

Dependence of Optical Properties on the Preparation Methods of Poly[(9,9'-dialkylfluorene-2,7-diyl)-*alt*-(1,3,4-oxadiazole-2,5-diyl)]

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ABSTRACT: A blue-light-emissive fluorene-based polyoxadiazole, an *n*-type polyfluorene derivative, was synthesized by both one-step and two-step methods. Directly polymerized poly[(9,9'-didodecylfluorene-2,7-diyl)-*alt*-(1,3,4-oxadiazole-2,5-diyl)] (PFOx-DP) exhibited a higher molecular weight and a more efficient photoluminescence quantum yield than poly[(9,9'-didodecylfluorene-2,7-diyl)-*alt*-(1,3,4-oxadiazole-2,5-diyl)] (PFOx) prepared via a polyhydrazide precursor, poly[9,9'-didodecylfluorene-2,7-(2,5-dihydrazide-1,3,4-oxadiazole)]. Both polymers, differently prepared, showed similar photoluminescent properties in 1,2-dichloroethane. However, in a film state, the influence of the interchain interactions on the photoluminescence of PFOx

with the lower molecular weight was larger than on the photoluminescence of PFOx-DP. The electron-deficient property of an oxadiazole group in the polymer backbone resulted in low-lying highest occupied molecular orbital and lowest unoccupied molecular orbital energy levels of -6.29 and -3.26 eV, respectively, of the polymer suitable for electron-transport/hole-blocking layers and emissive layers in multilayer electroluminescence devices. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3112–3118, 2004

Key words: conjugated polymers; photophysics; luminescence

INTRODUCTION

Polyfluorenes (PFs) have been intensively studied as very promising electro-optical polymers for electroluminescence (EL) devices, laser diodes, and biochemical sensors.^{1,2} The major advantages of PFs, the structure of which is based on poly(*p*-phenylene), are their facile solubility control through the introduction of long alkyl groups in the 9,9'-positions of fluorene, their large band gaps for blue emissions, and the high photooxidation stability of the fully aromatic structures in the main chain.¹ For tuning the optical properties and improving the charge-injection/transport properties for efficient EL devices, various derivatives of PF have been designed and synthesized.³ PFs have been known to exhibit good hole-transport properties.⁴ For the enhanced efficiency of an EL device, a balance of charge carriers for efficient recombination is essentially demanded. To meet this demand, some PF derivatives with electron-transport (*n*-type) moieties have been reported. Most well-known *n*-type PF derivatives are poly(fluorene-*co*-benzothiadiazole)s; however, these polymers have green emissions be-

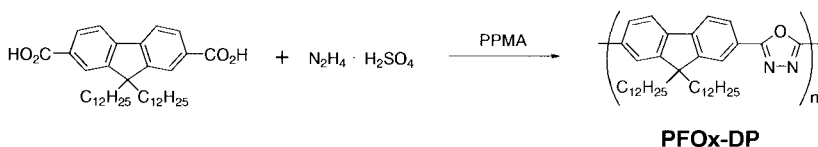
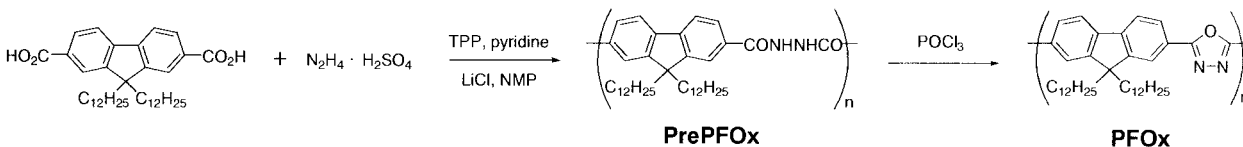
cause of their small band gaps attributed to benzothiadiazole groups.⁵ Also, the introduction of quinoline,^{6,7} quinoxaline,⁷ pyridine,⁸ cyanobenzene,⁸ *p*-dicyanobenzene,⁹ fluorinated benzene,¹⁰ and thiophene-*S,S*-dioxide¹¹ to the PF structure has been reported. Very recently, PF copolymers with an 1,3,4-oxadiazole group in the main chain, the most well-known electron-transport moiety for EL materials,^{12,13} have been developed by our group and some other groups.^{7,14–16} The incorporation of these *n*-type polymers into multilayer devices has been evaluated as a key technique for enhancing the efficiency and performance of EL devices.

