

Self-Assembled Aromatic Conjugated Polymers
with Advanced Optical Properties

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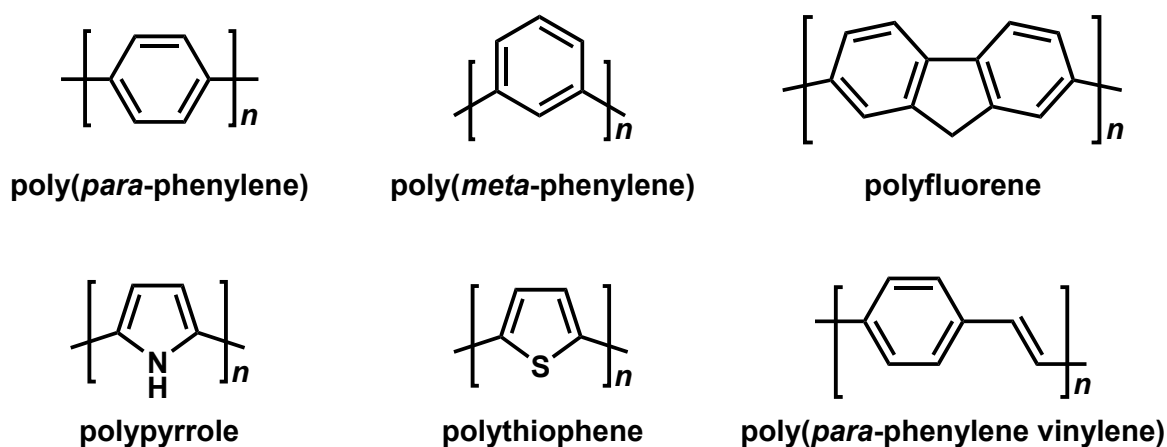
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General Introduction

Background

1. Aromatic Conjugated Polymers

Aromatic conjugated polymers (ACPs) have a main chain consisting of aromatic rings and hence they are chemically stable even in air. Due to the π -electrons delocalized over the main chain, ACPs have semiconducting properties such as electroconductivity, luminescence, and photo-harvesting behavior, and are therefore regarded as promising materials for next-generation optoelectronic devices.¹⁻⁷ Effective conjugation length, which represents the degree of π -electron delocalization, is one of the most important index for the properties of ACPs. In general, ACPs consisting of highly coplanar aromatic rings show the relatively longer effective conjugation length as well as lower band gap energy. For example, poly(*para*-phenylene) and polyfluorene have a wide band gap, resulting in blue-colored luminescence. Meanwhile polythiophene, which has a narrow band gap, exhibits red-colored luminescence, good photo-harvesting properties, and high carrier conductivity. The representative ACPs are shown in Scheme 1.



Scheme 1. Representative aromatic conjugated polymers.

It is well known that the semiconducting properties of ACPs has anisotropy because these properties arise from π -electrons on ACP main chain. This means that both the primary structure and the higher-order structures of ACPs are indispensable factors to be accounted for in achieving advanced optoelectronic properties and functions.⁶⁻¹¹ Thus, various methods such as self-organization,¹²⁻¹⁴ macroscopic alignment,¹⁵⁻²⁰ and intra- and inter-molecular interactions²¹⁻²⁵ have been proposed so as to control the conformation, arrangement, and alignment of the main chains.

2. Ionic Conjugated Polymers

Ionic conjugated polymer (ICP) is an amphiphilic polymer consisting of a hydrophobic conjugated main chain and hydrophilic ionic side chains. Because ICPs can interact with other ionic molecules via the electrostatic interaction, they were used as the optical probes of the chemical and biological sensors.²⁶⁻³⁰ In other case, ICPs are regarded as promising candidates for self-assembling materials due to their amphiphilic property.³¹⁻⁴⁰ Moreover, ICPs can form various helical structures by interacting with chiral molecules.^{41-46, 22-25, 46-56} Thus, ICPs are much attractive from the viewpoint of the supramolecular construction.

3. Circular Dichroism and Circularly Polarized Luminescence (g factor)⁵⁷

When the left- and right-handed circularly polarized lights are absorbed to a different extent, the difference is called circular dichroism (CD). The difference in absorption intensity of circularly polarized light is often observed in the absorption region of optically-active molecules. The differential molar extinction coefficient ($\Delta\varepsilon$) is defined as follows:

$$\Delta\varepsilon = \varepsilon_L - \varepsilon_R$$

Here, ε_L and ε_R are the molar extinction coefficients for left- and right-handed circularly polarized lights. The average molar extinction coefficient is defined as

$$\varepsilon = (\varepsilon_L + \varepsilon_R)/2$$

The strength of the circular polarization is evaluated with the dissymmetry factor. The

dissymmetry factor in absorption (g_{abs}) is defined as the ratio of CD and unpolarized absorption:

$$g_{\text{abs}} = \Delta\epsilon/\epsilon = (\epsilon_L - \epsilon_R)/\epsilon = 2(\epsilon_L - \epsilon_R)/(\epsilon_L + \epsilon_R)$$

Circularly polarized luminescence (CPL) is the analogue of CD. When there is difference in intensity between the left- and right-handed luminescence, the luminescence is called CPL. Similarly to CD, the differential luminescent intensity (ΔI) is defined as follows:

$$\Delta I = I_L - I_R$$

Here, I_L and I_R are the left- and right-handed luminescent intensity, respectively. The average luminescent intensity is given by

$$I = (I_L + I_R)/2$$

Thus, the dissymmetry factor in luminescence (g_{lum}) is defined as follows:

$$g_{\text{lum}} = \Delta I/I = (I_L - I_R)/I = 2(I_L - I_R)/(I_L + I_R)$$

The dissymmetry factor is a convenient quantity to compare different systems quantitatively. Moreover, the g_{abs} and g_{lum} factors are related to the absorption and luminescence of molecules, and therefore their values reflect the molecular chirality in the ground and excited states, respectively.

4. Excitation Chirality Method⁵⁸

Excitation chirality method is one of the most powerful methods to determine the absolute configuration of chiral molecules. When two (or more) chromophores are located nearby in space and constitute a chiral system, their transition dipole moments interact spatially, causing the split of the energy level of the excited state. The split, which is called Davydov splitting (Figure 1a), affects both the absorption and CD bands, and consequently provides the split of CD band, i.e., the CD couplet consisting of two Cotton effects. Figure 1b shows representative UV-vis absorption and CD spectra of the axially chiral binaphthyl derivatives. The CD bands at longer and shorter wavelengths are called 1st and 2nd Cotton effects and are related with the excitation to

α and β states, respectively. Such CD couplet is also called a bisignate Cotton effect. Positive bisignate Cotton effect means that positive and negative Cotton effects of CD couplet are observed at longer and shorter wavelengths, respectively. On the other hand, negative bisignate Cotton effect means that negative and positive Cotton effects of CD couplet are observed at longer and shorter wavelengths, respectively. When a chiral molecule shows positive bisignate Cotton effect in the CD spectra, the chirality of the transition moments on the chromophores is clockwise (Figure 1c). Meanwhile, when the chiral molecule shows negative bisignate Cotton effect, the chirality is counterclockwise (Figure 1d). The signs of the bisignate Cotton effect completely depend on the configuration of the chromophores, and hence the absolute configuration is always determined by using CD spectra.

