

Transfer of Photoenergy in π -Conjugated Polymers. Two Types of Photoluminescence that Involve Energy Transfer along a Polymer Chain

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Two types of energy transfer in π -conjugated polymers have been investigated using time-resolved photoluminescence (PL) techniques: type i, perpendicular-type energy transfer from the 2,3-di(*p*-tolyl)-quinoxaline unit to the π -conjugated main chain of poly[2,3-di(*p*-tolyl)quinoxaline-5,8-diyl], and type ii, parallel-type energy transfer from the oligo(pyridine-2,5-diyl) (O–Py) unit to the oligo(selenophene-2,5-diyl) (O–Se) unit in a block-type copolymer of O–Py and O–Se. Both types of energy transfer were very fast with a time constant shorter than approximately 0.1 ns; in particular, the type ii energy transfer took place with a time constant of approximately 5 ps. Both π -conjugated polymers were considered to contain segments with various effective π -conjugation lengths, and the energy transfer to the segment with a larger effective π -conjugation length and a smaller π – π^* transition energy required a longer transition time. A polarizing film was obtained by utilizing the perpendicular-type energy transfer.

Introduction

Energy transfer in photo- or electro-activated π -conjugated polymers is gaining interest,^{1–5} and information on such an energy transfer is expected to provide bases for the application of π -conjugated polymers in photonic and electronic devices such as polymer light-emitting diodes, polymer solar cells, and nonlinear optical devices.^{6,7} Various types of energy transfer are considered to occur in carrier-transporting and light-emitting processes in such devices, thus obtaining basic information on energy transfer is considered to be important.

Previously, we reported the following two types of energy transfer occurring along π -conjugated polymer chains. Herein, we report the results of the two types of energy transfer studied by time-resolved photoluminescence spectroscopy.

Results and Discussion

Perpendicular-Type Energy Transfer. UV–Vis Spectra of P(5,8-Qx(diTol)). Figure 1a shows the UV–vis spectrum of a cast film of P(5,8-Qx(diTol)) on a quartz glass plate. As shown in Figure 1a, P(5,8-Qx(diTol)) shows two main UV–vis peaks at approximately 380 (band A) and 420 nm (band B) in the solid state;⁸ a diphenyl analogue of P(5,8-Qx(diTol)) gives similar UV–vis data. Because monomeric 2,3-di(*p*-tolyl)-quinoxaline and 2,3-diphenylquinoxaline exhibit UV–vis peaks at 353 and 344 nm, respectively, and the lowest energy π – π^* transition of naphthalene is considered to have a transition moment along the long axis (*x* in Scheme 2),^{9,10} the UV–vis peak of P(5,8-Qx(diTol)) at 380 nm (band A) is considered to be associated mainly with the π – π^* transition along the *x* axis in the monomeric 2,3-di(*p*-tolyl)quinoxaline unit (Qx(diTol) unit) shown in Scheme 1. An AM-1 Hamiltonian calculation also indicates that the lowest energy π – π^* transition of 2,3-di(*p*-tolyl)quinoxaline ($\lambda_{\text{max}} = 353$ nm; Scheme 2) has a transition moment along the *x* axis.

However, the UV–vis peak of P(5,8-Qx(diTol)) at 420 nm (band B) is considered to correspond to a π – π^* transition with a transition moment along the polymer main chain (*y* axis in Scheme 1).

A poly(vinyl alcohol) (PVA) film was painted with a solution of P(5,8-Qx(diTol)) and dried, and a free-standing film containing P(5,8-Qx(diTol)) molecules was stretched for a dichroism measurement to obtain experimental evidence for this view. Such stretching of the PVA film induces the alignment of the main chain of π -conjugated P(5,8-Qx(diTol)) molecules in the stretching direction, as depicted in Figure 2, similar to the cases of previously reported π -conjugated poly(pyridine-2,5-diyl), poly(1,10-phenanthroline-3,8-diyl), and related polymers,^{4d,11} and gives the assignment for the π – π^* transition that occurred along the π -conjugated polymer main chain.