Polyoxadiazoles can generally be prepared by a one-step or two-step method.¹⁷ The one-step method is the direct polymerization of a dicarboxylic acid monomer with a dihydrazide monomer or hydrazine salt in the dehydrating medium, such as oleum, poly(phosphoric acid), or phosphorus pentoxide/methanesulfonic acid (PPMA).^{17,18} The two-step method involves a polycondensation step for polyhydrazides as polyoxadiazole precursors and a subsequent conversion of polyhydrazides into corresponding polyoxadiazoles by thermal or chemical dehydrocyclization.^{17–22} In comparison with the one-step method, the two-step method largely leads to lower molecular weight products.¹⁸

In this work, we prepared a polyoxadiazole based on fluorene, poly[(9,9'-didodecylfluorene-2,7-diyl)-

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A: the one-step method**B**: the two-step method**Scheme 1** Polymer preparation schemes.

alt-(1,3,4-oxadiazole-2,5-diyl)], by both one-step and two-step methods. The synthesized polymer was expected to exhibit blue emissions, good electron-transport properties, and good thermal stability.¹⁴ The dependence of the optical properties of the polymer on the preparation method was also investigated.

EXPERIMENTAL**Materials**

Pyridine and POCl₃ were purified by distillation under reduced pressure. All other chemicals were purchased from Aldrich, TCI, or Acros and were used as received.

Synthesis

Synthesis of 2,7-dicyano-9,9'-didodecylfluorene

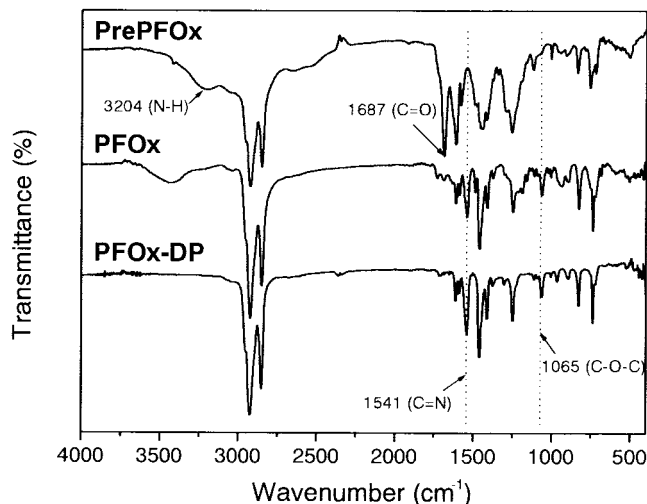
A solution of 2,7-dibromo-9,9'-didodecylfluorene^{14,23} (35.7 g, 54 mmol) and CuCN (13.4 g, 150 mmol) in dry *N,N*-dimethylformamide (50 mL) was refluxed for 20 h under N₂. After the mixture cooled to 80°C, a solution of hexahydro-FeCl₃ (40.6 g) and concentrated HCl (100 mL) in water (100 mL) was added. The solution was stirred at 70–80°C for 1 h and then overnight at room temperature. The light-brown precipitate was filtered off, washed with water and methanol, dissolved in chloroform, and filtered through a short silica gel column. Pure, pale-yellow, crystalline 2,7-dicyano-9,9'-didodecylfluorene was obtained by the removal of chloroform *in vacuo* and then recrystallization from ethanol.

Yield: 29.2 g (98%). mp: 85–86°C. ¹H-NMR (CDCl₃, δ): 7.82 (d, H²), 7.69 (d, H²), 7.65 (s, H²), 2.01 (t, H⁴), 1.05–1.23 (br, H³⁶), 0.86 (br, H⁴), 0.54 (br, H⁶). ¹³C-NMR (CDCl₃, δ): 152.1, 143.5, 131.6, 126.8, 121.5, 119.2,

112.0, 56.1, 39.9, 31.9, 29.3–29.6 (br), 23.8, 22.7, 14.1. IR (KBr): 3084, 3060 (aromatic C—H), 2920, 2850 (aliphatic C—H), 2226 cm⁻¹ (C—N).

