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New π-conjugated polymers containing oxazole in the main chain: Optical and electrochemical properties

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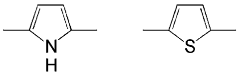
Abstract

Oxazole-containing π-conjugated polymers, an alternating copolymer of 9,9-dioctylfluorene-2,7-diyl and 2,5-bis(*p*-phenylene)oxazole (**P(Flu-DPOxz)**) and an alternating copolymer of 2,5-dialkoxy-*p*-phenylene and 2,5-bis(*p*-phenylene(oxazole)) (**P(ROPh-DPOxz)**), have been synthesized by Pd-catalyzed organometallic polycondensation. They were soluble in organic solvents, and had number average molecular weights of 18 600 and 24 700, respectively, in GPC analysis. **P(Flu-DPOxz)** and **P(ROPh-DPOxz)** showed UV–vis absorption peaks at about 380 nm in $CHCl_3$. Powder XRD patterns and UV–vis data of the polymers indicated that the polymer solid was amorphous. The polymers were photoluminescent both in chloroform and in solid. In chloroform, the emission peak appeared at about 420 nm with a high quantum yield of about 70%. The polymers were electrochemically active, and electrochemical data revealed that the oxazole unit behaved as a moderate electron-accepting unit.

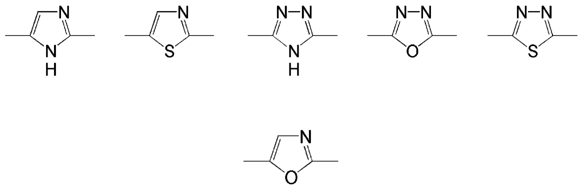
Keywords: π-Conjugated polymer; Oxazole; Optical properties

1. Introduction

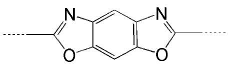
π-Conjugated polymers with electronic and optical functionalities have been attracting much attention [1]. Especially π-conjugated polymers consisting of five-membered hetero-aromatic units, *e.g.*, pyrrole and thiophene units have been attracting strong interest; the pyrrole and thiophene units are typical electron-donating units.



When the five-membered hetero-aromatic units contain imine −C=N− nitrogen(s), as in the cases of imidazole [2], thiazole [3], triazole [4], oxadiazole [5], and thiadiazole units [4a,c,6], π-conjugated polymers consisting of the five-membered hetero-aromatic units usually possess an electron-accepting nature because of the electron-withdrawing ability of the imine −C=N− group.



Oxazole is another candidate for the electron-accepting five-membered ring building block of π-conjugated polymers. However, examples of π-conjugated polymers consisting of the oxazole unit are not many, in spite of many reports on rigid-rod polymers of benzobisoxazole [7,8]:



Curtis reported an example of the main-chain type oxazole homopolymer, head-to-head type poly(4-nonyloxazole-2,5-diyl)

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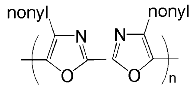
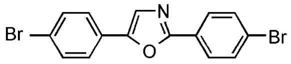
[9], however, usability of the oxazole unit in π-conjugated copolymers has not been examined well.



Herein, we report the synthesis of new π-conjugated copolymers of oxazole and optical and electrochemical properties of the copolymers. Oxazole sometimes undergoes a ring opening reaction via the attack of reagents at the 2-position of oxazole. For example, such a ring opening reaction takes place when oxazole is treated with BuLi (Bu = butyl) [10]. Based on the high reactivity of oxazole, we used the following compound **1**, whose 2- and 5-position was protected with the phenyl groups, as a stable starting monomer. From the monomer **1**, π-conjugated polymers consisting of the oxazole unit were successfully obtained.