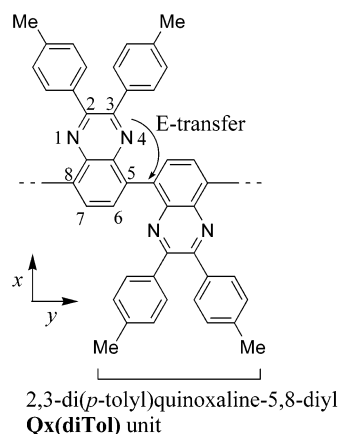
As shown in part b of Figure 1, P(5,8-Qx(diTol)) in the PVA film also gives two absorption bands, band A and band B.¹² When the PVA film was stretched to a stretching ratio, R_s , (for R_s , cf. the caption of Figure 2) of 4.9 (part b-2 of Figure 1) and irradiated with \parallel and \perp polarized lights (\parallel and \perp indicate that the directions of the oscillating electric field of the polarized light are parallel and perpendicular, respectively, to the direction of the stretching of the film), a clear dichroism was observed. The absorption at band B is enhanced upon irradiation with \parallel polarized light, whereas it is weakened upon irradiation with \perp polarized light. These results indicate that band B is assigned to the π – π^* transition occurring mainly along the π -conjugated polymer main chain.

For band A shown in part b-2 of Figure 1, it became clearer upon irradiation with \perp polarized light, supporting the above-described assignment of band A.

Homologues of P(5,8-Qx(diTol)) and P(5,8-Qx(diPy))⁸ with two 2-pyridyl groups at the 2,3-positions and P(5,8-Qx(PhBu))⁸ with phenyl and butyl groups at the 2,3-positions showed similar dichroisms (cf. S1 in the Supporting Information). P(5,8-Qx(PhBu)) was soluble in nonacidic solvents such as chloroform, and the UV–vis spectrum of P(5,8-Qx(PhBu)) in chlo-

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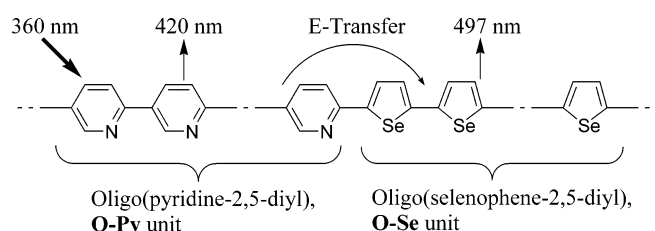
[‡] Saitama University.

SCHEME 1: Two Types of Energy Transfer(i) Perpendicular-type energy transfer in π -conjugated quinoxaline polymer^{4g}

Absorption:

 $\lambda_{\max} = 380 \text{ nm}$ and 420 nm

The **Qx(diTol)** unit accepts the energy of x-polarized light (absorption peak = 380 nm). The absorbed photoenergy is transferred to the π -conjugated system along the polymer chain (absorption peak = 420 nm) and emits y-polarized light with $\lambda_{\max} = 492 \text{ nm}$.

Poly(2,3-di-*p*-tolylquinoxaline-5,8-diyl), **P(5,8-Qx(diTol))**⁸(ii) Parallel-type energy transfer in block type π -conjugated copolymer^{4d}Block copolymer^{4d}

$\lambda_{\max} = 360 \text{ nm}$ for the **O-Py** unit,
 420 nm for the **O-Se** unit.

The photoenergy absorbed by the **O-Py** unit (absorption peak = 360 nm) is partly transferred to the **O-Se** unit (absorption peak = 420 nm), and the copolymer emits 497 nm light from the **O-Se** unit. The molar ratio of the pyridine unit to the selenophene unit is 4:1.

roform gave two peaks sharper than those of the polymer in the film at 340 nm (band A') and 393 nm (band B'), as exhibited in the Supporting Information (S1). The broader UV-vis peaks of the π -conjugated polymer in the solid phase (in the cast film and PVA film) suggest the presence of some intermolecular interaction between the polymer molecules. The excitation spectrum of P(5,8-Qx(PhBu)) in chloroform normally showed two peaks at the positions of bands A' and B'. For other polyquinoxalines, the measurement of UV-vis and PL spectra in nonacidic solutions was not possible.