Synthesis of 9,9'-didodecylfluorene-2,7-dicarboxylic acid

2,7-Dicyano-9,9'-didodecylfluorene (5.5 g, 10 mmol) and KOH (7.9 g, 120 mmol) were stirred and refluxed in a triethylene glycol/water mixture (80 mL/10 mL) for 20 h. The solution was filtered to remove insoluble parts, and then the filtrate was cooled to room temperature. The viscous filtrate was cooled to 0°C and acidified by excess concentrated HCl to pH ~ 2. The white precipitate was filtered off, washed with water, and dried at 80°C *in vacuo*. The pure product was

**Figure 1** IR spectra of PrePFOx, PFOx, and PFOx-DP.

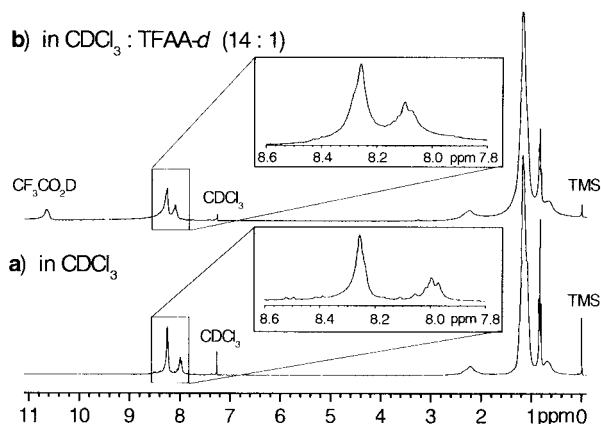


Figure 2 ^1H -NMR spectra of PFOx-DP in (a) CDCl_3 and (b) a mixture of CDCl_3 and TFAA-*d* (14:1).

obtained after recrystallization from aqueous methanol.

Yield: 5.6 g (95%). mp: 186–191°C. ^1H -NMR ($\text{DMSO}-d_6$, δ): 12.99 (s, H^2), 8.00 (m, H^6), 2.05 (t, H^4), 0.97–1.18 (br, H^{36}), 0.83 (br, H^4), 0.45 (br, H^6). ^{13}C -NMR ($\text{DMSO}-d_6$, δ): 168.2, 152.0, 144.5, 131.1, 129.5, 125.2, 121.3, 55.7, 32.0, 29.6 (br), 24.0, 22.8, 14.7. IR (KBr): 2400–3600 (O—H), 2924, 2852 (aliphatic C—H), 1686 cm^{-1} (C=O).

Synthesis of directly polymerized poly[(9,9'-didodecylfluorene-2,7-diyl)-*alt*-(1,3,4-oxadiazole-2,5-diyl)] (PFOx-DP)

In a 25-mL, three-necked flask under a dry nitrogen flux, 9,9'-didodecylfluorene-2,7-dicarboxylic acid (0.296 g, 0.5 mmol) and hydrazine sulfate (0.065 g, 0.5 mmol) were added to PPMA (5 mL). While stirring, the solution

TABLE I
Molecular Weights and Thermal Properties of the Polymers

Polymer	M_w (g/mol) ^a	M_n (g/mol) ^a	PDI ^b	DP_n^c	T_g^d (°C)	T_d^e (°C)
PFOx-DP	80,100	37,600	2.1	66	119	423
PFOx	21,200	7,300	2.9	13	93	422

M_w = weight-average molecular weight; M_n = number-average molecular weight.

^a Molecular weights of a tetrahydrofuran-soluble part determined by GPC.

^b Polydispersity index (PDI) = M_w/M_n .

^c Degree of polymerization based on M_n .

^d Glass-transition temperature measured by DSC under N_2 .