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2. Experimental

2.1. Materials and measurements

^{1}H NMR and IR spectra were recorded on a JEOL EX-400 spectrometer and a JASCO IR 810 spectrophotometer, respectively. UV–vis and photoluminescence (PL) spectra were measured with Shimadzu UV-3100 and Hitachi F-4010 spectrophotometers, respectively. The UV–vis and PL spectra were measured with chloroform solutions of the polymers (concentration = approximately 1×10^{-5} M based on the repeating unit of the polymer) and cast films (thickness = approximately 0.1 μm) on non-fluorescent glass plates. Thermal analysis was performed with a Shimadzu TA-50 WS thermal analyzer equipped with a Shimadzu DSC-50 differential scanning calorimeter and a Shimadzu TGA-50 thermogravimetric analyzer. GPC curves were obtained with a Shimadzu liquid chromatography system with a Shodex 80M column and a 6A refractive index detector; eluent was $CHCl_3$. $[Pd(PPh_3)_4]$ [11], monomer **1** [12], and monomer **3** [13] were prepared according to the literature. Monomer **2** and 1-methoxy-4-(2′-ethylhexyloxy)benzene were purchased from Aldrich, and other reagents were purchased from Tokyo Kasei Kogyo Co., Ltd.

2.2. Synthesis of polymers

2.2.1. *P(Flu-DPOxz)*

To a dry toluene (6 mL) solution containing 9,9-dioctylfluorene-2,7-bis(trimethyleneborate) **2** (1.12 g, 2.00 mmol) and 2,5-bis(4-bromophenyl)-1,3-oxazole **1** (0.758 g, 2.00 mmol), a degassed aqueous solution of K_2CO_3 (2 M, 3 mL), several drops of Aliquat 336, and $[Pd(PPh_3)_4]$ (0.069 g, 0.060 mmol) were added. After the mixture was stirred at 80 °C for 24 h, it was poured into an excess amount of MeOH. The precipitate was collected by filtration, washed by distilled water and MeOH, and dried in vacuo. Yield: 1.04 g (1.72 mmol, 86%). Anal. Calcd for $(C_{44}H_{49}NO \cdot 0.9H_2O)_n$: C, 84.68%; H, 8.20%; N, 2.24%. Found: C, 84.60%; H, 7.92%; Br, 0%; N, 2.48%. IR (KBr, cm^{-1}): 3032, 2925, 2852, 1610, 1507, 1465, 1436, 1407, 1376, 1250, 1134, 1107, 1061, 1013, 953, 892, 849, 816, 747, 710. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (br, 2H, Ph–*H*), 7.88–7.78 (br, 8H, Ph–*H*), 7.70–7.63 (br, 4H, Ph–*H*), 7.55 (s, 1H, Oxz–*H*), 2.09 (br, 4H, $^{\alpha}CH_2$), 1.21–1.00 (br, 20H, CH_2), 0.82–0.79 (br, 10H, $^{\beta}CH_2$ and CH_3).

2.2.2. *P(ROPh-DPOxz)*

P(ROPh-DPOxz) was prepared analogously by using **3** (97 mg, 0.30 mmol) and **1** (110 mg, 0.30 mmol). A light-green solid was obtained. Yield: 110 mg (0.23 mmol, 78%). Anal. Calcd for $(C_{30}H_{31}NO_3 \cdot 0.8H_2O)_n$: C, 76.99%; H, 7.02%; N, 2.99%. Found: C, 76.84%; H, 6.62%; Br, 0%; N, 3.03%. IR (KBr, cm^{-1}): 3036, 2956, 2927, 2871, 1612, 1558, 1514, 1485, 1419, 1387, 1337, 1310, 1260, 1209, 1134, 1109, 1048, 1014, 953, 844, 751, 713, 542, 476. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (br, 2H, Ph–*H*), 7.90–7.70 (br, 6H, Ph–*H*), 7.54 (br, 1H, Oxz–*H*), 7.06 (br, 2H, RO–Ph–*H*), 3.86 (br, 5H, $^{\alpha}CH_2$ and OCH_3), 1.65 (br, 1H, $^{\beta}CH$), 1.45–1.20 (br, 8H, CH_2), 0.86 (br, 6H, CH_3).