Photoluminescence, Energy Transfer, and Polarizing Film.

As shown in Figure 3, the irradiation of the PVA-P(5,8-Qx(diTol)) film with light at 420 nm (the peak position of the band B) gives PL with a peak position at 492 nm , which agrees with the onset position of band B, indicating that this simple PL takes place normally by the electronic transition between the electronic states associated with band B.

The dichroism of PL also supports this view. When non-polarized light at 420 nm was irradiated to the stretched PVA-P(5,8-Qx(diTol)) film, the parallel (\parallel) component of the emitted light was stronger than the perpendicular (\perp) component to give dichroic ratios (R_d) of 3.6 and 4.2 at stretching ratios (R_s ; cf. Figure 2) of 4.9 and 7.3, respectively.

$$R_d = \frac{\text{int}(\parallel)}{\text{int}(\perp)}$$

where $\text{int}(\parallel)$ and $\text{int}(\perp)$ represent the intensities of the \parallel and \perp

components of emitted light, respectively, and \parallel represents a direction parallel to the stretching direction. Irradiation with \parallel -polarized 420-nm light gave larger R_d values of 4.5 and 9.5 at R_s values of 4.9 and 7.3, respectively. These data are consistent with the notion that this simple PL has a transition moment mainly along the direction of the π -conjugated polymer main chain and is associated with the electron transfer between electronic states associated with band B. Similar dichroic PL behavior of the π -conjugated polymer has been reported.^{11b}

Irradiation with light at 380 nm (the peak position of the band A) gives essentially the same PL spectrum with a peak at 492 nm , suggesting that the photoenergy captured by the monomeric 2,3-di(*p*-tolyl)quinoxaline unit is transferred to the π -conjugation system along the polymer chain.

Irradiation with \perp -polarized light and monitoring the \parallel -polarized PL at 492 nm gives the excitation spectra depicted in Figure 4. As shown in Figure 4, the excitation spectrum obtained at a high R_s values exhibits a peak only at the position of band A, and the peak at the position of band B becomes unobservable, although the UV-vis spectrum of the stretched film has both absorption bands, as depicted in Figure 1. The results in Figure 4 indicate that when R_s is large ($R_s = 7.3$; curve b), the light absorbed at band A contributes mainly to the \parallel mode PL at 492 nm ; Figure 5 shows this situation of the stretched film.

Time-Resolved PL Spectra Associated with Energy Transfer. As described above, the photoenergy absorbed at band A is transferred to the electronic states associated with band B (the perpendicular-type energy transfer depicted in Scheme 1)

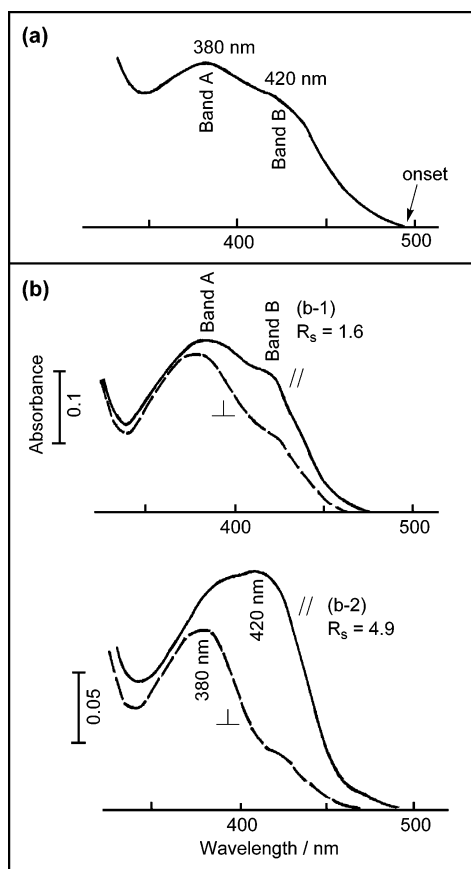
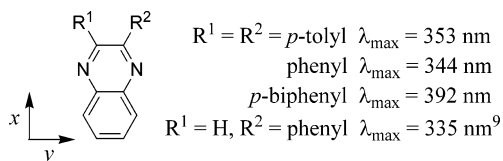