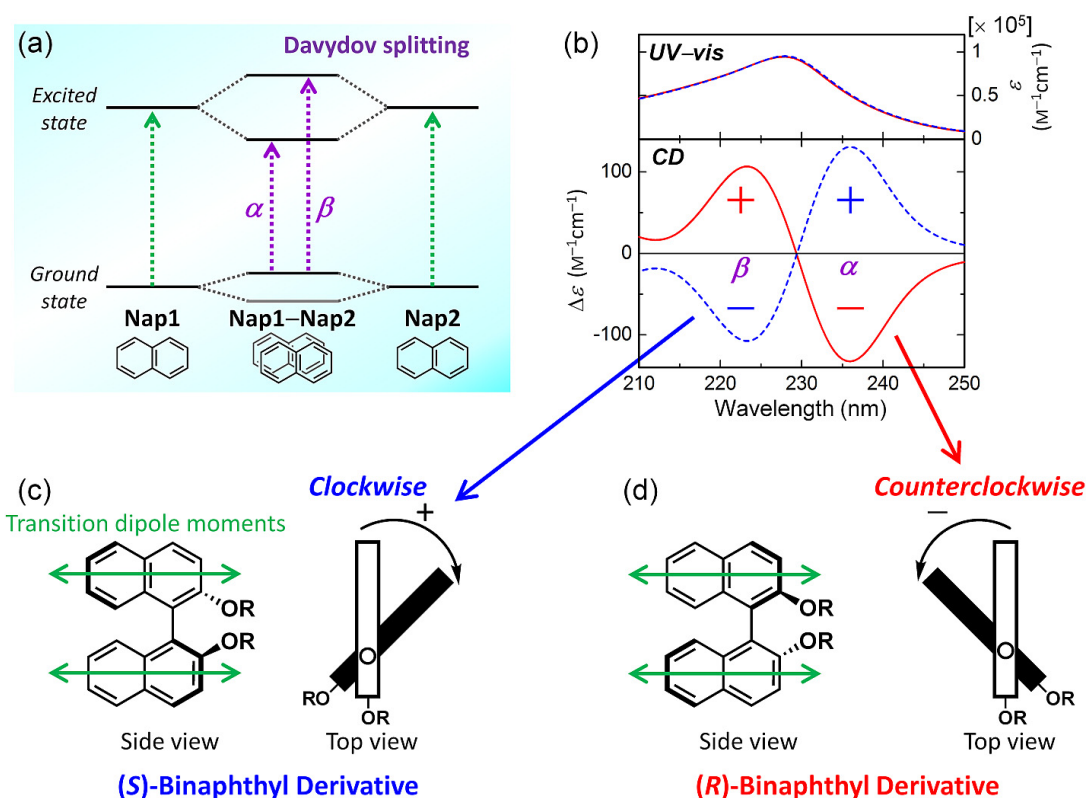


Figure 1. (a) Schematic diagram of exciton coupling between two naphthyl rings. (b) UV-vis absorption and CD spectra of axially chiral binaphthyl derivatives. (c,d) Schematic models of binaphthyl derivatives with (c) (*R*)- and (d) (*S*)-configurations.

5. Helical Conjugated Polymers

Helical conjugated polymers have attracted considerable interest because they provide unique optical functions such as circular polarizations in absorption and luminescence^{22, 59-61} and novel physico-chemical properties.⁶² In addition, helical conjugated polymers can also be used as chiral templates and chiral sensors.¹ Various types of helical conjugated polymers, represented by helical polyacetylenes,⁶³ amino acid-containing substituted polyacetylene derivatives,^{64, 65} poly(phenylacetylene) derivatives,^{12, 21, 66} poly(*meta*-phenylene arylene) derivatives,⁶⁷⁻⁷⁰ and polythiophene derivatives,⁷¹ have been proposed. These helical conjugated polymers are constructed with intrachain-spiral, intrachain-twisted, or interchain-helically π -stacked structures (Figure 2).^{13, 72} Among these structures, the interchain-helically π -stacking interaction is intriguing, because it enables ACPs to self-assemble into an interchain helix thereby generating amplified chiroptical properties such as CPL. CPL is a fascinating property of ACPs that arises from their molecular chirality or helicity, eliminating the requirement for macroscopic alignment of the polymers that is required for linearly polarized luminescence.