^e Onset decomposition temperature measured by TGA under N_2 .

was heated to 80°C for 1 h and then to 120°C for 2 h under N_2 . The viscous gum solution clung to the stirrer. The resultant gum solution was poured into a diluted NaOH solution, crushed with a spatula, filtered off, washed with water and methanol several times, and dried at 80°C *in vacuo*. Two precipitations from 1,2-dichloroethane (DCE)/trifluoroacetic acid (TFAA) solution into a mixture of methanol and triethylamine were carried out for further purification.

Yield: 0.20 g (98%). ^1H -NMR (CDCl_3 , δ): 8.25 (br, H^4), 8.00 (d, H^2), 2.20 (br, H^4), 1.18 (br, H^{36}), 0.83 (br, H^4), 0.69 (br, H^6). ^{13}C -NMR (CDCl_3 , δ): 165.1, 152.4, 143.5, 126.4, 123.5, 121.6, 121.2, 56.0, 40.3, 31.8, 29.5 (br), 23.9, 22.6, 14.0. IR (KBr): 3080, 3045 (aromatic C—H), 2925, 2853 (aliphatic C—H), 1613, 1591, 1541 (C=N in oxadiazole), 1461, 1413, 1249, 1065, 828, 739 cm^{-1} .

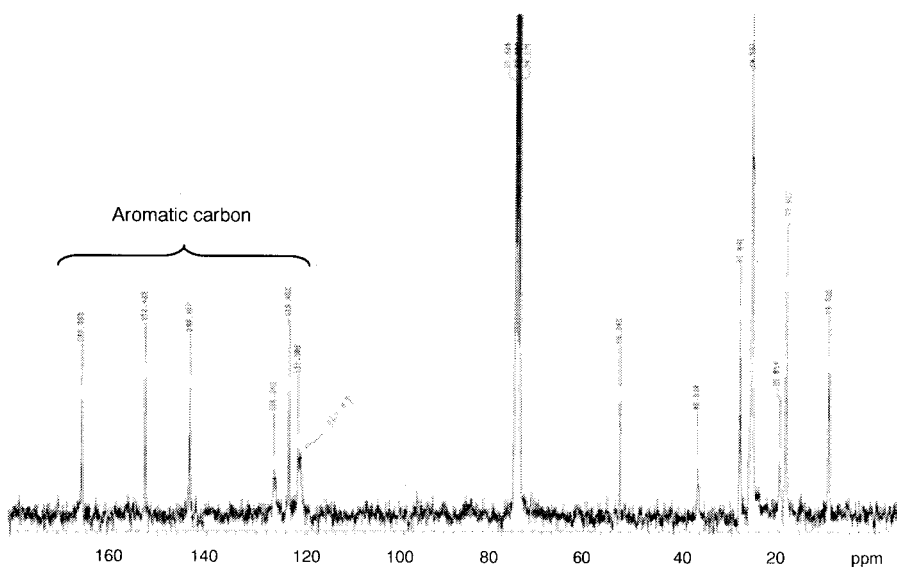


Figure 3 ^{13}C -NMR spectra of PFOx-DP in CDCl_3 .

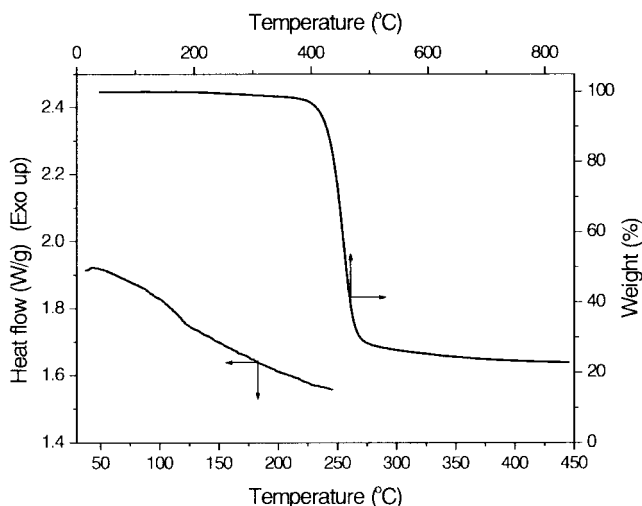


Figure 4 DSC and TGA thermograms of PFOx-DP.

