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Helically π -Stacked Conjugated Polymers Bearing Photoresponsive and Chiral Moieties in Side Chains: Reversible Photoisomerization-Enforced Switching Between Emission and Quenching of Circularly Polarized Fluorescence

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Novel multifunctional conjugated polymers, [poly(*p*-phenylene)s and poly(bithienylene-phenylene)s with (*R*)- and (*S*)-configurations], which have fluorescence, chirality, and photoresponsive properties, have been designed and synthesized. The polymers are composed of π -conjugated main chains, where poly(*p*-phenylene) and poly(bithienylene-phenylene) are fluorescence moieties, and the side chains of the photochromic dithienylethene moiety are linked with chiral alkyl groups. The polymer films exhibit right- or left-handed circularly polarized fluorescence (CPF) and also show reversible quenching and emitting behaviors as a result of photochemical isomerization of the dithienylethene moiety upon irradiation with ultraviolet and visible light. This is the first report realizing the reversible switching of CPF using chirality and photoresponsive properties.

1. Introduction

Conjugated polymers are promising materials for use in organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), photovoltaic cells, and biosensors.^[1–5] Chiral conjugated polymers are expected to show circularly polarized luminescence when they form helical structures. They can be prepared by the introduction of a chiral moiety into a side chain.^[6–8] However, the circularly polarized fluorescence (CPF) cannot be controlled in intensity like a switching between emitting and non-emitting (quenching) states, which is desirable for dynamic control of

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Recently, the photochemical control of linearly polarized fluorescence (LPF) has been performed by using liquid crystalline and conjugated copolymers with photoresponsive dithienylethene moieties in the side chain.^[12e] When the polymer-based device of LPF is fabricated, the relative arrangement between the LPF polymer film and the linear polarizer should be rigorously controlled. Namely, the aligned LPF polymer film must be exactly arranged

parallel or perpendicular to the linear polarizer. Otherwise, the light passing through the LPF film and the polarizer is insufficiently polarized, which gives rise to incompletely polarized light. Nevertheless, this type of fabrication becomes much more difficult and time consuming when the size of the device becomes smaller in the micro- or nano-order. One way to avoid such a difficulty in the device fabrication of LPF is to deal with CPF. This is because CPF is free from the macroscopic alignment of the polymer, and the degree of circular polarization of the polymer film depends on that of one-handed screwing in the helical polymer and/or that of the helical π -stacking of polymers. Besides, CPF is easily transformed into LPF by passing the light of CPF through a 1/4 (quarter) wave plate.

Here, we have designed and synthesized multifunctional conjugated polymers, [poly(*p*-terphenylene)s and poly(bithienylene-phenylene)s with (*R*)- and (*S*)-configurations], which have fluorescence, chiral, and photoresponsive properties. The polymers are composed of π -conjugated main chains where poly(*p*-terphenylene) and poly(bithienylene-phenylene) are fluorescence moieties, and photochromic dithienylethene moieties^[9] are linked with chiral alkyl groups in the side chains.

Scheme 1 depicts the structures of the polymers composed of a main chain, where the π -conjugated aromatic unit is a fluorescent moiety (green frame), and a side chain bears a photochromic







Scheme 1. Structures of photoresponsive chiral conjugated polymers.

dithienylethene moiety (red frame) linked with the chiral moiety (blue frame).

The present polymer films exhibit right- or left-handed CPF owing to a helically π -stacked or weakly twisted structure, and also show reversible quenching and emitting behaviors in CPF as a result of photochemical isomerization of the dithienylethene moiety upon irradiation of ultraviolet and visible lights. This is the first report realizing the reversible switching of CPF emission by using chiral and photoresponsive properties.

2. Results and Discussion

2.1. Synthesis and Characterization of Polymers

Synthetic routes of monomer (*R*)-**5** and polymers (*R*)-**P1** and (*R*)-**P2** are shown in Scheme 2. Ethyl-4-[(*R*)-1-methyloctoxy]benzoate [(*R*)-**2**] was synthesized by Mitsunobu coupling of **1** with (*S*)-2-nonanol in tetrahydrofuran (THF).^[14] The hydrolysis of (*R*)-**2** with NaOH in a mixed solvent of MeOH and water gave 4-[(*R*)-1-methyloctox-y]benzoic acid [(*R*)-**3**]. The esterification between the hydroxy group of the dithienylethene derivative $4^{[12e]}$ and (*R*)-**3** gave (*R*)-**5** in the presence of dicyclohexylcarbodiimide (DCC) and 4-



Scheme 2. Synthetic routes and photoisomerization. Conditions: a) (*S*)-2-nonanol, DIAD, PPh₃, THF. b) NaOH, H₂O, MeOH. c) DCC, DMAP, CH_2Cl_2 . d) 4,4'-Biphenyldiboronic acid bis (neopentylglycol)cyclic ether, Pd (PPh₃)₄, NaHCO₃, THF, H₂O. e) 5,5'-Bis-trimethylstannyl-2,2'-bithiophene, Pd₂(dba)₃ (2-furyl)₃P, THF. DCC = dicyclohexylcarbodiimide, DMAP = 4-(dimethylamino)pyridine, DIAD = diisopropyl azodicarboxylate, dba = dibenzilideneacetone, * = chiral substituent.