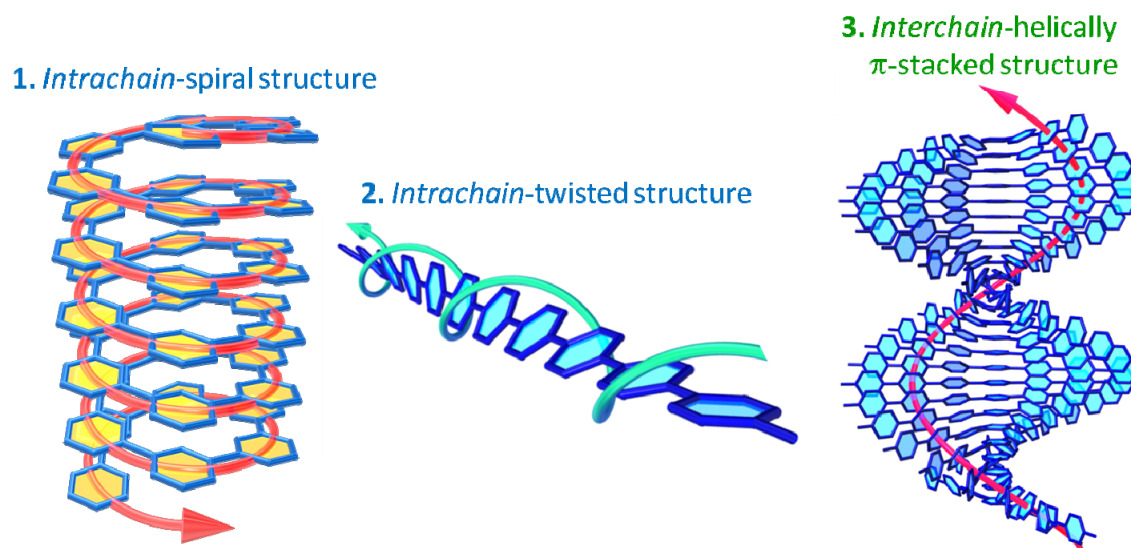


Figure 2. Various helical structures of conjugated polymers

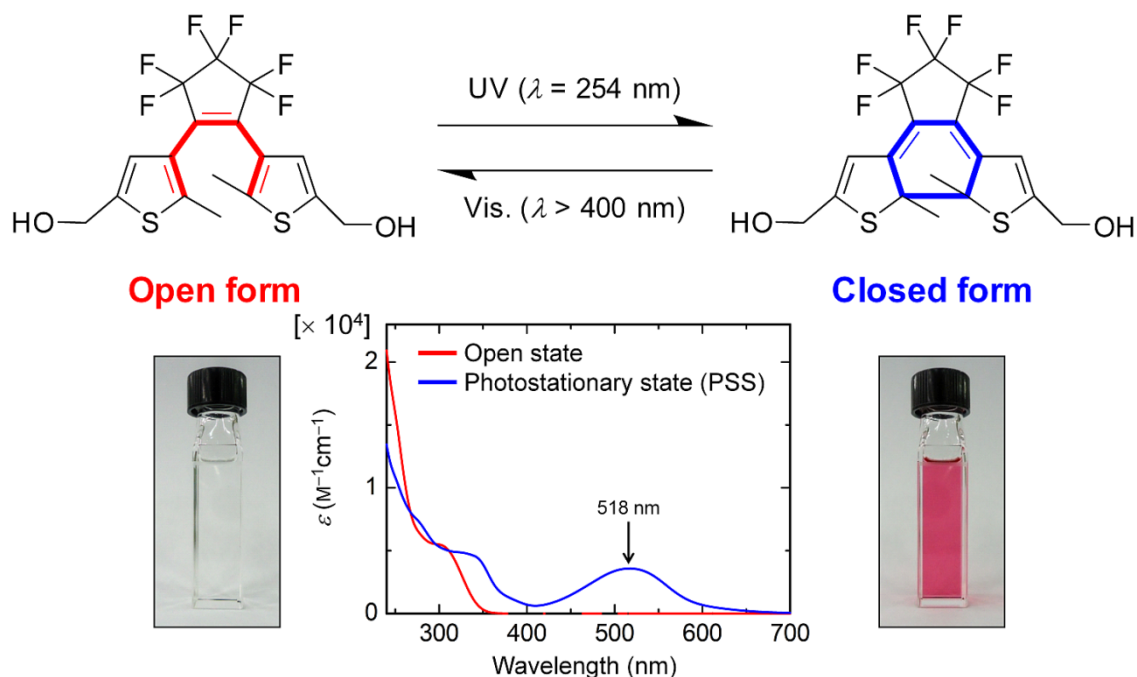


Figure 3. The structural, spectral, and color changes of a dithienylethene derivative via photoisomerization under irradiation of UV ($\lambda = 254 \text{ nm}$) and visible ($\lambda > 400 \text{ nm}$) lights.

6. Dithienylethene

Photochromic molecules are well known to show reversible change of color upon irradiation of light, which results from the photo-induced transformation of their molecular structures. The photoisomerization involves the change in various molecular properties such as light absorption, refractive indices, dielectric constants, and redox potentials. Thus, the photochromic molecules are regarded as the advanced functional materials that have reversibly switchable properties by light stimulus. Azobenzenes, spiropyrans, fulgides, and dithienylethene (DE) are the representative photochromic molecules. Especially, DE derivatives⁷³⁻⁷⁷ are one class of the most attractive photochromic materials because of their outstanding fatigue resistance, thermal stability, and ability to undergo conformational changes between open and closed forms via photoisomerization (see Figure 3). DE derivatives are also known to display luminescent color changes via photoisomerization.^{76, 78-87} Similarly, conjugated polymers that contain DE moieties in the polymer backbones exhibit

photochromism.^{76, 88-91} The chromism in both absorption and luminescence of the conjugated polymers is attributed to structural changes in the conjugated backbones resulting from the DE photoisomerization. Figure 3 displays the structural and spectral changes of a representative DE molecule in the open and closed forms. Hence, DE derivatives are regarded as the core block to produce the fluorescent color-tuning by external light stimuli.

7. Polymer Nanosphere

A polymer nanosphere is a nanometer-scale spherical aggregate of polymers. When dispersing in solution, the nanosphere can be considered as an intermediate state between solution and film because the polymer nanoparticles are uniformly dispersed in the solvent, similar to the solution state, and also aggregate with each other, similar to the film state. Such bilateral character of the nanosphere causes the polymer to exhibit high processability and fluidity as well as aggregation effects. Moreover, the individual nanoparticles can inhibit the energy transfer between different polymers, so that the fluorescence of each polymer nanosphere may be maintained even in the cast film consisting of the mixture of various colored fluorescent nanospheres.

In addition, the polymer nanosphere solution enables quantitative analysis of the aggregated state of polymers from the spectroscopic point of view. Hence, the polymer nanosphere solution is useful for understanding the aggregation effect on ACPs as compared with the solution and solid film states. Furthermore, each polymer nanosphere can freely move and rotate in solution and hence no linear dichroism is observed even if the nanosphere is linearly polarized. This feature is suitable for chiroptical measurements because an artifact corresponding to the linear polarization can be excluded from the CD and CPL spectra of the nanosphere solution.