Figure 1. UV-vis spectra of (a) P(5,8-Qx(diTol)) film on a quartz plate and (b) stretched PVA film containing P(5,8-Qx(diTol)) molecules at stretching ratios (R_s) of 1.6 (b-1) and 4.9 (b-2). The // and \perp marks in part b indicate the UV-vis spectra observed upon irradiation with polarized light with the oscillating electric field parallel and perpendicular, respectively, to the stretching direction of the film.

SCHEME 2: UV-Vis Data of 2,3-Diarylquinoxaline (in Ethanol)



and is emitted through the electronic transition related to band B. The time-resolved PL data obtained by irradiation with light at band A will give basic information on the perpendicular-energy transfer.

A 347-nm laser pulse was irradiated to the cast film of P(5,8-Qx(diTol)) on a quartz glass plate and the PVA-P(5,8-Qx(diTol)) film to avoid the direct excitation of band B at its slope absorption. Examples of the emission decay curves monitored at 450, 470, 500, and 600 nm at 293 K are shown in Figure 6. Films of P(5,8-Qx(diPh)) and P(5,8-Qx(PhBu)) showed similar decay curves. From the initial linear part of the $\log(\text{intensity})-t$ decay curves, the lifetime (τ) of the PL was evaluated, and the τ values obtained under various conditions are summarized in Tables 1 and 2. Some of the data are given in the Supporting Information (S2).

The data shown in Tables 1 and 2, which were obtained with a cast film of P(5,8-Qx(diTol)) on a quartz glass plate and PVA-P(5,8-Qx(diTol)) films, show the following features of energy transfer: (i) When PL is monitored at 460 nm for the P(5,8-Qx(diTol)) film cast on a quartz glass plate, a lifetime of

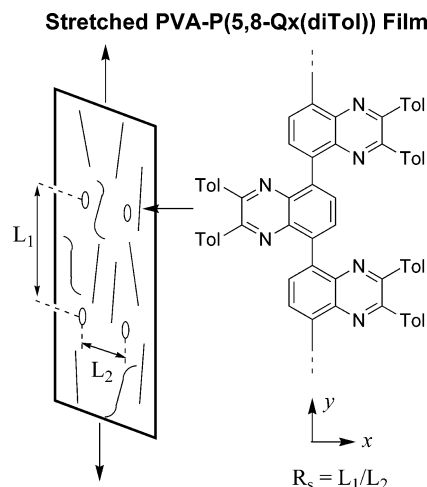


Figure 2. Alignment of P(5,8-Qx(diTol)) in the surface region of stretched PVA film. Four \circ marks were made to form a square before stretching the film. After the stretching, the stretching ratio (R_s) was determined from the size of the rectangle. $R_s = L_1/L_2$.