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(dimethylamino)pyridine (DMAP) in CH_2Cl_2 . The copolymerization between the monomer (*R*)-**5** and 4,4'-biphenyldiboronic acid bis(propyl glycol)cyclic ester in a mixture of THF and water in the presence of Pd(PPh₃)₄ as a catalyst was carried out through a Suzuki coupling reaction to give (*R*)-**P1**.^[15] The copolymerization of (*R*)-**5** and 5,5'-bis-trimethylstannyl-2,2'-bithiophene in THF in the presence of Pd₂(dba)₃ (dba = dibenzylideneacetone) and (2-furyl)₃P as catalysts was carried out through a Stille polycondensation reaction to give (*R*)-**P2**.^[16] The polymers (*S*)-**P1** and (*S*)-**P2** were obtained by synthetic routes similar to those for (*R*)-**P1** and (*R*)-**P2**, respectively.

All polymers synthesized were fusible and soluble in organic solvents such as THF, toluene, and CHCl₃. The number-average molecular weights (M_n) of (R)-P1 and (S)-P1 were 1.4 × 10⁴ and 1.1 × 10⁴, respectively, while those of (R)-P2 and (S)-P2 were 1.0 × 10⁴ and 8.0 × 10³, respectively. The degree of polymerization (DP) was calculated to be 9–15, indicating that the polymer main chain consists of 27–45 aromatic rings.

Photoisomerization of the dithienylethene moiety upon irradiation with UV ($\lambda = 254$ nm) and visible ($\lambda > 400$ nm) light was confirmed by ¹H NMR analysis in CDCl₃. Two broad signals observed at 5.30 and 5.34 ppm were assigned to the methylene protons neighboring the dithienylethene moiety with an open form. Irradiation of UV light ($\lambda = 254$ nm, 16 W) caused the photoisomerization, giving new broad signals at 5.05 and 5.08 ppm that corresponded to the methylene protons neighboring the dithienylethene moiety with a closed form. The integrated intensities of the proton signals indicated that the open forms of 44% and 30% were converted into the closed forms in the photostationary states (PSS) of P1 and P2, respectively. Here, the PSS is defined as {[closed form]/([open form] + [closed form])} \times 100.^[9a,12c,e] In other words, the dithienvlethene moieties of 56% and 70% remained unchanged in the open forms of P1 and P2, respectively, even upon UV light irradiation. Meanwhile, the degrees of conversion from the open into the closed form in the

cast films of **P1** and **P2** were 10% and 9–7%, respectively. Note that the degree of conversion in the cast film was evaluated in the following way: The cast film, after irradiation by UV light, was stripped off from the substrate and then dissolved in CDCl₃ for ¹H NMR measurement.

After subsequent irradiation with visible light, all proton signals of the open form reappeared. The results of polymerization and the conversion value are summarized in Table 1.

Thermal properties of the polymers were examined through differential scanning calorimetry (DSC) and polarized optical microscopy (POM). Broad peaks associated with the phase transition were observed by DSC. The broadening may be attributed to a high viscosity and wide polydispersity of the polymer. As summarized in Table 1, the phase transition temperatures during the heating process of (*R*)-**P1** (open) and (*S*)-**P1** (open) were 69 and 70 °C, respectively, while those in the cooling one are 65 and 68 °C, respectively. Similarly, the phase transition temperatures in the heating



Table 1. Polymerization results, conversion rates from the open to the closed form in the dithienylethene moiety, and transition temperature of the polymers.

Polymer	M _n [a]	<i>M</i> _w [b]	$M_{\rm w}/M_{\rm n}$	DP [c]	Conversion rate [d]		Transition temperature [e] [°C]	
					in $CDCl_3$	film	heating	cooling
(R)- P1	14 000	255 000	18	15	44	10	69	65
(S)- P1	11000	104 000	10	12	44	10	70	68
(R)- P2	10 000	30 000	3.0	11	30	9	52	50
(S)- P2	8 000	14 000	1.8	9	30	7	69	64

[a] Number-average molecular weight evaluated with a polystyrene (PS) standard. [b] Weight-average molecular weight evaluated with a PS standard. [c] Degree of polymerization. [d] Conversion rate from the open form into the closed form under irradiation of UV light. [e] Transition temperature between glass and meso phases in the open form.

process of (*R*)-**P2** (open) and (*S*)-**P2** (open) were 52 and 69 $^{\circ}$ C, respectively, while those in the cooling one are 50 and 64 $^{\circ}$ C, respectively (see also Supporting Information Fig. S1 and S2). The polymers showed mesophases in both heating and cooling processes over a wide range of temperatures, which indicates an enantiotropic nature.