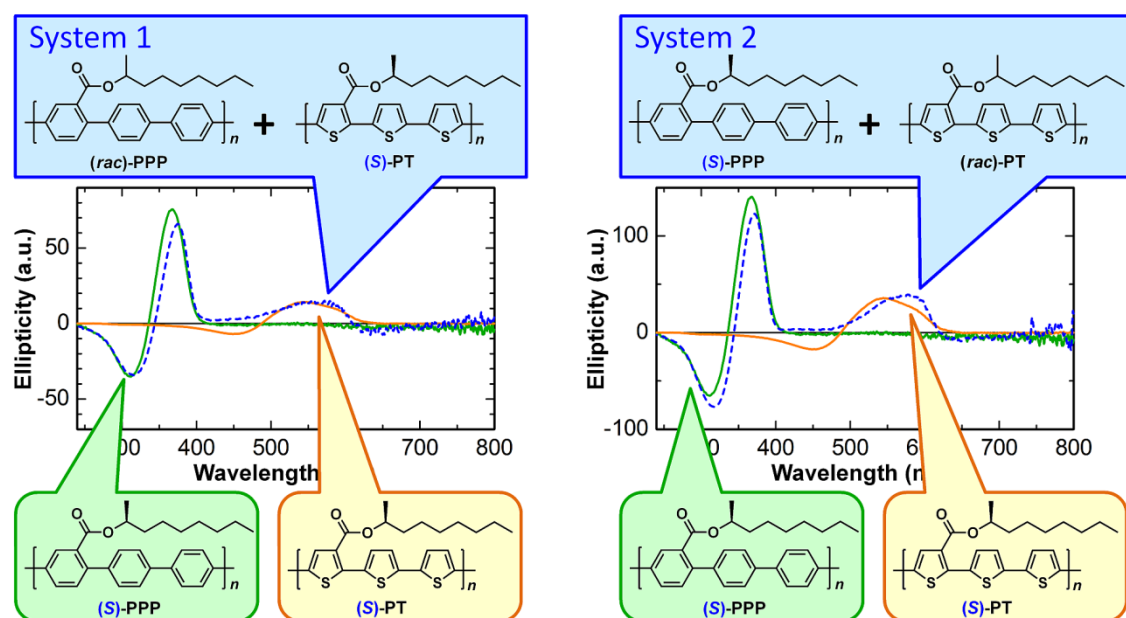
Outline of this Thesis

In *Chapter 1*, the author synthesized phenylene- and thienylene-based copolymers by introducing chiral (2-nonyloxy)carbonyl substituents into their side chains. Most of these polymers showed enantiotropic main-chain liquid crystallinity at high temperatures and across a wide range of elevated temperatures. They exhibited fluorescence that ranged in color from blue to orange in chloroform solutions and from blue to red in films. The bisignate Cotton effect was observed in the π - π^* transition region of the polymers main chains, which was attributed to the formation of a polymer assembly with an interchain helically π -stacked structure. The dependence of UV-vis absorption and CD spectra on the concentration and temperature of the solution indicated that the polymer assembly exists, even in dilute concentration at room temperature, but it dissociated into single polymers at high temperatures. Additionally, the polymer films exhibited an enhanced Cotton effect caused by the strengthening of the helical π -stacking in the polymer assembly.



Outline of Chapter 1

Both the polymer solutions and films generated circularly polarized fluorescence with the dissymmetry factor (g_{lum}) on the order of 10^{-3} and 10^{-2} , respectively. Values for g_{lum} as high as 10^{-1} were obtained by annealing the polymer films at temperatures that the polymer exhibited the liquid crystalline phase, which were due to the self-ordering of their chiral nematic phases. Furthermore, a mixture of red, green, and blue fluorescent polymers generated a unique, circularly polarized white luminescence not only in solution but also in the cast film prepared by dispersing the mixture in an excess of polystyrene.



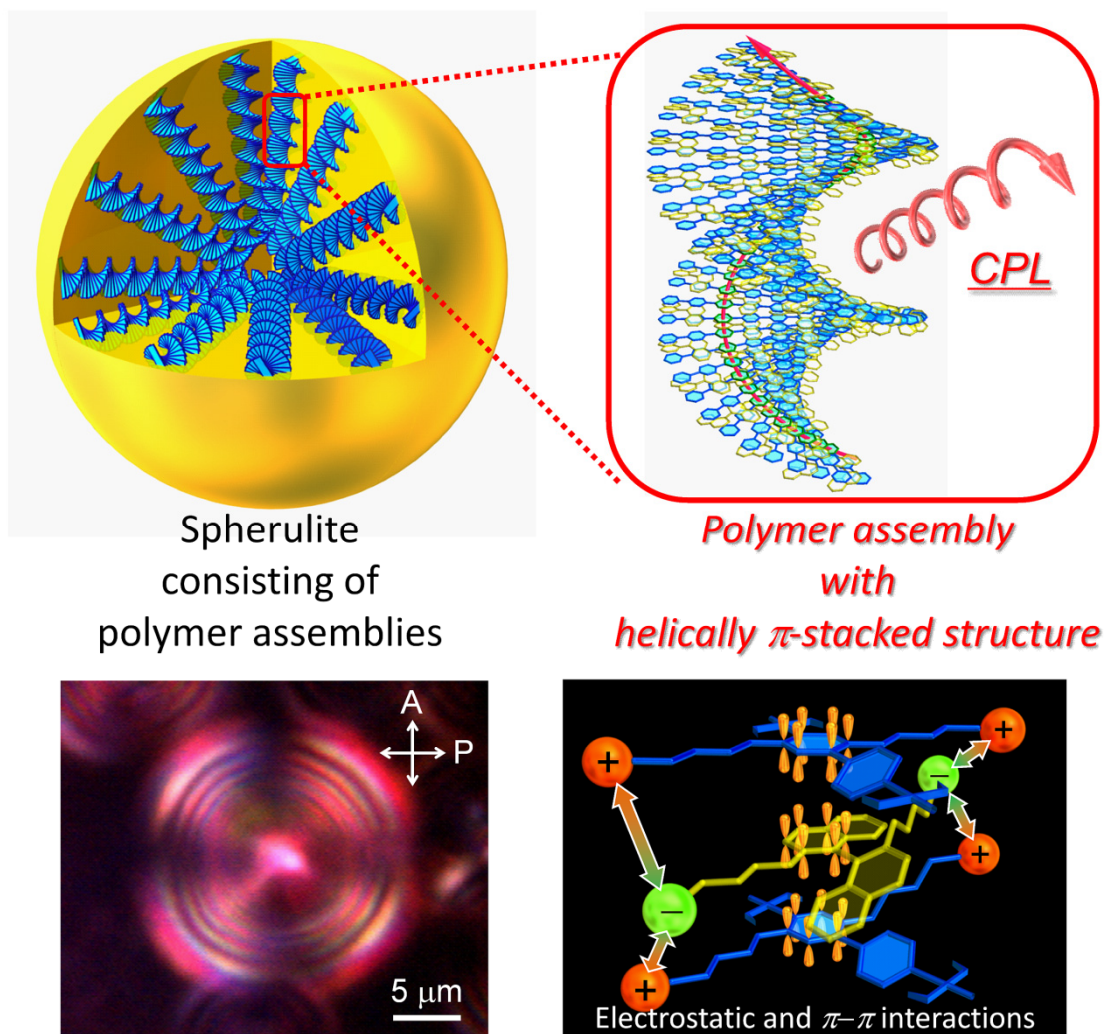
Outline of Chapter 2

In **Chapter 2**, the author synthesized 3-ring type ACPs, poly(*para*-terphenylene) and poly(terthiophene) derivatives (**PPPs** and **PTs**, respectively), by introducing the racemic or optically-active (2-nonyloxy)carbonyl side chains and then collected the soluble parts by Soxhlet extraction. The chiroptical measurements revealed that **PPPs** and **PTs** existed as isolated chains in chloroform solution and showed no circular polarization in both absorption and luminescence regardless of the presence or absence of chiral side chains. Meanwhile, in the aggregated state such as a polymer nanosphere, chiral **PPPs** and **PTs** respectively self-assembled into the interchain helical

π -stacking, exhibiting circular polarization in absorption and luminescence. Thus it is clarified that the circular polarization of **PPP**s and **PT**s arises from the interchain helicity in polymer aggregates. Subsequently the author demonstrated that chirality transferred from the chiral polymer to the achiral polymer through the interchain π - π interaction by mixing these polymers into a polymer nanosphere. The mixed system consisting of (*rac*)-**PPP** and chiral **PT** showed a circular dichroism (CD) spectrum that coincided with the sum of the CD spectra of chiral **PPP** and chiral **PT** in the aggregated state. This indicates that not only chiral **PT** but also (*rac*)-**PPP** have the interchain π -stacked structure with same helical sense according to the side chain chirality of chiral **PT**. The same result was obtained in the mixed system of chiral **PPP** and (*rac*)-**PT**. Consequently, it was successfully demonstrated that the interchain π - π interaction can play an important role in the appearance of circular polarization on ACP main chain and the chiral transfer between ACPs.