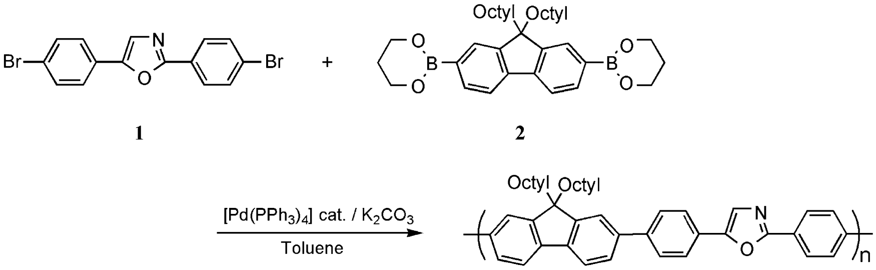
3. Results and discussion

3.1. Synthesis of polymers

The following organometallic polycondensations of **1** with **2** and **3** were carried out utilizing Pd-catalyzed Suzuki cross-coupling reaction to yield **P(Flu-DPOxz)** and **P(ROPh-DPOxz)**, as shown in Eqs. (1) and (2). **P(Flu-DPOxz)** was obtained in 86% yield as a green powder. Poly(fluorene)s are the subject of recent strong interest because of their excellent light emitting properties, and various copolymers of fluorenes to tune the optical properties of the polymer have been synthesized [14]. **P(ROPh-DPOxz)** was obtained in 78% yield as a light-green powder.

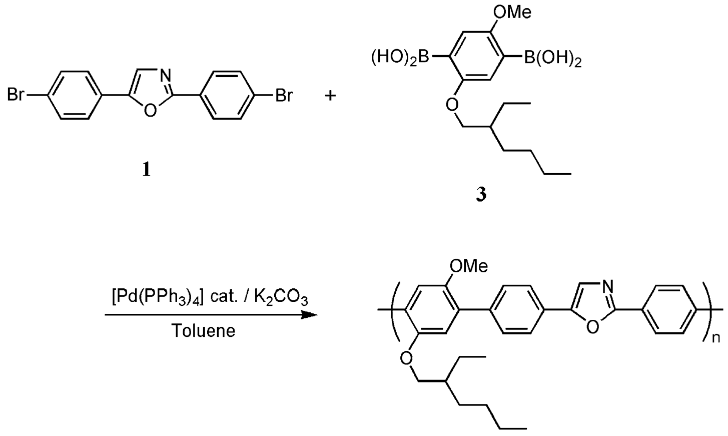
P(Flu-DPOxz) and **P(ROPh-DPOxz)** were soluble in organic solvents such as $CHCl_3$, THF, toluene, NMP, and trifluoroacetic acid. The solutions containing the polymer displayed strong blue emission when irradiated with UV light. Data from elemental analysis, ^{1}H NMR, and IR agreed with the polymer structures, and Br was not detected. **P(Flu-DPOxz)** and **P(ROPh-DPOxz)** had number average molecular weights (M_n's) of 18 600 and 24 700 (*vs.* polystyrene standards) with M_w/M_n (M_w = weight average molecular weight) values of 2.5 and 2.4, respectively. The M_n values correspond to degrees of polymerization of about 30 and 55, respectively.

Fig. 1 shows IR spectra of **P(Flu-DPOxz)**, **P(ROPh-DPOxz)**, and their starting monomers. The IR spectra of the polymers show a ν(C=N) peak of the oxazole ring at about 1610 cm^{-1}. Fig. 2 discloses ^{1}H NMR spectra of the polymers. The ^{1}H NMR spectra of **P(Flu-DPOxz)** and **P(ROPh-DPOxz)** show a signal of the oxazole ring-H at δ 7.55 and 7.54, respectively, as a single peak. The polymers may have both the



P(Flu-DPOxz), M_n = 18 600

(1)



P(ROPh-DPOxz), M_n = 24 700

(2)

head-to-tail and head-to-head microstructures, which may cause splitting of the oxazole ring-H according to the difference in the microstructure.

However, such a splitting of the oxazole-H signal is not observed presumably due to enough separation of each oxazole unit from other oxazole units by the long π-conjugated system (*e.g.*, the two *p*-phenylene units and the fluorene unit in the case of **P(Flu-DPOxz)**) between the oxazole units.

All the ^{1}H NMR signals appear at reasonable positions and with reasonable areas. In the case of **P(Flu-DPOxz)**, the ^{1}H NMR signal of the β-CH_2 group of the octyl side chain in the fluorene unit appears at a high magnetic field of about δ 0.8, and the peak is overlapped with the signal of the terminal CH_3 group of the octyl group. Appearance of the β-CH_2 group at a relatively high magnetic field, owing to location of the β-CH_2 group on the fluorene ring, has been reported [15]. The IR and NMR data support that the polymers shown in Eqs. (1) and (2) were obtained without the ring opening reaction of the oxazole unit. Data from elemental analysis agreed with hydrated structures of the polymers.