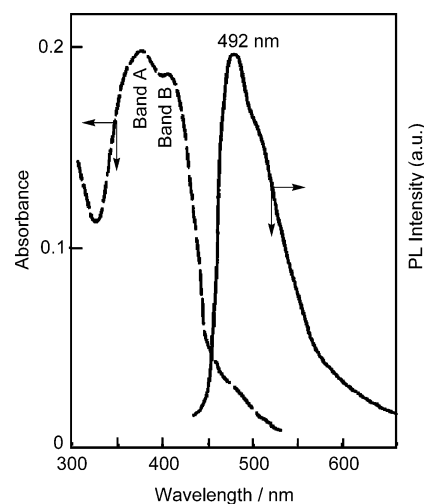


Figure 3. PL (—) and UV-vis (---) spectra of PVA-P(5,8-Qx(diTol)) film. The PL spectrum was obtained by irradiation with 420-nm light. Irradiation with 380-nm light gave a similar PL spectrum.

about 0.3 ns is obtained (Table 1). (ii) When PL is monitored at a longer wavelength with a larger Stokes shift, its lifetime becomes longer, and the slowing down of decay is more obvious at a lower temperature, suggesting that emission at a longer wavelength involves thermal processes. In contrast, the PL lifetime of monomeric 2,3-di(p -tolyl)quinoxaline (cf. Scheme 2), measured by irradiation with 370-nm light, remains constant (about 0.3 ns in a cast film at 293 K) in the PL monitoring range of 390–460 nm, as depicted in the Supporting Information (S3). For the thermal process, two processes are conceivable. First, the activated polymer molecule may form an excimer-like adduct with a polymer molecule in the ground state and emit PL light with a longer wavelength. Such a formation of the excimer-like adduct is often observed with linear π -conjugated polymers, such as poly(pyridine-2,5-diyl) and poly-(1,10-phenanthroline-3,8-diyl).¹¹ Another explanation is based on the possibility that P(5,8-Qx(diTol)) contains various segments with different effective π -conjugation lengths. The thermal movement of the polymer chain will give various segments with various effective π -conjugation lengths, which will be in dynamic equilibrium. Generally, an activated π -conjugated unit with a smaller π -conjugation length and a higher $\pi-\pi^*$ transition energy transfers its energy to a π -conjugated

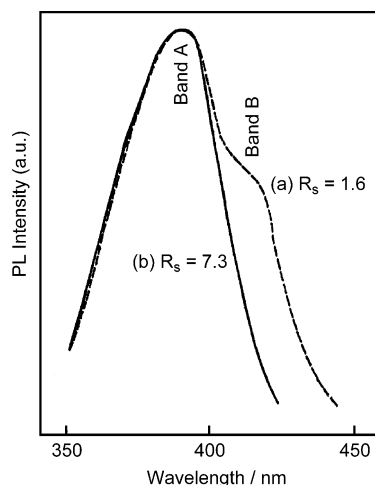


Figure 4. Excitation spectra of PVA-P(5,8-Qx(diTol)) film at (a) R_s (stretching ratio of the film) = 1.6 (---) and (b) R_s = 7.3 (—). The \perp -polarized light is irradiated and the PL intensity is measured in the \parallel mode at 492 nm. The \perp and \parallel directions indicate perpendicular and parallel directions, respectively, to the direction of the stretching of the film.

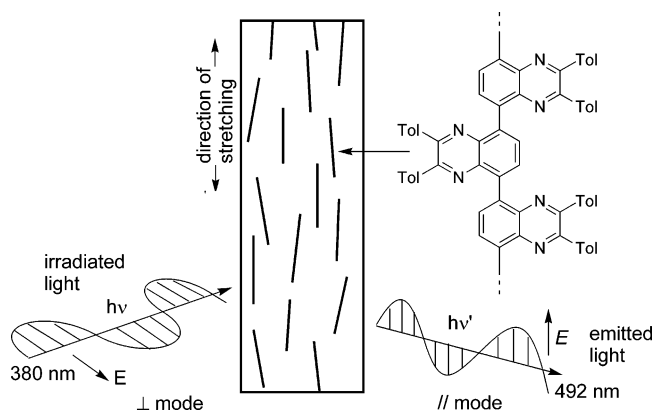


Figure 5. PVA-P(5,8-Qx(diTol)) film for rotating 380-nm \perp mode light to 492-nm \parallel mode light.