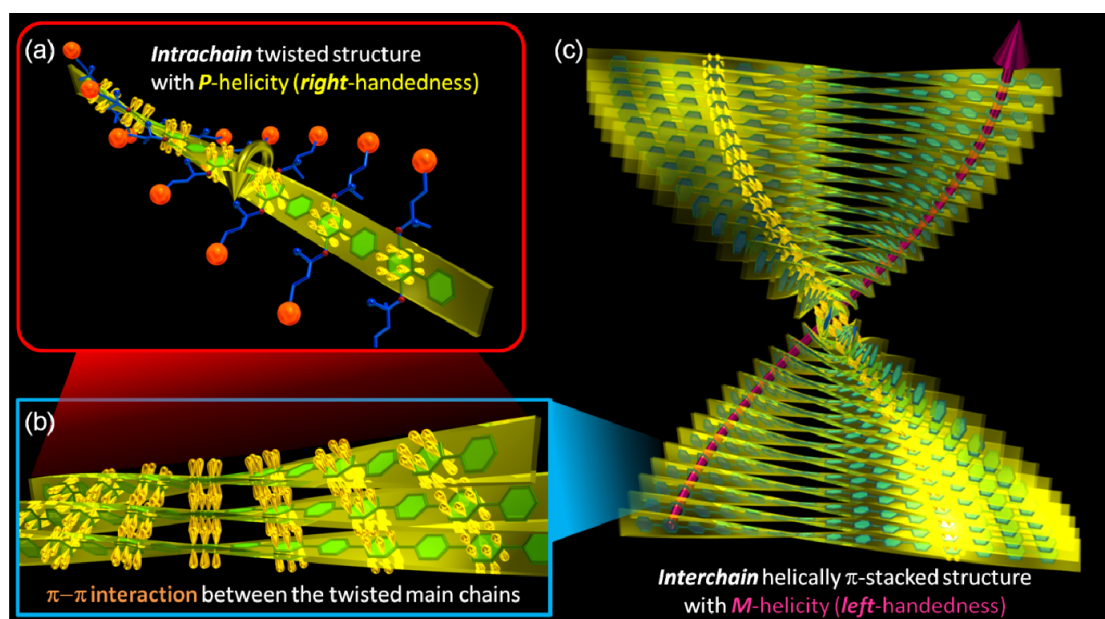
In **Chapter 3**, a cationic π -conjugated polymer is synthesized by introducing tetraalkylammonium groups onto both side chains of poly(*para*-phenylene) (**PPP**). An anionic axially chiral binaphthyl derivative (**BNP**) is also synthesized by introducing two anionic sulfonate groups onto the 2 and 2' positions of the binaphthyl ring. The chiroptical properties of the mixture of **PPP** and **BNP** (**PPP-BNP**) in a mixed solvent were investigated by UV-vis absorption, photoluminescence, circular dichroism (CD), and circularly polarized luminescence (CPL) spectra. It is found that **PPP** and **BNP** form a hierarchically self-organized assembly with an interchain helical π -stacked structure stabilized by both electrostatic and π - π interactions. The assembly shows large dissymmetry factors on the order of $|10^{-2}|$ - $|10^{-1}|$ in the absorption and luminescence spectra, even in solution. Signs of the Cotton effect in the CD and CPL spectra indicate that **PPP-(R)-BNP** and **PPP-(S)-BNP** have left-handed (*M*-helicity) and right-handed (*P*-helicity) helical structures, respectively. Measurements of scanning electron microscope micrographs and dynamic light scattering reveal that the assembly forms spheres with an average size of 220 ± 57 nm. Furthermore, the spheres show a Maltese Cross and extinction rings in the polarized optical microscope.

This demonstrates that the spheres are semicrystalline spherulites constructed from helically π -stacked assemblies of **PPP-BNP**, and the spheres exhibit a circularly polarized blue luminescence.



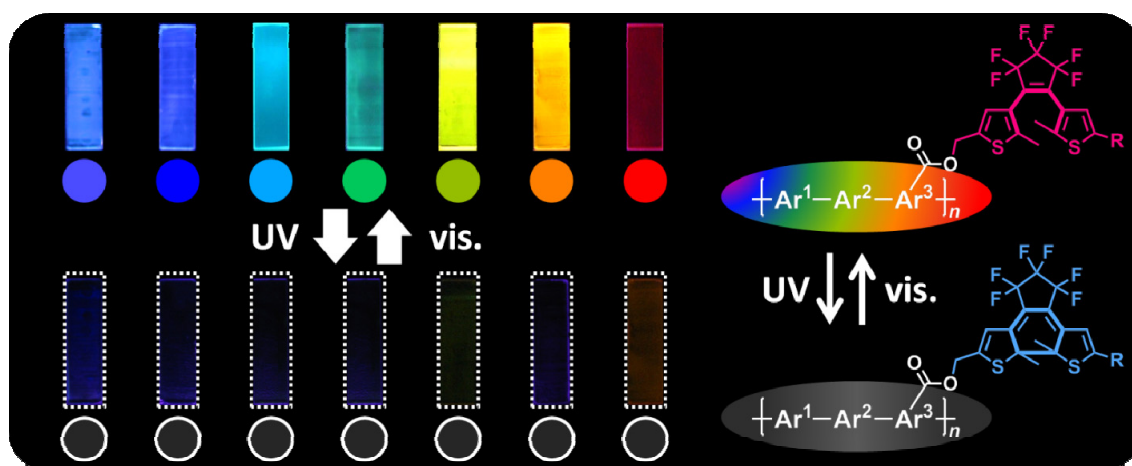
Outline of Chapter 3

In **Chapter 4**, novel approach for preparing ionic and helically π -stacked polymer assemblies with high dissymmetry factors is presented. The author synthesized cationic and chiral poly(*para*-biphenylene) [PBP] and poly(*para*-terphenylene) [PTP] derivatives by introducing chiral substituents containing both asymmetric centers and quaternary ammonium cations into the side chains of the polymers. The author found that these polymers have intrachain helical structure bearing one-handed twisted main chains in solution although there is only a slight preference for one twisted conformation over the opposite. Subsequently, by adding an anionic π -conjugated molecule to the cationic polymers, the author prepared a polymer assembly between the polymers and the molecules. It is clarified that the anionic molecule plays the role of a binding species that closes the cationic π -conjugated polymers through both electrostatic and π - π interactions. After thermal heating, PTP derivatives in the polymer assembly were arranged and then formed interchain helically π -stacked structure, whereas PBP derivatives formed the interchain structure just by mixing with the anionic molecules. The helically π -stacked polymer assembly showed circular dichroism in absorption and luminescence, giving high dissymmetry factors of 10^{-2} – 10^{-1} . The present approach using the cooperative intermolecular electrostatic and π - π interactions should be useful for preparing various types of electrically and chiroptically active polymer assemblies.