3.2. Thermal stability

P(Flu-DPOxz) and **P(ROPh-DPOxz)** had high thermal stability, and gave 5% weight loss temperature ($T_{5\%}$) at 409 and 415 °C, respectively, as estimated by thermogravimetric analysis. These values are comparable to $T_{5\%}$ (452 °C) of the head-to-head type poly(4-nonyloxazole-2,5-diyl) [9].

3.3. UV–vis and photoluminescence (PL) spectra

Figs. 3 and 4 show UV–vis and photoluminescence (PL) spectra of **P(Flu-DPOxz)** and **P(ROPh-DPOxz)**, respectively, and Table 1 summarizes optical data of the polymers. The UV–vis peaks (λ_{max}'s) of **P(Flu-DPOxz)** and **P(ROPh-DPOxz)** in $CHCl_3$ appear at 383 and 374 nm, respectively, and the λ_{max} values are comparable with that of poly(*p*-phenylene) (PPP; $\lambda_{max} = ca.$ 380 nm) [1]. Cast films of **P(Flu-DPOxz)** and **P(ROPh-DPOxz)** show λ_{max} at 383 and 379 nm, respectively. The minor shift of the absorption peak in going from the solution to the film indicates the absence of significant electronic interaction between the polymer molecules in the solid state, and suggests that the polymers are amorphous in solid. Powder X-ray diffraction (XRD) patterns of the polymers confirmed this view. However, the onset position of the UV–vis absorption band of **P(ROPh-DPOxz)** in chloroform at 420 nm is significantly shifted to 460 nm when measured with the film. These results suggest **P(ROPh-DPOxz)** partly forms an aggregate which gives intermolecular electronic interaction in the solid state.

P(Flu-DPOxz) and **P(ROPh-DPOxz)** exhibit PL peaks at $\lambda_{em} = 421$ and 424 nm, respectively, in chloroform. The λ_{em} positions agree with the onset positions of the UV–vis absorption bands. The PL spectra have substructures (*e.g.*, emissions at 446 and 470 nm for **P(Flu-DPOxz)**), which are considered to arise owing to the presence of vibronic coupling. In $CHCl_3$, **P(Flu-DPOxz)** and **P(ROPh-DPOxz)** gave quantum yields of 66% and 71%, respectively. The quantum yield of