Synthesis of poly[9,9'-didodecylfluorene-2,7-(2,5-dihydrazide-1,3,4-oxadiazole)] (PrePFOx)

In a 20-mL Schlenk tube, 9,9'-didodecylfluorene-2,7-dicarboxylic acid (0.296 g, 0.5 mmol), hydrazine sulfate (0.065 g, 0.5 mmol), dry LiCl (0.1 g), and triphenylphosphite (0.341 g, 1.1 mmol) were placed, and then *N*-methylpyrrolidinone (2 mL) and pyridine (0.5 mL) were added. The solution was stirred at 105°C for 3 h under N₂ and poured into methanol. The white precipitate was filtered, washed with methanol and water several times, and dried at 80°C *in vacuo*.

Yield: 0.246 g (84%). IR (KBr): 3204 (N—H), 3049 (aromatic C—H), 2925, 2853 (aliphatic C—H), 1687 (C=O), 1613, 1581, 1445, 1417, 1289, 1256, 1121, 838, 758, 722 cm⁻¹.

Synthesis of poly[(9,9'-didodecylfluorene-2,7-diyl)-*alt*-(1,3,4-oxadiazole-2,5-diyl)] (PFOx)

PrePFOx (0.165g) in POCl₃ (10 mL) was refluxed for 3 h under N₂, then poured into water, filtered, washed

with water and methanol, and dried at 80°C *in vacuo*. The powder was dissolved in DCE/TFAA and then precipitated into a mixture of methanol and triethylamine.

Yield: 0.124 g (78%). ¹H-NMR [CDCl₃/TFAA-*d* (1:1), δ]: 8.31 (br, H⁴), 8.19 (d, H²), 2.29 (br, H⁴), 1.21 (br, H³⁶), 0.85 (br, H⁴), 0.69 (br, H⁶). ¹³C-NMR [CDCl₃/TFAA-*d* (1:1), δ]: 165.9, 153.9, 145.7, 127.9, 126.8, 122.6, 120.6, 56.9, 40.3, 32.1, 29.8 (br), 24.2, 22.8, 13.8. IR (KBr): 3068, 3041 (aromatic C—H), 2924, 2852 (aliphatic C—H), 1613, 1588, 1541 (C=N in oxadiazole), 1461, 1412, 1248, 1065, 936, 894, 828, 739 cm⁻¹.

Measurements

NMR spectra were obtained with a Varian VXR-300 FT-NMR spectroscope (Palo Alto, CA) and were referenced to tetramethylsilane. IR spectra were recorded on a Nicolet 360 Fourier transform infrared spectroscope (Middleton, WI). The molecular weights were measured with a Waters gel permeation chromatography (GPC) system (a 410 differential refractometer, Styragel HR-4, HR-3, HR-1, and HR-5E columns, and tetrahydrofuran as an eluent) (Milford, MA).

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed with a TA Instruments SDT 2960 simultaneous DSC-TGA instrument and a TA Instruments DSC 2010 instrument, respectively, at heating rates of 10 and 5°C/min, respectively, under N₂.

Ultraviolet-visible (UV-vis) absorption and photoluminescence (PL) spectra were recorded on a Shimadzu UV-2101PC UV-vis scanning spectrophotometer and a Shimadzu RF 5301PC spectrofluorophotometer (Japan), respectively. The PL quantum yield (Φ_{PL}) values were calculated with 9,10-diphenylanthracene in cyclohexane as a reference:

$$\Phi_{PLs} = \Phi_{PLr}(A_r/A_s)(F_s/F_r)(n_s/n_r)^2$$

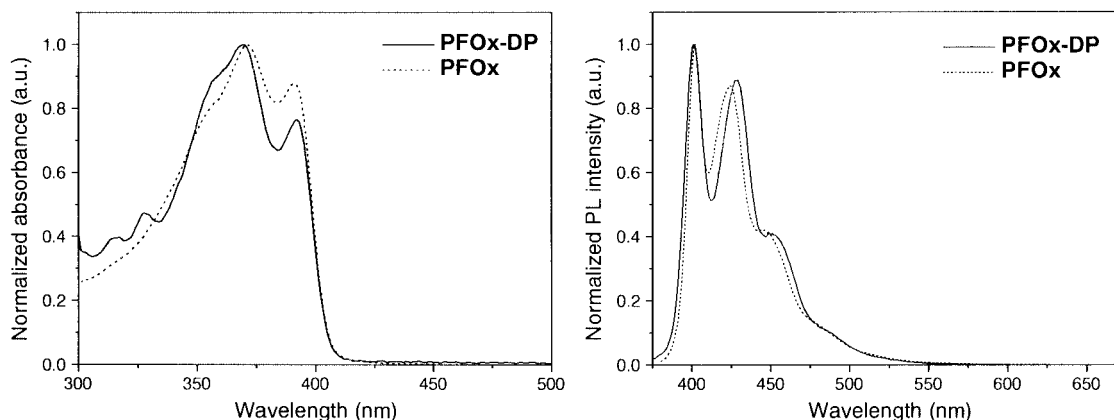


Figure 5 Abs (left) and PL (right) spectra of PFOx-DP and PFOx in DCE.

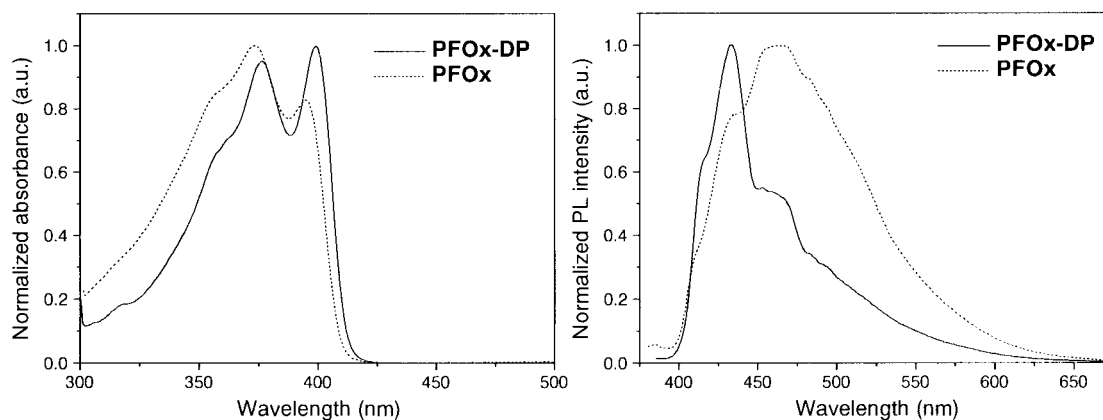


Figure 6 Abs (left) and PL (right) spectra of PFOx-DP and PFOx as films.

where A , F , and n are the absorbance at the excitation wavelength, the integral over the PL spectrum, and the refractive index of the solvent, respectively, and subscripts s and r refer to the sample and reference solution specimens, respectively.²⁴

Cyclic voltammetry was conducted with an EG&G model 273A potentiostat (Gaithersburg, MD) and a three-electrode electrochemical cell composed of a Pt wire dip-coated with a polymer as a working electrode, a platinum plate as a counter electrode, and a Ag/Ag^+ reference electrode [Ag wire/ 0.1M AgNO_3 / 0.1M $(\text{C}_4\text{H}_9)_4\text{NPF}_6$ /acetonitrile] supported by an electrolyte of 0.1M $(\text{C}_4\text{H}_9)_4\text{NPF}_6$ /acetonitrile at a scanning rate of 50 mV/s .

RESULTS AND DISCUSSION

Polymer preparation and characterization

As shown in Scheme 1, we attempted both one-step (route A) and two-step (route B) methods for the preparation of a polymer. PFOx-DP (via route A) was prepared from 9,9'-didodecylfluorene-2,7-dicarboxylic acid and hydrazine sulfate with PPMA,^{18,20,25} known as an Eaton's reagent, as a condensation agent and reaction solvent. In the two-step method, the polyhydrazide precursor PrePFOx was prepared via a phosphorylation polyamidation known as a Yamazaki-Higashi reaction^{20,21,26} and then was converted into

PFOx by dehydrocyclization in POCl_3 (via route B).^{19,22} To our knowledge, this is the first report about a phosphorylation polyamidation with hydrazine as a diamine monomer.