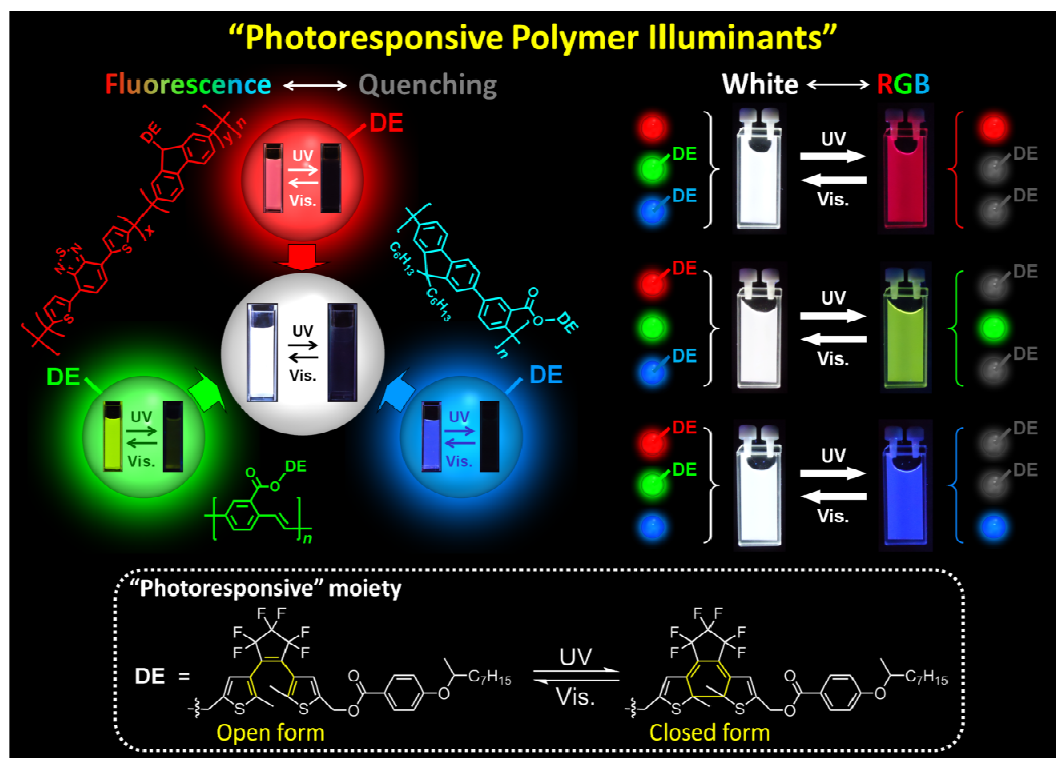
Outline of Chapter 4

In **Chapter 5**, the author synthesized a series of photoresponsive full-colored conjugated copolymers by combining phenylene- and thienylene-based main chains with photochromic dithienylethene (DE) side chains. Solutions and cast films of the polymers exhibited various colored fluorescence in visible wavelengths of 400–700 nm corresponding to emissions of the conjugated main chain. The fluorescence was reversibly photoswitched between emission and quenching through DE photoisomerization using external stimuli from ultraviolet and visible light irradiation. The reprecipitation method with ultrasonication enabled the polymers to form spherical aggregates with diameters of 20–70 nm in water. After investigating and comparing the optical properties, the resulting nanosphere solutions were assumed to exist in an intermediate state between an isolated state (i.e., in solution) and an aggregated state in cast film. The majority of the nanosphere solutions also exhibited the same photoswitchable fluorescence behavior as those in the solutions and the cast films. These results demonstrated that the visible fluorescence of the conjugated copolymers was reversibly switchable between emission and quenching using the photoisomerizing DE side chain regardless of the fluorescent colors and the polymer chain aggregation.



Outline of Chapter 5

In **Chapter 6**, π -conjugated aromatic polymers have attracted much interest due to their semi-conducting and luminescent properties, and are therefore regarded as promising materials for next-generation optoelectronic devices. Especially, it is considered as one of indispensable steps for advanced function to control the optoelectronic properties by external stimuli. Herein, the author show photochemically fluorescent color-tunable systems consisting of photoresponsive conjugated polymer nanospheres. The author design and synthesize photoresponsive conjugated polymers with red, green, and blue fluorescence by introducing photoisomeric dithienylethene moieties in the side chains. A mixture of the red-, green-, and blue-fluorescent polymer nanospheres exhibits photoswitchable white fluorescence between emission and quenching by irradiating external lights in both the nanosphere solution and film state. In addition, reversible change in fluorescent color between white and RGB is also achieved by replacing a photoresponsive polymer with a non-photoresponsive analogue in the mixture. Thus, the author successfully demonstrate “photoresponsive polymer illuminant” systems bearing photochemically color-tunable white fluorescence.



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Chapter 1

Helically π -Stacked Thiophene-Based Copolymers with Circularly Polarized Fluorescence: High Dissymmetry Factors Enhanced by Self-Ordering in Chiral Nematic Liquid Crystal Phase

Introduction

Aromatic π -conjugated polymers, such as polythiophenes and poly-*p*-phenylenes, are regarded as promising materials for advanced electronic and optoelectronic devices due to their profound electrical and optical properties.^{1–8} The polarized optical properties of π -conjugated polymers, which are controlled by their molecular and higher-order structures, have attracted much interest in both industry and academia.^{9,10} Our laboratory previously reported the synthesis of side-chain liquid crystalline (LC) π -conjugated polymers^{11–15} with linearly polarized fluorescence generated under high magnetic fields by virtue of the macroscopic orientation of the polymers.^{16–19}