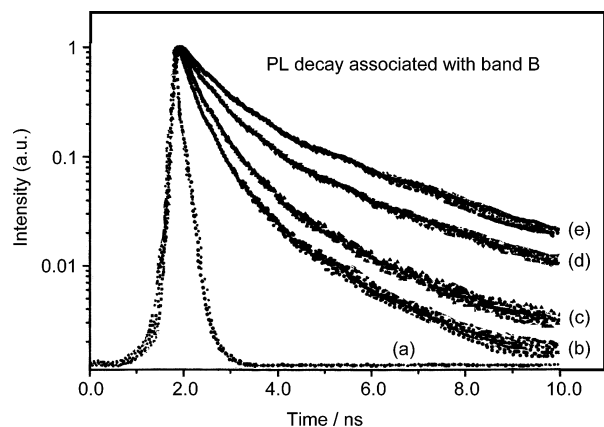


Figure 6. Emission decay curves of PVA-P(5,8-Qx(diTol)) film (stretching ratio R_s = 4.9) measured at 293 K. (a) Laser pulse (347 nm) profile; intensity decay monitored at (b) 450, (c) 470, (d) 500, and (e) 600 nm. A laser pulse at 347 nm corresponding to band A was irradiated.

unit with a larger π -conjugation length and a lower π - π^* transition energy.^{3a,4a} If one assumes such an energy transfer to π -conjugated segments with a lower π - π^* transition energy, the longer PL lifetime observed at a longer PL wavelength is accounted for. (iii) A PVA-P(5,8-Qx(diTol)) film with a small

TABLE 1: Emission Lifetimes of P(5,8-Qx(diTol)) Film Cast on a Quartz Glass Plate at 293 and 77 K^a

wavelength of monitoring light (nm)	293 K	77 K
	lifetime τ (ns)	lifetime τ (ns)
450		0.36
460	0.29	
475		0.49
500	0.44	0.55
525		0.67
550	0.61	0.74
580	0.53	1.55

^a Excitation wavelength = 347 nm.

TABLE 2: Emission Lifetimes of PVA-P(5,8-Qx(diTol)) Film^a

(I) R_s = 1.6 at 293 and 77 K		
wavelength of monitoring light (nm)	293 K	77 K
	lifetime τ (ns)	lifetime τ (ns)
450		0.41
460	0.34	
470	0.39	0.51
500	0.42	0.67
530	0.47	1.1
550	0.53	
560		1.4
580	0.53	1.6
(II) R_s = 4.9 at 293 and 77 K		
wavelength of monitoring light (nm)	293 K	77 K
	lifetime τ (ns)	lifetime τ (ns)
450	0.36	0.63
460	0.39	
470	0.41	0.63
500	0.48	0.84
530	0.64	1.1
550	0.78	
560		1.4
580	0.97	1.7

^a Excitation wavelength = 347 nm.

R_s of 1.6 gives time-resolved PL data similar to those observed with a P(5,8-Qx(diTol)) film cast on a quartz glass plate (Table 2-I). Because the rate of the above-described excimer forming reaction, if it occurs, is considered to be slower in the PVA-P(5,8-Qx(diTol)) film than in the P(5,8-Qx(diTol)) film due to the separation of P(5,8-Qx(diTol)) molecules in the PVA matrix, then these data suggest the importance of the energy transfer between the segments described above (ii). (iv) At a larger R_s value of 4.9 (Table 2-II), the PL lifetime is extended, particularly at 450–470 nm at 77 K.