2.2. Absorption and CD Spectra

(*R*)-**P1** (open) and (*R*)-**P2** (open) dissolved in CHCl₃ showed absorption bands at 343 and 429 nm, respectively, which correspond to $\pi - \pi^*$ transitions of the polymer main chains. The band at 250 nm in the open form of the dithienylethene moiety decreased in intensity after irradiation with UV light for 1 min. At the same time, the bands around 350 and 520 nm, attributable to

the closed form of the dithienvlethene moiety, gradually increased in intensity. Subsequent irradiation with visible light for 5 min caused an increase in intensity at 250 nm and a decrease in intensity around 350 and 520 nm, as shown in Figure 1a and 1c. The cast films of (R)-P1 and (R)-P2, prepared from the mixture of CHCl₃ and toluene at room temperature, showed absorption bands at 360 and 470 nm, respectively, assignable to $\pi - \pi^*$ transitions of the conjugated main chain. The results are shown in Figure 2a and 2d. It is worth noting that the absorption band attributed to the main chain of the (R)-P2 showed a large red-shift of 41 nm in the cast film, while that of (R)-P1 showed a red-shift of only 17 nm. This is likely because the coplanarity of the main chain increased more in the (R)-P2 cast film than in the (R)-P1 one. Figure 2b and 2e show difference absorption spectra between the open form and the PSS of the (R)-P1 and (R)-P2 films, respectively. The reversible change between the open form and the PSS, which is a result of the photoisomerization of the dithienylethene



moiety in the side chain, was observed in both polymer films.

The polymers, **P1** and **P2**, dissolved in CHCl₃, toluene, or THF, showed no Cotton effect in the region of the $\pi - \pi^*$ transition of the conjugated main chain in circular dichroism (CD) spectra, although they gave imperceptible signals in the shorter wavelength region such as 253–258 nm, due to overlapped absorption bands between the dithienylethene moiety and the phenylene one linked with the chiral alkyl moiety (see Supporting Information Fig. S3 and S4). This result suggests that the main chain of the polymer does not form an intrachain one-handed helical structure in solution, even though the polymer has a chiral alkyl moiety in the side chain. This might be rationalized by the fact that the center of chirality in the side chain is far from the conjugated main chain, which makes through-bond and/or through-space intramolecular interactions difficult. The chirality only effects the phenylene and dithienylethene moieties in the side chain.

However, the cast films showed CD signals with Cotton effects in the $\pi - \pi^*$ transition region of the polymer main chain. CD spectra of P1 and P2 films are shown in Figure 2c and 2f, respectively. The (R)-P1 film exhibited a split CD band, where the positive and negative Cotton effects were observed from the longer to shorter wavelengths. The (S)-P1 film also showed a split CD band, giving a mirror image to that of the (R)-P1 film. This implies that the polymers in the film are each assembled to form a onehanded helical interchain π -stacking structure. It is also understandable that the direction of the helical π -stacked structure depends on the configuration of the chiral moiety in the side chain. According to the bisignate exciton coupling theory,^[17] it can be assumed that the (R)-P1 film has a P-helicity with a right-handed (clockwise) π -stacked structure. The (S)-P1 film has a M-helicity with a left-handed (counterclockwise) π -stacked structure. On the other hand, the (R)-P2 and (S)-P2 films showed CD bands with mirror images of each other. However, the CD bands gave no splitting shape and relatively weak signals compared with those of



Figure 1. a) UV-vis absorption and b) fluorescence spectra of (*R*)-**P1** and those (c and d) of (*R*)-**P2** in CHCl₃ (4.0×10^{-5} M). The wavelength of excitation for fluorescence was 350 nm. Insets show photographs of emitting and quenching between the open form and the PSS in solution (excitation wavelength of 370 nm, 4 W, handheld lamp).







Figure 2. UV-vis absorption spectra and difference spectra between the PSS and the open form of (R)-P1 (a and b) and (R)-P2 (d and e) cast films, respectively, and CD spectra of P1 (c) and P2 (f) cast films upon photoisomerization between the open form and the PSS of the dithienylethene moiety.

P1 films. This suggests that the P2 polymers form loosely π -stacked helical structures. The non-straight and rather bent backbone of P2, which consists of bithiophene-monophenylene repeat units, might be less suitable for the formation of interchain π -stacking, and results in a weak CD signal.

Interestingly, there is no difference in CD spectra between the open form and the PSS, irrespective of **P1** and **P2** films and also of the (*R*)- and (*S*)-configuration. This indicates that the helical π -stacked structure of the **P1** film and the chiral structure of the **P2** film remain unchanged even after the reversible photoisomerization between the open form and PSS in the side chain. This may allow us to exploit the chiroptical properties such as CPF during the photochemical isomerization, as will be mentioned below.