As shown in Figure 1, a comparison of the IR spectra of PrePFOx and PFOx indicates the complete conversion from a hydrazide group to an 1,3,4-oxadiazole group in the polymer backbone,^{18,19,21,22} and the IR spectra of PFOx-DP and PFOx are almost identical.

Both PFOx-DP and PFOx were soluble in common organic solvents such as chloroform, DCE, 1,4-dioxane, and tetrahydrofuran at room temperature. However, the polymer solution prepared by these solvents showed turbidity to a slight extent at a concentration of 10 mg/mL , and this revealed that the polymers were not completely soluble in these organic solvents. Upon heating, however, they were completely soluble without any turbidity, and the addition of a small amount of TFAA dramatically increased the polymer solubility; this was due to the acid-base-complex formation between TFAA and imine-type ($\text{C}=\text{N}$) nitrogen atom(s) in the oxadiazole group.^{18,22} As shown in the $^1\text{H-NMR}$ spectra of PFOx-DP (Fig. 2), aromatic hydrogen signals in a fluorene group shifted to a lower field region because of the enhancement of the electron deficiency triggered by this complex formation in the oxadiazole group. $^{13}\text{C-NMR}$ spectra of both polymers show seven aromatic carbon signals; this

TABLE II
Optical Properties of the Polymers

Polymer	$\lambda_{\text{max}}(\text{DCE})$ (nm) ^a	$\lambda_{\text{max}}(\text{film})$ (nm) ^a	$\text{PL}_{\text{max}}(\text{DCE})$ (nm) ^b	$\text{PL}_{\text{max}}(\text{film})$ (nm) ^b	Φ_{PL}^c
PFOx-DP	369, 392	376, 399	401, 429, 450	417, 432, 452	1.00
PFOx	371, 391	373, 395	402, 424, 446	412, 436, 461	0.76

^a UV–v is absorption maxima (italic data indicate major band peaks).

^b PL maxima excited at 370 nm (italic data indicate major band peaks).

^c With respect to 9,10-diphenylanthracene ($\Phi_{\text{PL}} = 0.90$ in cyclohexane) excited at 350 nm.

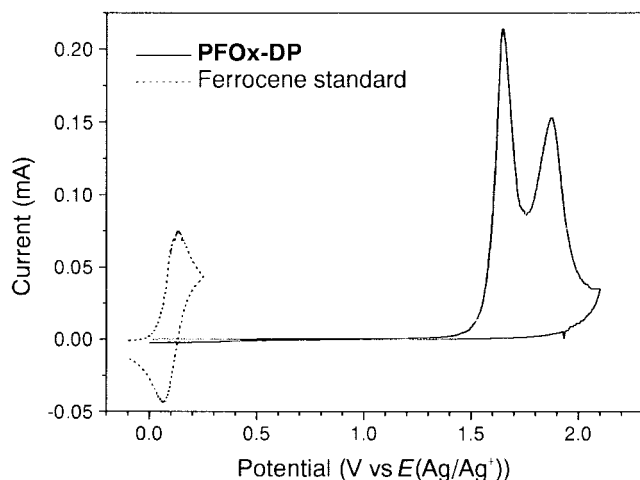


Figure 7 Cyclic voltammogram of PFOx-DP.

agrees well with the proposed chemical structure of the repeating unit of the polymers (Fig. 3). A robust, pinhole-free, and transparent film was readily obtained from a polymer solution with a small amount of TFAA by a spin-coating or solution-casting technique. As determined with IR, a small trace of TFAA could not be found in these films dried *in vacuo* at 40°C overnight.