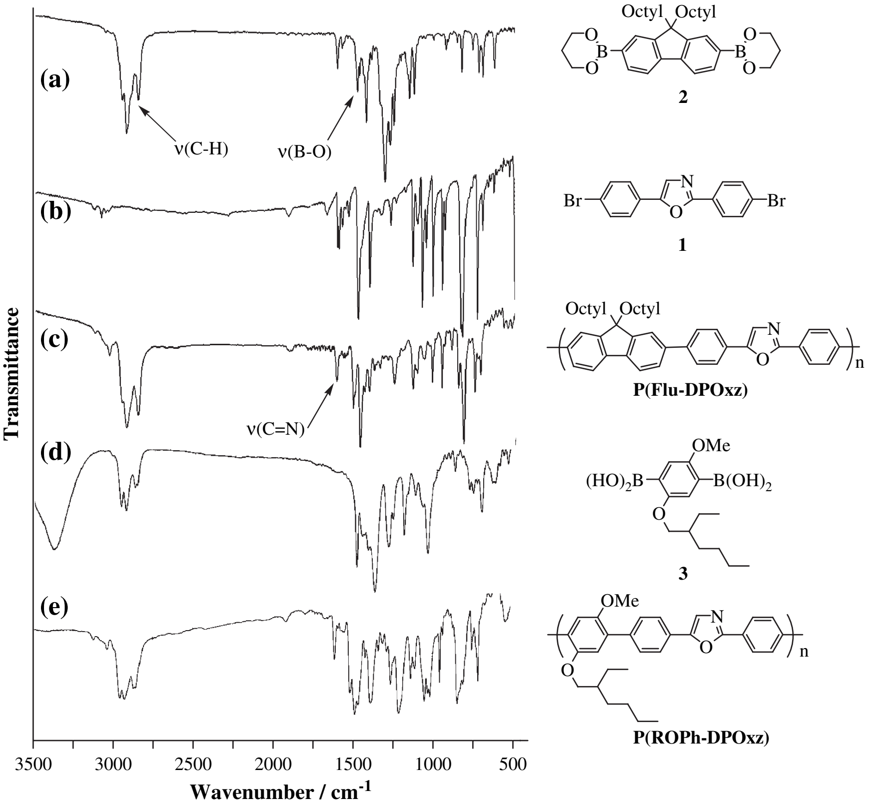


Fig. 1. FT-IR spectra of: (a) 9,9-dioctylfluorene-2,7-bis(trimethyleneborate), (b) 2,5-bis(4-bromophenyl)-1,3-oxazole, (c) **P(Flu-DPOxz)**, (d) [2-(2′-ethylhexyloxy)-5-methoxy-1,4-phenylene]bisboronic acid, and (e) **P(ROPh-DPOxz)**.

P(Flu-DPOxz) is comparable to those of reported poly(fluorene)s [15a,16].

In the cast film, **P(Flu-DPOxz)** shows a shift of the PL peak by about 10 nm to a longer wavelength. However, the shift is not large and indicates that the emission in the film is essentially originated from a single molecule and formation of an excimer is prevented even in the solid state, presumably due to a strong retardation effect of the two octyl groups in the fluorene unit on the intermolecular electronic interaction. In the cast film, **P(ROPh-DPOxz)** shows a large shift of λ_{em} to 478 nm, as depicted in Fig. 4. **P(ROPh-DPOxz)**, which has a basically flat molecular structure, seems to form an excimer-like adduct [17] between photoactivated **P(ROPh-DPOxz)**

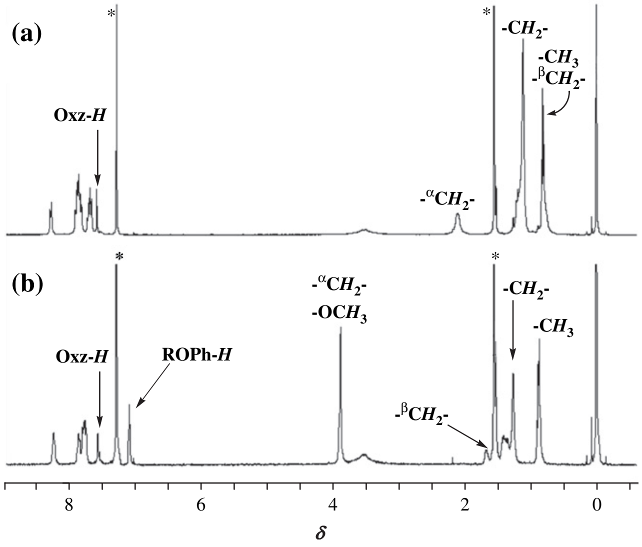


Fig. 2. ^{1}H NMR spectra of: (a) **P(Flu-DPOxz)** and (b) **P(ROPh-DPOxz)** in $CDCl_3$. The peaks with the * mark are due to solvent impurities ($CHCl_3$ and H_2O).