The above-described features of PL support the view that the energy captured by the 2,3-di(*p*-tolyl)quinoxaline unit is transferred rapidly to segments in the π -conjugated main chain of P(5,8-Qx(diTol)) before the emission of PL light from the 2,3-di(*p*-tolyl)quinoxaline unit (approximately 0.3 ns; cf. S3 in the Supporting Information). When the segment with a smaller effective π -conjugation length accepts the energy, it further transfers the obtained energy to a segment with a larger effective π -conjugation length. Because light emission at a relatively short wavelength of 450–470 nm has a lifetime of about 0.3 ns, which essentially agrees with the PL lifetime of 2,3-di(*p*-tolyl)-

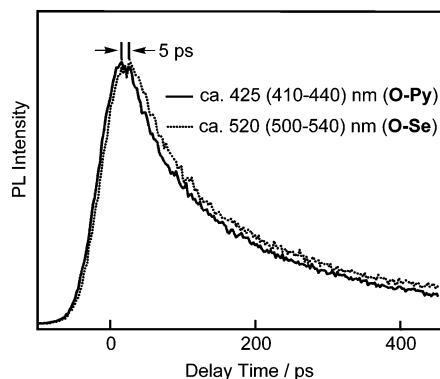


Figure 7. Temporal profiles of the PL intensity of the copolymer in formic acid monitored at approximately 425 (—, from the O-Py unit) and 520 nm (···, from the O-Se unit), excited with a 360-nm 130-fs laser pulse at room temperature and at the UV-vis peak of the O-Py unit. The streak camera method was used.

quinoxaline, the perpendicular-type energy transfer from the 2,3-di(*p*-tolyl)quinoxaline unit to the main chain π -conjugated system is considered to take place within a short time (presumably 0.1 ns or less). However, the perpendicular-type energy transfer may be delayed at 77 K in the PVA-P(5,8-Qx(diTol)) film with a larger R_s value of 4.9 (Table 2-II).

Parallel-Type Energy Transfer. As shown in (ii) of Scheme 1 and previously reported,^{4d} the photoenergy at 360 nm captured by the O-Py unit is transferred partly to the O-Se unit in the block copolymer to emit two types of PL light at 420 (from the O-Py unit) and 497 nm (from the O-Se unit). The additional UV-vis and PL data shown in the Supporting Information (S4 through S8) also support such an energy transfer.

Because the block-type copolymer gives emission from both the O-Py and O-Se units after irradiation of the O-Py unit, the time lag of the two types of emission is expected to give information on the rate of the parallel-type energy transfer. For this purpose, a picosecond time-resolved fluorescence spectrometer consisting of a streak camera and a femtosecond laser system were used.

Figure 7 shows the data of the time-resolved PL monitored at 425 and 520 nm after irradiation of a 360-nm (UV-vis peak of the O-Py unit) laser pulse. In Figure 7, the rapid rise and decay of PL are observed at both 425 and 520 nm. A rise-time difference of about 5 ps is observed between the PL at 425 nm and that at 520 nm, indicating that the parallel-type energy transfer takes approximately 5 ps. A shift of the PL band to a longer wavelength was also observed after 150 ps using the streak camera technique, as shown in the Supporting Information (S9), supporting the energy transfer from the O-Py unit to the O-Se unit.

When a 420-nm laser pulse, corresponding to the absorption by the O-Se unit, was irradiated, only PL from the O-Se unit was emitted, as shown in the Supporting Information (S6). In this case, the shift of the PL band to a longer wavelength was observed after approximately 155 ps, as shown in Figure 8, and this shift is considered to be caused by the energy transfer from an O-Se unit with a smaller effective π -conjugation length to other O-Se units with larger effective π -conjugation lengths, similar to the case of P(5,8-Qx(diTol)).

Supporting data for the above-described time delay of about 5 ps between PL from the O-Py unit at 420 nm and that from the O-Se unit at 525 nm were obtained by femtosecond time-resolved fluorescence spectroscopy using an upconversion technique. The data are shown in the Supporting Information (S10 and S11), which support the notion that PL from the O-Se