2.3. Fluorescence Spectra

The fluorescence band at 410 nm of (R)-**P1** (open) and that at 530 nm of (R)-**P2** (open) in CHCl₃ drastically decreased in intensity and then quenched upon the irradiation with UV light after 50 to



60 s. However, the quenched fluorescence was regenerated by irradiation with visible light for 5 min, which leads to a reversible photoswitching of fluorescence, as shown in Figure 1b and 1d. The ratio of fluorescence intensity between the open form and the PSS (I_{open}/I_{PSS}) was 180 for (R)-P1 and 20 for (R)-P2. The fluorescence quantum yields of the open form and PSS for (R)-P1 were 0.65 and 0.005, respectively, and those for (R)-P2 were 0.23 and 0.01, respectively. The quantum yields of the open form and PSS for (S)-P1 and (S)-P2 were very similar to those of the corresponding polymers with (R)configurations (see Table 2). The fluorescence quantum yield was evaluated by using quinine sulfate in 1.0 M sulfuric acid as a standard solution. The quenching of the fluorescence might be a result of an efficient energy transfer from the excited polymer main chain to the closed form of the dithienylethene moiety. However, the excited dithienylethene of the closed form changes to its ground state through a non-radiative transition. A similar quenching behavior in fluorescence was observed in the cast film, as shown in Figure 3a and 3c. The results of fluorescence intensity (I_{open}/I_{PSS}) in

CHCl₃ and cast films of **P1** and **P2** are summarized in Table 2. The ratio of fluorescence intensity (I_{open}/I_{PSS}) at 413 nm in the (R)-**P1** film was 240, and the corresponding value at 570 nm in the (R)-**P2** film was 80.

Here it is useful to compare the fluorescence quantum yields of the cast films with those in solution. As seen in Table 2, the absolute fluorescence quantum yields of (*R*)- and (*S*)-**P1** films were 0.16 and 0.14, respectively; those of (*R*)- and (*S*)-**P2** films were 0.04 and 0.03, respectively. It is evident that the quantum yields of **P1** films are about 4 to 6 times larger than those of **P2** ones. The relative strength in quantum yield between **P1** and **P2** films is consistent with the case of solution where the quantum yield (0.65) of **P1** dissolved in chloroform is about three times larger than that (0.23–0.24) of **P2** in chloroform. Note that the fluorescence quantum yields of the polymer films are substantially smaller in absolute value than those in solution. This may be a result of concentration quenching in the film, because the film is composed of neat polymer. Whereas the polymer in solution is dispersed in chloroform, so is free from concentration quenching.

Table 2. Fluorescence quantum yields and CPF intensity ratios between the open and PSS states in CHCl₃ (4×10^{-5} M) and cast films of P1 and P2.

Polymer	In CHO	Cl ₃	Film				
	I _{open} /I _{PSS} (E _m [nm]) [a]	$\phi_{\sf open}$ ($\phi_{\sf PSS}$) [a][b]	I _{open} /I _{PSS} (E _m [nm])	$\phi_{ m open}$	$\Delta I_{\rm open}/\Delta I_{\rm PSS}$ [d] ($E_{\rm m}$ [nm])	$g_{ m em}$ [e] (± 0.005)	
(R)- P1	180 (410)	0.65 (0.005)	240 (413) [a]	0.16 [a]	13 (414) [a]	-1.0×10^{-2} [a]	
(S)- P1	130 (410)	0.65 (0.005)	200 (413) [a]	0.14 [a]	12 (422) [a]	$+1.0 \times 10^{-2}$ [a]	
(R)- P2	20 (530)	0.23 (0.01)	80 (570) [c]	0.04 [c]	7 (650) [c]	$+1.0 \times 10^{-2}$ [c]	
(S)- P2	24 (530)	0.24 (0.01)	73 (575) [c]	0.03 [c]	5 (630) [c]	-1.5×10^{-2} [c]	

[a] Excitation at 350 nm. [b] Quinine sulfate in 1.0 \times sulfuric acid as a standard solution. [c] Excitation at 380 nm. [d] Δl : CPF intensity. [e] Dissymmetric factor defined as the ratio between fluorescence and CPF intensities; $g_{em} = (I_L - I_R)/[(I_L + I_R)/2] = \Delta I/I$.



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Figure 3. Fluorescence spectra of a) (*R*)-**P1** and c) (*R*)-**P2** and CPF spectra of b) **P1** and d) **P2** cast films. The wavelength of excitation light for fluorescence was 350 nm for **P1** and 380 nm for **P2**. The inset shows photographs of the emitting film of the open form and the quenching film of the PSS of (*R*)-**P1** and (*R*)-**P2** (excitation wavelength $\lambda = 370$ nm, 4 W, handheld lamp).