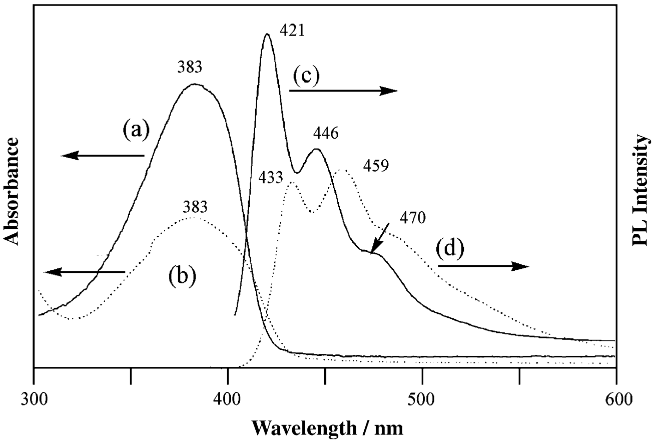


Fig. 3. (a) UV–vis spectrum of **P(Flu-DPOxz)** in $CHCl_3$ (solid line); (b) UV–vis spectrum of a cast film of **P(Flu-DPOxz)** (dashed line); (c) PL spectrum of **P(Flu-DPOxz)** in $CHCl_3$ (solid line); (d) PL spectrum of a cast film of **P(Flu-DPOxz)** (dashed line). PL spectra of the solution and film were measured with an excitation wavelength of 383 nm.

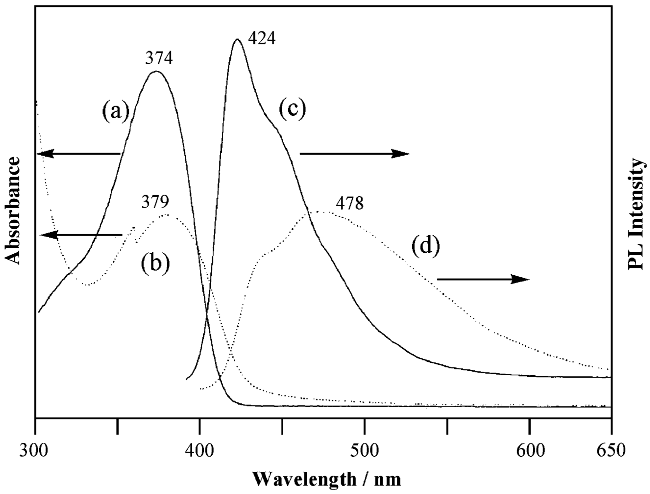


Fig. 4. (a) UV–vis spectrum of **P(ROPh-DPOxz)** in $CHCl_3$ (solid line); (b) UV–vis spectrum of cast film of **P(ROPh-DPOxz)** (dashed line); (c) PL spectrum of **P(ROPh-DPOxz)** in $CHCl_3$ (solid line); (d) PL spectrum of cast film of **P(ROPh-DPOxz)** (dashed line). PL spectra of the solution and film were measured with excitation wavelengths of 374 nm (in $CHCl_3$) and 379 nm (cast film), respectively.

and **P(ROPh-DPOxz)** in the ground state. However, the interacting site(s) to form the excimer-like adduct has not been clarified.

3.4. Electrochemical response

Electrochemical properties of the polymers were investigated by cyclic voltammetry (CV) using cast films of the polymers on a Pt plate electrode. As exhibited in Fig. 5, the polymers are electrochemically active in both oxidation and reduction regions, and show two redox couples. The one couple appears in a region from about 1 to 1.3 V *vs.* Ag^+/Ag, and is assigned to a p-doping and p-dedoping couple, and the other couple appears at about −2.5 V *vs.* Ag^+/Ag, and is assigned to an n-doping and n-dedoping couple. Color of the film changes according to the electrochemical oxidation and reduction (electrochromism) as depicted in Fig. 5. Light-green film of **P(Flu-DPOxz)** turns purple both in the oxidized and reduced states. In the case of the yellowish green film of **P(ROPh-DPOxz)**, it turns reddish purple in the oxidized state and purple in the reduced state.

Table 1
Optical data of the polymers

Polymer	Solution[a]			Cast film[b]	
	λ_{max}/nm	λ_{em}/nm	Φ^c/%	λ_{max}/nm	λ_{em}/nm
P(Flu-DPOxz)	383	421, (441), (470)	66	383	433, 459
P(ROPh-DPOxz)	374	424	71	379	478

λ_{max} = absorption peak; λ_{em} = PL peak.

[a] Solvent = $CHCl_3$.

[b] Cast from $CHCl_3$.

[c] PL quantum yield (Φ) was calculated by comparing with the standard of quinine sulfate (*ca.* 10^{-5} M solution in 0.5 M H_2SO_4, having Φ of 54.6%).