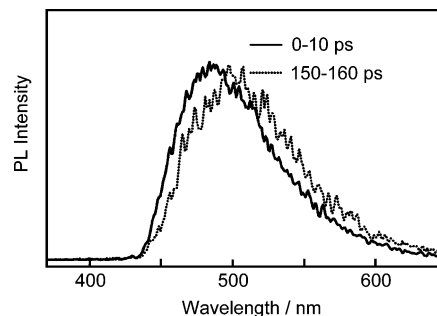


Figure 8. PL profiles of the copolymer in formic acid after irradiation of a 420-nm (UV-vis peak of the O-Se unit) laser pulse at room temperature. The streak camera method was used. A shift of the PL peak to a longer wavelength is observed after 150–160 ps, which is assigned to the shift in energy from a shorter O-Se unit to a longer O-Se unit with a smaller π - π^* transition energy.

unit has a delay time of approximately 5 ps compared with that from the O-Py unit. The deconvolution of the decay curves shown in Figure 7 gave a short-lifetime component with $\tau_1 = 70$ ps (for PL from the O-Py unit) or 78 ps (for PL from the O-Se unit) and a long-lifetime component with $\tau_2 = 300$ ps (for PL from the O-Py unit) or 360 ps (for PL from the O-Se unit), respectively.

Experimental Section

Materials. P(5,8-Qx(diTol)) (molecular weight = 24 000) and its analogues⁸ and a copolymer (molar ratio of Py units to Se units = 4:1)^{4d} were prepared according to the literature. 2,3-Di(*p*-tolyl)quinoxaline was prepared following a method developed by Bost and Towell.¹³ Poly(vinyl alcohol) (degree of polymerization = 4000) was kindly donated by the Nippon Synthetic Chemical Industry Co., Ltd.

Preparation of Film Samples. A P(5,8-Qx(diTol)) film was prepared by casting its formic acid solution on a quartz glass plate. After removing formic acid by evaporation, the film was immersed in aqueous ammonia and dried under vacuum. An ethanol solution of 2,3-di(*p*-tolyl)quinoxaline was cast on a quartz glass plate, which was then dried under vacuum; this resulted in a 2,3-di(*p*-tolyl)quinoxaline film (powdery). Poly(vinyl alcohol) film, which was prepared by casting from a 4:1 mixture of water and ethanol and drying, was painted with a formic acid solution of P(5,8-Qx(diTol)) and dried under vacuum. The cast P(5,8-Qx(diTol)) film on the quartz glass plate and PVA-P(5,8-Qx(diTol)) had absorbances of approximately 0.1–0.2.

Measurements. A time-correlated photocounting system with a mode-locked Nd:YAG laser, a synchronously pumped dye laser, a photomultiplier tube, and a time-amplitude converter was used for P(5,8-Qx(diTol)) (perpendicular-type energy transfer). For the parallel-type energy transfer in the copolymer, an optical system using a femtosecond Ti/sapphire regenerating amplifier (Clark-MXR CPA-2000), a femtosecond optical parametric amplifier (Clark-MXR IR-OPA), and a streak camera (Hamamatsu Photonics C4334) were used. For the upconversion method, the optical system used is shown in the Supporting Information, and the cross-correlation time between the pump pulse (360 nm) and the gate pulse (775 nm) was about 560 fs.

Conclusions

The photoenergy absorbed by a 2,3-di(*p*-tolyl)quinoxaline unit in P(5,8-Qx(diTol)) is transferred to the π -conjugated main chain system of the polymer. For such an energy transfer, a transition

time of less than 0.1 ns was estimated. The π -conjugated main chain was considered to contain segments with various effective π -conjugation lengths, and the energy transfer to a segment with a larger effective π -conjugation length required a longer time. The energy transfer from the O–Py unit to the O–Se unit in the copolymer occurred with a transition time of about 5 ps. These results are expected to provide the bases for understanding basic electronic and photonic processes in π -conjugated polymers and the application of π -conjugated polymers in photonic and electronic devices.

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Supporting Information Available: Wavelength dependence of PL lifetime of PVA-P(5,8-Qx(diTol)), emission lifetime of 2,3-di(*p*-tolyl)quinoxaline, UV–vis and PL spectra of copolymer, PL profiles of copolymer at approximately 5 and 155 ps, optical system for upconversion method, and data obtained by upconversion method. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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