PFOx-DP had a higher molecular weight than PFOx.^{17,18} Determined by the number-average molecular weight, the degree of polymerization of PFOx-DP was about five times greater than that of PFOx. The glass-transition temperature, 119°C, of PFOx-DP was higher than that of PFOx because of the higher molecular weight (Table I). Both PFOx-DP and PFOx showed good thermal stability up to about 400°C under N₂ (Table I and Fig. 4).

Optical properties

Table II and Figures 5 and 6 show the optical properties of PFOx-DP and PFOx, including UV-vis absorption (Abs), PL, and Φ_{PL} , analyzed by means of Abs and PL spectroscopy. The Abs spectrum of PFOx-DP as a film ($\lambda_{\text{max}} = 376$ and 399 nm) was redshifted with respect to that in DCE ($\lambda_{\text{max}} = 369$ and 392 nm); this suggested that its π delocalization in the solution was interrupted to a great extent by the twisted conformation of the main chain caused by the increased disorder of the long alkyl chains in a fluorene group, whereas its planar conformation formed well and, as a result, increased the π delocalization in a solid phase such as a film because of the chain packing.²⁷ Despite the difference in the molecular weights, the Abs spectra of both polymers in solution were almost identical, with a deviation of 1 nm (corresponding to 0.0091 eV) between the Abs maxima of both polymers; this re-

vealed that PFOx had a sufficient number of repeating units for an effective conjugation length.^{28,29}

Both polymers exhibited efficient blue PL with almost identical vibronic patterns (PL maxima at 401–402 nm) in DCE. The Φ_{PL} values of the polymers in dilute DCE were determined in comparison with 9,10-diphenylanthracene in cyclohexane as a reference ($\Phi_{\text{PL}} = 0.90$ at 350-nm excitation).²⁴ PFOx-DP showed quantitative Φ_{PL} values, whereas PFOx had a lower yield than PFOx-DP. The lower Φ_{PL} values of PFOx were due to the impurities introduced during the polyhydrazide synthesis, the minor structural defects caused by incomplete dehydrocyclization, and the relatively large end-group effect in the low-molecular-weight one that probably acted as exciton traps to quench its PL.

The PL spectrum of PFOx-DP as a film was redshifted with respect to that in DCE, with the changes in the vibronic band pattern due to interchain interactions, such as aggregation formation,^{1,30} and the enhancement of the rigid conformation in a solid phase.²⁷ PFOx-DP as a film exhibited PL with a maximum band at 432 nm corresponding to the second vibronic band, whereas PFOx had broadened PL in the lower energy region at 461 nm. This result indicated that interchain interactions including aggregation and/or excimers were more effective in a lower molecular weight part.³¹

Electronic structure

Figure 7 shows an anodic scan plot of the cyclic voltammetry of PFOx-DP, the potential of which is called the electrochemical potential of Ag/Ag⁺. PFOx-DP displayed a *p*-doping process with well-defined and irreversible signals at the maxima of +1.64 and +1.88 V versus E(Ag/Ag⁺). Determined by both the band gap, calculated from the absorption edge of the polymer film, and the ionization potential, calculated from the *p*-doping onset potential referred to ferrocene,³² PFOx-DP had highest occupied molecular orbital and lowest unoccupied molecular orbital energy levels of 6.29 and 3.26 eV, respectively, which were below the vacuum level because of the electron deficiency of an 1,3,4-oxadiazole unit.^{12,13} This result of low-lying electronic energy levels of PFOx-DP indicated that it could be used as a competitive electron-transport/hole-blocking material for multilayer EL devices.¹³

CONCLUSIONS

A PF copolymer with an 1,3,4-oxadiazole group in the main chain was successfully synthesized by the one-step and two-step preparation methods for a polyoxadiazole. PFOx-DP, prepared by the one-step method in PPMA, had a higher molecular weight than PFOx prepared via a corresponding polyhydrazide, PreP-

FOx. Both PFOx-DP and PFOx showed high solubility in common organic solvents with the aid of a small amount of TFAA. Also, PFOx-DP exhibited better optical properties, such as the PL color and Φ_{PL} , than PFOx with a lower molecular weight. The investigation of the electronic energy levels of the polymer suggests that it has promise as of which a blue-emissive material and as an electron-transport/hole-blocking EL material.

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