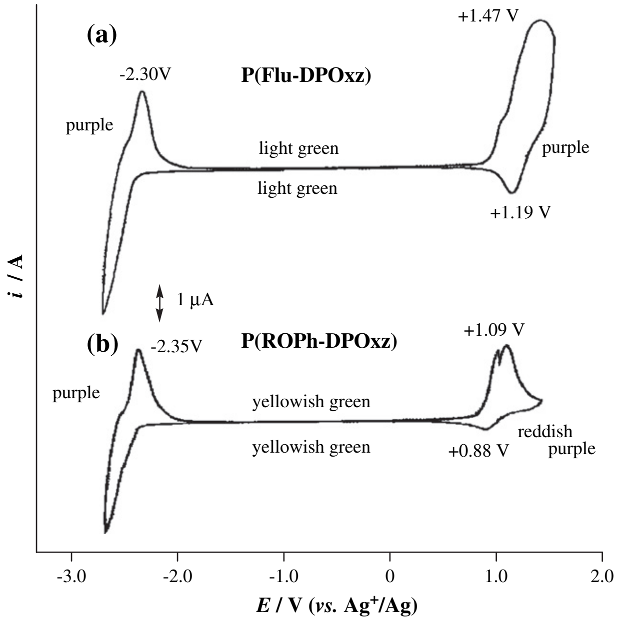


Fig. 5. Cyclic voltammograms of: (a) a film of **P(Flu-DPOxz)** and (b) a film of **P(ROPh-DPOxz)** on a Pt plate in an MeCN solution of $[Et_4N][BF_4]$ (0.10 M) under N_2. Sweep rate is 30 mV s^{-1}.

Electrochemical data of **P(Flu-DPOxz)** and **P(ROPh-DPOxz)** are summarized in Table 2, and Table 3 shows comparison of electrochemical data of **P(Flu-DPOxz)** with other π-conjugated poly(fluorene)s [18,19a]. As shown in Table 3, **P(Flu-DPOxz)** gives the peak current anodic potential, E_{pa}, at a relatively high potential, suggesting that an electron-accepting nature of the oxazole unit makes oxidation of **P(Flu-DPOxz)** difficult. However, in the electrochemical reduction, the electron-accepting effect of the oxazole unit is not obvious, and the electrochemical reduction requires a moderate peak current cathodic potential, E_{pc}.

It is reported that $E_{pa}^{onset} - E_{pc}^{onset}$ (E_{pa}^{onset} = onset potential for the anodic peak; E_{pc}^{onset} = onset potential for the cathodic peak) corresponds to a band gap of π-conjugated polymers [19]. **P(Flu-DPOxz)** gives an $E_{pa}^{onset} - E_{pc}^{onset}$ value of 3.11 eV (or 25 100 cm^{-1} and 399 nm), which roughly agrees with the band gap of **P(Flu-DPOxz)** estimated from the onset position of the UV–vis absorption band of **P(Flu-DPOxz)** in film (430 nm or 2.88 eV).

The HOMO and LUMO levels of **P(Flu-DPOxz)** and **P(ROPh-DPOxz)** have been calculated from the

Table 2
Electrochemical data of the copolymers

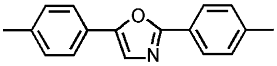
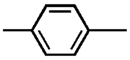
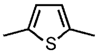
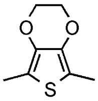
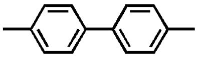
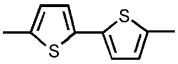
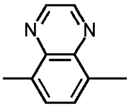
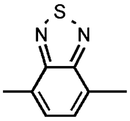
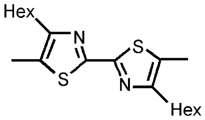
Polymer	Redox peak potential[a] (V *vs.* Ag^+/Ag)			
	n-doping	n-dedoping	p-doping	p-dedoping
P(Flu-DPOxz)	–[b]	−2.30	1.47	1.19
P(ROPh-DPOxz)	−2.50[c]	−2.35	1.09	0.88

[a] Measured by cyclic voltammetry in an MeCN solution of $[Et_4N][BF_4]$ (0.10 M) under N_2. Sweep rate = 30 mV s^{-1}.

[b] Not clearly observed due to overlapping with decomposition current of the solvent.

[c] At the second scan.