2.4. CPF Spectra

It is of interest that the polymers show CPF as well as CD in cast films, although they show neither CPF nor CD in solution, except the weak CD signal that corresponds to overlapped absorption bands of the dithienylethene and the phenylene moieties linked with the chiral alkyl moiety. The formation of helical π -stacking structures of P1 is supported by the observation of CPF in cast films, as shown in Figure 3b. The open forms (R)- and (S)-P1, show negative and positive signs in the CPF spectra, respectively. The sign in the CPF spectra is defined as $\Delta I = I_{\rm L} - I_{\rm R}$, where $I_{\rm L}$ and $I_{\rm R}$ represent left- and right-handed fluorescence intensities, respectively. The positive and negative signs in CPF indicate the formation of the left- and right-handed helical structures, respectively. It follows that the (R)- and (S)-P1 films have rightand left-handed screw structures, respectively, which is consistent with the results of CD spectra. Figure 3b also shows that the CPF intensity of the P1 film drastically decreases, irrespective of the



Figure 4. Reversible changes of CPF intensities of (R)-**P1** and (S)-**P1** at 414 nm in a cast film upon alternating irradiations of UV (light blue area) and visible (yellow area) light.

configuration, upon photoisomerization from the open form to the PSS. Namely, the quenching of CPF occurs in the PSS, which is associated with the quenching of fluorescence itself. The reverse photoisomerization from the PSS to the open form causes a reappearance of the CPF band. Such a photoswitching behavior was observed over 10 cycles, as shown in Figure 4. It should be noted that the (R)- and (S)-P2 films exhibit CPF spectra with positive and negative signs, respectively, as shown in Figure 3d. These signs are opposite to those of the (R)- and (S)-P1 films, which suggests that the loosely π -stacked structure of the P2 film has an opposite helical sense to that of the P1 film, although the detailed mechanism remains unclear.^[8c,18]

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The ratio of CPF intensities ($\Delta I_{\text{open}}/\Delta I_{\text{PSS}}$) between the open form and the PSS of the (*R*)-**P1** film at 414 nm and that of the (*R*)-**P2** film at 650 nm were 13 and 7, respectively, which are smaller than the corresponding ratios of the fluorescence intensities (240 and 80 in $I_{\text{open}}/I_{\text{PSS}}$ for (*R*)-**P1** and (*R*)-**P2**, respectively). The

ratios of the CPF intensities ($\Delta I_{\rm open}/\Delta I_{\rm PSS}$) in cast films of P1 and P2 are also summarized in Table 2. The remaining weak CPF emission observed in the PSS is a result of a small amount of the open form, which isomerized from the closed form during the CPF measurement. The degree of circular polarization in fluorescence was evaluated using the dissymmetry factor, $g_{\rm em}$. This factor is defined by the equation; $g_{em} = (I_L - I_R)/[(I_L + I_R)/2] = \Delta I/I = V_{AC}/2$ $V_{\rm DC}$. $I_{\rm R}$ and $I_{\rm L}$ denote the right- and left-handed CPF intensities, respectively, and V_{DC} and V_{AC} are measured values that correspond to the fluorescence and CPF intensities. As shown in Figure 5 and Table 2, the gem values for the P1 and P2 films were estimated to be in the order of 10^{-2} at 414 nm and 650 nm, respectively. Finally, it should be emphasized that the helical π -stacked structure formed in the films of the present conjugated polymers is so rigid that it is not affected by the photochemical opening and closing isomerization reaction of the dithienylethene moiety in the solid state. This allowed us to control the reversible switching of the CPF between emission and quenching states through photochemical irradiations, by maintaining the chirality of the polymers.

3. Conclusions

Novel photoresponsive chiral π -conjugated polymers have been synthesized by introducing dithienylethene moieties linked with chiral alkyl groups into the polymer side chains. It is implied that the cast films of **P1** polymers, which consist of a straight backbone of terphenylene moieties as repeat units, have helical π -stacked structures of their main chains. Meanwhile, the cast films of **P2**, which consists of a bent backbone of bithienylene-monophenylene moieties as repeat units, are suggested to have a weakly π -stacked structure. The cast films of the two kinds of conjugated polymers exhibited right- or left-handed CPF with relatively large dissymmetry factors in the order of 10^{-2} . The emission and quenching of CPF of the cast films are reversibly switched



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(*R*)-P1 (open) (*R*)-P1 (PSS)

Figure 5. Dissymmetry factors (g_{em}) of a) P1 and b) P2 films in open form and the PSS.

through the photoisomerization of the dithienylethene moiety introduced in the side chain. The present polymers could be useful for advanced chiroptical materials with photochemically switchable CPF properties.

4. Experimental

Measurements: ¹H and ¹³C NMR spectra were measured in CDCl₃ using a JEOL AL-400 spectrometer. Chemical shifts were represented in parts per million downfield from tetramethylsilane (TMS) as an internal standard. Mass spectrometry was performed with a JEOL JMS-SX102A spectrometer. The molecular weights of polymers were determined by gel permeation chromatography (GPC) using a Shodex A-80M column and a JASCO HPLC 870-UV detector with THF used as solvent during measurements. The instrument was calibrated with a polystyrene standard. Phase transition temperatures were determined using a TA Instrument Q-100 differential scanning calorimeter with a constant heating/cooling rate of 10 °C min⁻¹, and texture observations were carried out under crossed nicols by using a Zeiss AxioImager M1m polarizing microscope equipped with a Zeiss AxioCam MRc5 digital camera and a Linkam TH-600PM heating and cooling stage with temperature control.