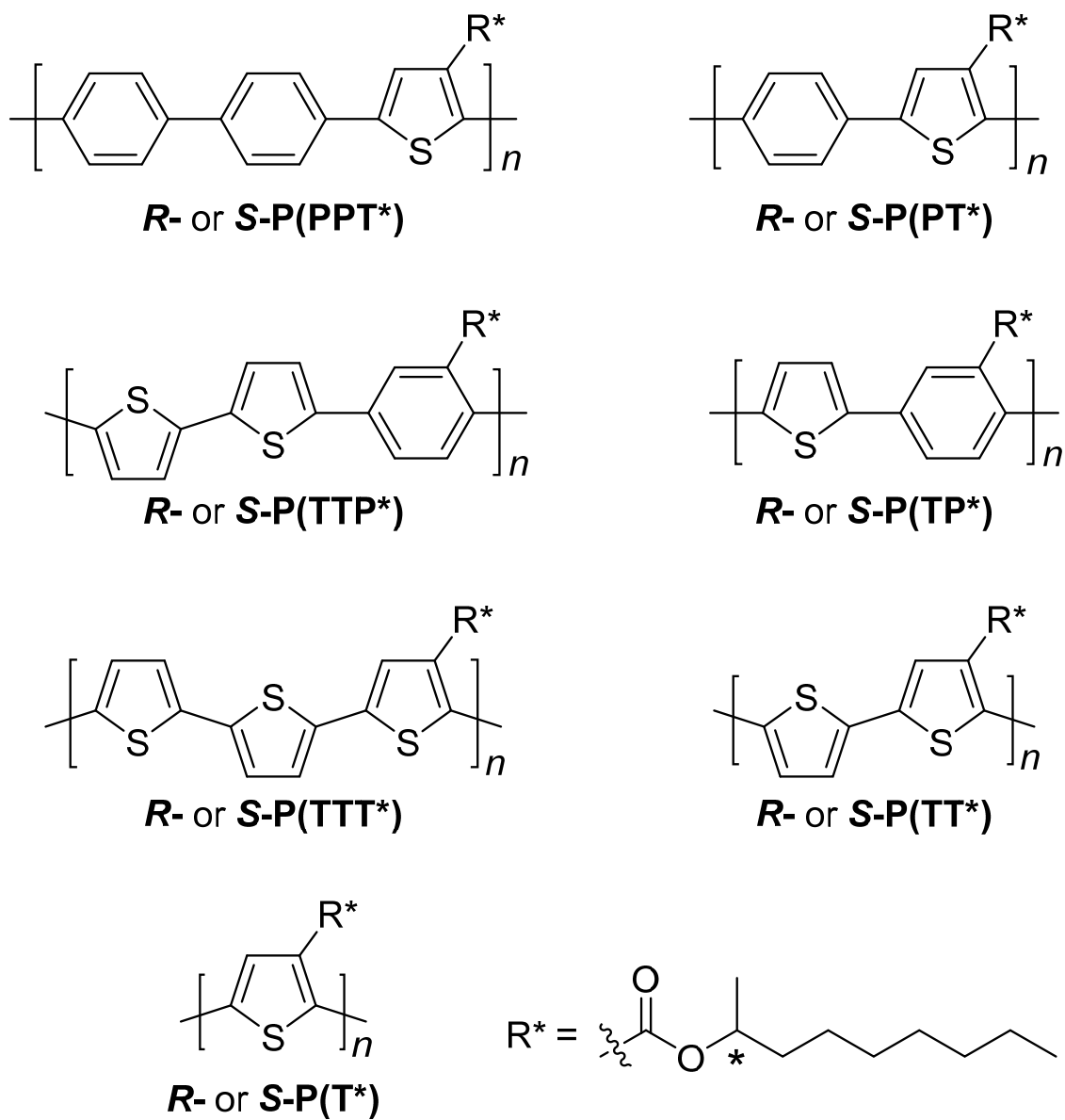
Circularly polarized luminescence (CPL) is another useful property of aromatic π -conjugated polymers that derives from their molecular chirality, eliminating the requirement for macroscopic alignment of the polymers. Chiral π -conjugated polymers can be prepared by polymerizing the corresponding monomer in a chiral reaction field using chiral nematic liquid crystals as the solvent,^{20–33} by introducing chiral moieties into the polymer side chains through either acid–base complexation^{34,35} or covalent bonds,^{36–47} and by incorporating torsional, asymmetric, aromatic rings in the main chain.⁴⁸ Several studies have reported synthesis of CPL of aromatic π -conjugated polymers. However, circular polarization in polymers with chiral side chains has only been achieved under aggregated conditions and not in dilute solutions.^{36,43–47} Previously, our laboratory reported preliminary results that homo- and copolymers based on thiophene with chiral alkoxy carbonyl side chains exhibited circular polarization in their absorption and fluorescence spectra even in dilute solutions,^{49,50}

which may suggest the intrachain helical structure of the single polymer and/or the interchain helically π -stacked structure of the polymer assembly formed as a result of its lower solubility.^{26–29}

Meanwhile, the circularly polarized fluorescence (CPF) due to the intrachain helical structure of the conjugated polymer is generally small ($<10^{-4}$) in its dissymmetry factor because the helical twisting distortion of the polymer backbone constructed with sp^2 -hybridized conjugated carbons is substantially restricted. Developing an appropriate way to enhance the circular polarization for absorption and luminescence is required for advancing these technologies. One of the promising ways is to add liquid crystallinity to the chiral conjugated polymers; the conjugated polymers tend to form an aggregate in a poor solvent or in a film, and the polymer aggregates further self-order in the mesophase when annealed at the LC temperature. This procedure can be regarded as a hierarchical arrangement of higher-order structure by liquid crystallinity.

Here, the author synthesizes polythiophene derivatives and thiophene-based copolymers by incorporating a chiral nonyloxy carbonyl group into their side chains and by detailing the chemical, optical, and LC properties of these polymers as well as their circularly polarized fluorescence in solution and film form. The chemical structures of the polymers are depicted in Scheme 1.

The carbonyl group located at the root of the chiral substituent is expected to enhance and stabilize the interactions between the chiral side chain and the conjugated main chain through a π bond, which results in strong main chain helicity. Furthermore, variation in the backbone structure can control the conjugation length and can afford the ability to tune the color of the polymers. Increasing the number of thiophene rings in the repeating unit can create a red shift in the π – π^* transition band, while increasing the number of phenylene rings a blue shift of the π – π^* transition band. The author found that self-ordering of the polymer aggregates in the chiral nematic phase during annealing at the LC temperature is essential for enhancing the CPF with a dissymmetry factor on the order of 10^{-1} . Additionally, the development of RGB-colored luminescence allows for white light emission by mixing the polymers in the appropriate ratios, which generates circularly polarized white luminescence.



Scheme 1. Polythiophene and thiophene-based copolymers with chiral nonyloxy carbonyl substituents.