Table 3
Electrochemical data (*vs.* Ag^+/Ag) of fluorene copolymers $-(Ar-Flu)_n-$ (Flu = 9,9-dialkylfluorene-2,7-diyl)

−Ar−	E_{pa}	E_{pc}	$E_{pa} - E_{pc}$	Ref.	E_{pa}^{onset}	E_{pc}^{onset}	$E_{pa}^{onset} - E_{pc}^{onset}$	Ref.
	1.47	*ca.* −2.5	*ca.* 4	This work	0.82	−2.29	3.11	This work
	1.43	−2.77	4.20	[18a]	1.07	−2.12	3.19	[18e]
	0.93	−2.73	3.66	[18a]	0.76	−1.89	2.65	[18e]
	0.85	–	–	[18a]	0.82	−1.56	2.38	[18f]
	1.17	−2.73	3.90	[18a]				
	0.74	−2.33	3.07	[18b]	0.69	−2.24	2.93	[18b]
	0.88	−2.39	3.27	[18c]	0.40	−1.40	1.80	[18c]
	0.83	−2.01	2.84	[18c]	0.76	−1.59	2.35	[18c]
	1.19	−2.16	3.35	[18d]				

E_{pa}: oxidation peak current potential (or peak anodic current potential).
E_{pc}: reduction peak current potential (or peak cathodic current potential).
E_{pa}^{onset}: onset potential of the oxidation peak.
E_{pc}^{onset}: onset potential of the reduction peak.

electrochemical data. The energy level of Fc^+/Fc is estimated at 4.8 eV below the vacuum level [20]. The cyclic voltammetry of **P(Flu-DPOxz)** and **P(ROPh-DPOxz)** was performed in a solution of $[NEt_4][BF_4]$ in dry acetonitrile at 30 mV s^{-1} under N_2 as shown in Fig. 5. Under the conditions, the redox couple of Fc^+/Fc was found to be $E^{1/2} = +0.05$ V (*vs.* Ag^+/Ag). According to the following empirical relationships [19],

$$\mathrm{HOMO} = -\left(E_{pa}^{onset} + 4.75\right)\ \mathrm{eV}$$

$$\mathrm{LUMO} = -\left(E_{pc}^{onset} + 4.75\right)\ \mathrm{eV},$$

where E_{pa}^{onset} and E_{pc}^{onset} are the onset potentials measured *vs.* Ag^+/Ag, the HOMO levels of **P(Flu-DPOxz)** and **P(ROPh-DPOxz)** were estimated to be −5.57 and −5.55 eV, and those of LUMO levels were estimated to be −2.46 and −2.45 eV, respectively (cf., Table 4). As described above, the electrochemically measured band gaps of **P(Flu-DPOxz)** and **P(ROPh-DPOxz)** are 3.11 and 3.10 eV, respectively. The optically measured band gaps of **P(Flu-DPOxz)** and **P(ROPh-DPOxz)** (about 2.90 eV) are smaller than the electrochemically measured band gaps; this may be due to the interfacial energy barrier for charge injection to the polymer film in the electrochemical process [21].

Table 4
Energy level data of the copolymers

Polymer	LUMO[a]	HOMO[a]	$E_g^{elec\,b}$ (eV)	$E_g^{\,c}$ (eV, nm)
P(Flu-DPOxz)	−2.46	−5.57	3.11	2.90, 428
P(ROPh-DPOxz)	−2.45	−5.55	3.10	2.90, 428

[a] HOMO and LUMO level estimated from anodic and cathodic onset of the cyclic voltammogram of the polymer film, respectively.
[b] Band gaps determined from the cyclic voltammogram.
[c] The optical gap, E_g, taken as the absorption onset of the UV–vis spectrum of the polymer film.

4. Conclusion

Two copolymers containing the oxazole unit in the main chain have been synthesized by the Suzuki cross-coupling reaction and characterized. The monomer **1** serves as a good starting material to introduce the oxazole unit in π-conjugated polymers. The obtained polymers show high solubility in organic solvents and high thermal stability. The UV–vis and XRD data indicate that the polymers are amorphous in the solid state. The polymers show strong photoluminescence with a quantum yield of about 70%. The polymers are electrochemically active both in the oxidation and reduction regions, and exhibit electrochromism.

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