Optical absorption (UV-vis) spectra were measured using a JASCO V-570 spectrometer. CD spectra were measured with JASCO J-820 spectrometer. Fluorescence spectra were measured using a JASCO FP-750 spectrometer. Fluorescence quantum yields were measured using a JASCO FP-6500 spectrometer equipped with an ILF-533 integrating sphere. CPF measurements were performed with a JASCO CPL 200S spectrometer with a quartz cell or substrate at room temperature. Photo-irradiation was



carried out using a UV ($\lambda\!=\!254\,\text{nm},\,4\,\text{W})$ or visible ($\lambda\!>\!400,\,100\,\text{W})$ mercury lamp as a light source at room temperature.

Samples for UV-vis, CD, PL, and CPF measurements were prepared by casting the polymer dissolved in a mixture of CHCl₃ and toluene on a quartz substrate. The thickness of the polymer film was in the range of 1.0–1.2 $\mu m.$

Materials: Compound 4 and bis-trimethylstannyl-2,2'-bithiophene were prepared by procedures described in the literature.^[12e] 4-Hydroxybenzoic acid ethyl ester, diisopropylazodicarboxylate (DIAD, 40 wt % in toluene, ~1.9 M), dicyclohexylcarbodiimide (DCC), and 4-(dimethylamino)pyridine (DMAP) were purchased from Tokyo Kasei (TCI). Triphenylphosphine (PPh₃), and (*R*)- and (S)-2-nonanol were purchased from Wako Pure Chemical Industries. 4,4'-Biphenyldiboronic acid bis(neopentylglycol) cyclic ether, *tris*(dibenzylideneacetone)dipalladium(0) [Pd₂(dba)₃], tri-2furylphosphine [(2-furyl)₃P], and *tetrakis*(triphenylphosphine)palladium(0) [Pd(PPh₃)₄] were purchased from Aldrich Co. Ltd THF was dried and distilled over sodium benzophenone ketyl under Ar. CH₂Cl₂ was distilled over CaCl₂ under argon atmosphere. MERCK Silicagel 60 (particle size 0.063–0.200 mm) was used for column chromatography.

Ethyl-4-[(R)-1-methyloctoxy]benzoate [(R)-2]: A solution of DIAD (4.0 mL, 7.69 mmol) in THF (5.0 mL) was added to a mixture of 4hydroxybenzoic acid ethyl ester 1 (1.02 g, 6.17 mmol), triphenylphosphine (1.80 g, 6.96 mmol), and (S)-2-nonanol (1.00 g, 6.94 mmol) in THF (20 mL). The reaction mixture was stirred at 0°C for 1h under Ar atmosphere. The resulting precipitate was extracted with CHCl₃, thoroughly washed with saturated NaCl solution, and dried over anhydrous sodium sulfate. The precipitate was removed by filtration, and the filtrate was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, CH₂Cl₂) to give 1.94 g (99%) of (R)-2 as a yellow oil. HRMS (EI, m/z):[M]⁺ calcd. for C₁₈H₂₈O₃: 292.2038; found, 292.2034. ¹H NMR (400 MHz, CDCl₃, δ): 0.88 (t, 3H, J = 6.8 Hz, $-CH_3$), 1.27–1.34 (m, 15H, $-OCHCH_3$ and $-OCH(CH_2)_6CH_3$), 1.37 (t, 3H, $J = 7.2 \text{ Hz}, -\text{COOCH}_2\text{CH}_3), 4.33 \text{ (q, 2H, } J = 7.2 \text{ Hz}, -\text{COOCH}_2\text{CH}_3), 4.43$ (sext, 1H, J = 6.8 Hz, $-OCH(CH_3)C_7H_{15}$), 6.87 (d, 2H, J = 8.8 Hz, ortho to $-OCH(CH_3)C_7H_{15}$, 7.96 (d, 2H, J = 8.8 Hz, meta to $-OCH(CH_3)C_7H_{15}$). ¹³C NMR (400 MHz, CDCl₃, δ): 14.0, 14.1, 19.6, 22.6, 25.4, 29.2, 29.5, 31.8, 36.3, 60.2 (sp³, -OCH₂CH₃), 74.0 (sp³, -OCH(CH₃)C₇H₁₅), 114.9 (sp², phenylene), 120.5 (sp², phenylene linked to carbonyl moiety), 131.7 (sp², phenylene), 162.3 (sp², phenylene carbon linked to ether type oxygen), $165.7 (sp^2, -COOC_2H_5).$

4-[(R)-1-Methyloctoxy]benzoic acid [(R)-3]: Compound (R)-2 (1.94 g, 6.65 mmol) was hydrolyzed by NaOH (3.10 g, 77.5 mmol) in 10 mL of water and 120 mL of MeOH at 60 °C for 4 h. The solvent was then evaporated, and the product was dissolved in water. The mixture was acidified to pH 1 with hydrochloric acid solution. The resulting precipitate was extracted with CHCl₃, thoroughly washed with saturated NaCl solution, and dried over anhydrous sodium sulfate. The precipitate was removed by filtration, and the filtrate was evaporated under reduced pressure to yield 1.65 g (94%) of a colorless oil. HRMS (EI, m/z): $[M]^+$ calcd. for C₁₆H₂₄O₃: 246.1725; found, 246.1725. ¹H NMR (400 MHz, CDCl₃, δ): 0.88 (t, 3H, J = 6.4 Hz, $-CH_3$), 1.28-1.75 (m, 15H, $-OCHCH_3$ and $-OCH(CH_2)_6CH_3)$, 4.45 (sext, 1H, J = 6.4 Hz, $-OCH(CH_3)C_7H_{15}$), 6.90 (d, 2H, J = 8.7 Hz, ortho to $-OCH(CH_3)C_7H_{15}$), 8.04 (d, 2H, J = 8.7 Hz, meta to -OCH(CH₃)C₇H₁₅). ¹³C NMR (400 MHz, CDCl₃, δ): 14.1, 19.6, 22.6, 25.4, 29.2, 29.5, 31.8, 36.3, 74.0 (sp³, -OCH(CH₃)C₇H₁₅), 114.9 (sp², phenylene), 120.9 (sp², phenylene linked to carbonyl moiety), 132.9 (sp², phenylene), 162.7 (sp², phenylene carbon linked to ether type oxygen), 171.4 (sp², -COOH).

1-{5-(2,5-Dibromobenzoyloxymethylene)-2-methylthien-3'-yl]-2-[5-{4-((R)-1-methyloctoxy)benzoyloxymethylene)}-2-methylthien-3-yl]-3, 3, 4, 4, 5, 5hexafluorocyclopentene [(R)-5]: A solution of compound 4 (0.68 g, 0.98 mmol), (R)-3 (0.24 mg, 0.89 mmol), DCC (0.22 mg, 1.0 mmol), and DMAP (0.13 mg, 1.1 mmol) in CH₂Cl₂ (20 mL) was stirred for 14 h at room temperature. The crude product was extracted with CHCl₃. The organic layer was washed with saturated NaCl solution and dried over anhydrous sodium sulfate. The precipitate was removed by filtration, and the filtrate was evaporated under reduced pressure. The residue was purified with column chromatography (silica gel; CHCl₃) to give 450 mg (54%) of (R)-5



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as a yellow oil. HRMS (EI, m/z): [M]⁺ calcd. for C₄₀H₁₆O₅Br₂F₆O₂: 934.0432; found, 934.0478. ¹H NMR (400 MHz, CDCl₃, δ): 0.87 (t, 3H, −CH₃), 1.27–1.73 (m, 15H, $-OCHCH_3$ $l = 6.5 \, \text{Hz},$ and $-OCH(CH_2)_6CH_3$, 1.89 (s, 6H, thienyl-CH₃), 4.43 (sext, 1H, J = 6.5 Hz, -OCH(CH₃)C₇H₁₅), 5.36 (s, 2H, -COOCH₂-), 5.40 (s, 2H, $-COOCH_2-$), 6.86 (d, 2H, J=8.9 Hz, ortho to $-OCH(CH_3)C_7H_{15}$), 7.08 (s, 1H, thienyl-H), 7.13 (s, 1H, thienyl-H), 7.45 (d, 1H, J=8.6 Hz, phenyl-H), 7.51 (d, 1H, J = 8.6 Hz, phenyl-H), 7.88 (s, 1H, phenyl-H), 7.96 (d, 2H, J = 8.9 Hz, meta to-OCH(CH₃)C₇H₁₅). ¹³C NMR (400 MHz, CDCl₃, δ): 14.1, 14.4 (2 × sp³ signals, thienyl-CH₃), 22.6, 25.4, 29.2, 29.5, 31.7, 36.3, 60.4 $(sp^3, -OCH_2-)$, 61.4 $(sp^3, -OCH_2-)$, 75.0 $(sp^3, -OCH$ -OCH(CH₃)C₇H₁₅), 115.0, 120.4, 120.9, 121.3 (sp², phenylene linked to carbonyl moiety), 124.4, 124.4, 127.3, 128.5, 131.7, 132.9 (sp², phenylene linked to carbonyl moiety), 134.1, 135.1, 135.6, 135.7, 136.7, 143.1, 143.7 162.3 (sp², phenylene carbon linked to ether type oxygen), 164.2 (sp², -OCO-), 165.7 (sp², -OCO-).

(R)-P1: A solution of (R)-5 (158 mg, 0.17 mmol), 4,4'-biphenyldiboronic acid bis(neopentylglycol)cyclic ether (64.3 mg, 0.17 mmol), and Pd(PPh₃)₄ (2.0 mg, 1.7 $\mu mol)$ in 10 mL of THF and 5 mL of 40% Na_2CO_3 aq. was stirred under Ar at 55 °C overnight. The reaction mixture was poured into a large amount of methanol (250 mL) and stirred for 15 min. The resulting precipitate was collected by filtration and dissolved in the minimum amount of THF (3 mL) and stirred in H₂O (300 mL) for 1 h. After filtration, the product was dried under vacuum to give 182 mg (99%) of a colorless powder. ¹H NMR (400 MHz, CDCl₃, δ): 0.86 (br, 3H, -CH₃), 1.25 (br, 15H, -OCHCH₃ and -OCH(CH₂)₆CH₃), 1.79 (br, 3H, thienyl-CH₃), 1.84 (br, 3H, thienyl-CH₃), 4.39 (br, 1H, -OCH(CH₃)C₇H₁₅), 5.30 (br, 2H, -COOCH2-), 5.34 (br, 2H, -COOCH2-), 6.89 (br, 2H, ortho to -OCH(CH₃)C₇H₁₅), 7.05 (br, 1H, thienyl-H in dithienylethene), 7.14 (br, 1H, thienyl-H in dithienylethene), 7.50-7.71 (br, 11H, phenyl-H in main chain), 7.94 (br, 2H, meta to $-OCH(CH_3)C_7H_{15}$) ¹³C NMR (400 MHz, CDCl₃, δ): 14.0, 14.3, 19.5, 22.6, 25.4, 29.2, 29.5, 31.7, 36.2, 60.4 (2 × sp³ signals, -OCH₂-), 74.0 (sp³, -OCH(CH₃)C₇H₁₅), 114.9 (sp², phenylene in side chain), 121.3 (sp², phenylene linked to carbonyl moiety), 124.2, 124.7, 127.4, 128.8, 131.6 (sp², phenylene in side chain), 136.7, 162.3 (sp², phenylene carbon linked to ether type oxygen), 165.7 (sp², -OCO-) (see Fig. S5 in the Supporting Information).

(R)-P2: A solution of Pd₂(DBA)₃ (3.5 mg, 3.4 µmol) and (2-furyl)₃P (3.5 mg, 13.5 μ mol) in 1 mL of THF was stirred under Ar at 50 °C for 15 min. 5,5'-bis-trimethylstannyl-2,2'-bithiophene (191 mg, 0.34 mmol) and (R)-5 (316 mg, 0.34 mmol) were then added to the mixture. After stirring at 50 °C for 3 days, the reaction mixture was poured into a large amount of methanol (400 mL) that contained 12 N HCl (3 mL) and vigorously stirred for 15 min. The resulting precipitate was collected by filtration and dissolved in a minimum amount of THF (3 mL) and stirred in methanol (300 mL) for 24 h. After filtration, the product was dried under vacuum to give 318 mg (99%) of an orange powder. ¹H NMR (400 MHz, CDCl₃, δ): 0.83 (br, 3H, -CH₃), 1.21-1.28 (m, 15 H, -OCHCH₃ and -OCH(CH₂)₆CH₃), 1.79 (br, 3H, thienyl-CH₃), 1.83 (br, 3H, thienyl-CH₃), 4.39 (br, 1H, -OCH(CH₃)C₇H₁₅), 5.28 (br, 2H, -COOCH₂-), 5.32 (br, 2H, $-COOCH_2-$), 6.83 (d, 2H, J = 8.8 Hz, ortho to $-OCH(CH_3)C_7H_{15}$), 6.98 (br, 2H, thienyl-H in dithienylethene), 7.13-7.96 ppm (m, 7H, phenyl-H and thienyl-H in main chain), 7.92 (d, 2H, J = 8.8 Hz, meta to-OCH(CH₃)C₇H₁₅). ¹³C NMR (400 MHz, CDCl₃, δ): 14.1, 19.5, 22.6, 25.4, 29.2, 29.5, 31.7, 36.2, 60.4 (sp³, -OCH₂-), 61.2 (sp³, -OCH₂-), 74.0 (sp³, -OCH(CH₃)C₇H₁₅), 114.9 (sp², phenylene in side chain), 121.3 (sp², phenylene linked to carbonyl moiety), 124.2, 124.7, 127.3, 128.0, 131.6 (sp², phenylene in side chain), 136.7, 143.0, 143.5, 162.3 (sp² phenylene carbon linked to ether type oxygen), 165.7 (sp^2 , -OCO-), 167.7 $(sp^2, -OCO-)$ (see Fig. S6 in the Supporting Information).

Similar chemical properties were obtained for the enantiomeric compounds (S)-2, (S)-3, (S)-5, (S)-P1, and (S)-P2.

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