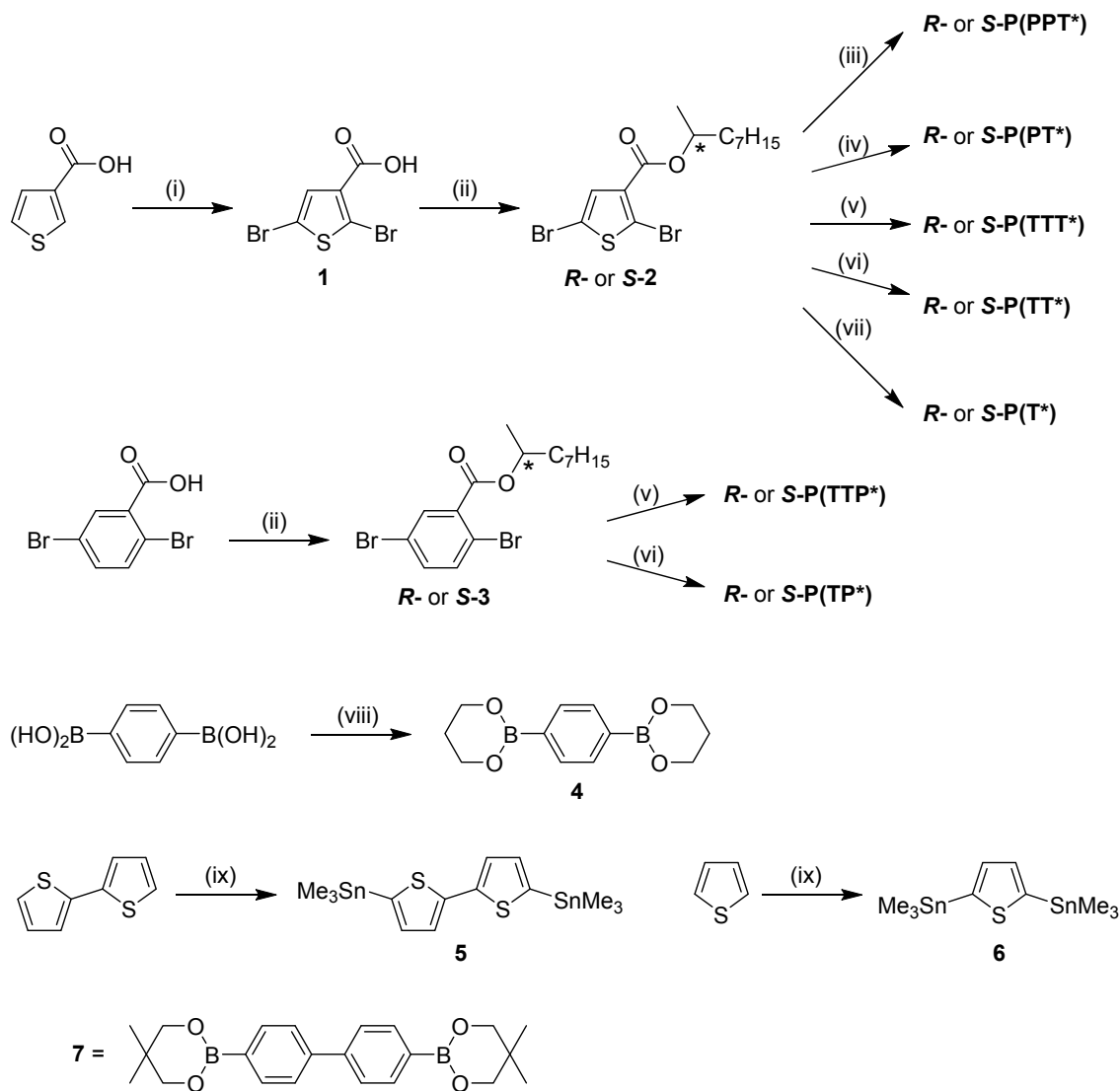
Results and Discussion

Synthesis of the Monomers. The synthetic routes for the target monomers and polymers are shown in Scheme 2. The 2- and 5-positions of 3-thiophenecarboxylic acid were brominated using *N*-bromosuccinimide (NBS) to create 2,5-dibromo-3-thiophenecarboxylic acid (**1**), which was followed by esterification with (*S*)-(+)-2- and (*R*)-(–)-2-nonanol using diethyl azodicarboxylate (DEAD) and triphenylphosphine (TPP), according to the Mitsunobu reaction,⁵¹ to yield **R-2** and **S-2**, respectively. The esterification of 2,5-dibromobenzoic acid with (*S*)-(+)- and (*R*)-(–)-2-nonanol was performed in the same way to yield **R-3** and **S-3**, respectively. 1,4-Phenylenediboronic acid bis(1,3-propanediol) cyclic ester (**4**) was obtained from 1,4-phenylenediboronic acid and 1,3-propanediol. 5,5'-Bis(trimethylstannyl)-2,2'-bithiophene (**5**) was prepared by lithiating bithiophene with *n*-BuLi and then quenching with trimethyltin chloride,⁵² 2,5-bis(trimethylstannyl)thiophene (**6**)⁵³ was prepared in the same manner.

Polymerization. **R-2** and **S-2** were copolymerized with 4,4'-biphenyldiboronic acid bis(neopentyl glycol) cyclic ester (**7**) using Pd(PPh₃)₄ as a catalyst according to the Suzuki coupling reaction⁵⁴ to give **R-P(PPT*)** and **S-P(PPT*)**, respectively. **R-P(PT*)** and **S-P(PT*)** were prepared by the copolymerization of **R-2** and **S-2**, respectively, with **4** using the same procedure. **R-3** and **S-3** were copolymerized with **5** through the Stille coupling reaction,⁵⁵ using Pd₂(dba)₃ as a catalyst, to give **R-P(TTP*)** and **S-P(TTP*)**, respectively. The preparations of **R-** and **S-P(TP*)**, **P(TTT*)**, and **P(TT*)** were also performed by Stille coupling. **R-P(T*)** and **S-P(T*)** were synthesized from **R-2** and **S-2**, respectively, via the Yamamoto polymerization method using Ni(cod)₂.⁵⁶

Polymerization Results. All of the synthesized polymers were soluble in common organic solvents, such as tetrahydrofuran (THF) and chloroform. Table 1 summarizes the chemical properties of both the *R* and *S* polymers. The degree of polymerization (DP), which stands for the number of repeating unit in the corresponding polymer, is evaluated by dividing the number-average molecular weight (*M_n*) by the molecular weight of the repeating units. The average quantity of aromatic rings in the main chain, which was evaluated by multiplying DP by the number of rings in the repeating unit, is

listed in the parentheses. The solubility of the polymers was lowered by increasing the number of non-substituted aromatic rings in the repeating unit because of the resultant increase in the rigidity of the polymer backbone.



Scheme 2. Synthetic Routes for monomers and polymers.

Reagents and conditions: (i) NBS, DMF, 50 °C; (ii) (*S*)-(+)-2-nonanol or (*R*)-(-)-2-nonanol, DEAD, TPP, THF, rt; (iii) **7**, Pd(PPh₃)₄, NaHCO₃, THF, H₂O, reflux; (iv) **4**, Pd(PPh₃)₄, NaHCO₃, THF, H₂O, reflux; (v) **5**, Pd₂(dba)₃, TFP, THF, 50 °C; (vi) **6**, Pd₂(dba)₃, TFP, THF, 50 °C; (vii) Ni(cod)₂, bpy, DMF, 80 °C; (viii) 1,3-propanediol, CH₂Cl₂, rt; (ix) *n*-BuLi, Me₃SnCl, TMEDA, -78 °C.

Table 1. Chemical Properties and Phase Transition Temperatures of the Polymers.

Polymer	M_n	M_w	M_w/M_n	DP ^{a, b}	heating (°C) ^c	cooling (°C) ^c
R-P(PPT*)	23000	230000	10.0	57 (171)	G 160 LC 300< I	G 160 LC 300< I
S-P(PPT*)	24000	140000	5.7	59 (177)	G 120 LC 300< I	G 112 LC 300< I
R-P(PT*)	11800	26600	2.3	36 (72)	G 85 LC 300< I	G 80 LC 300< I
S-P(PT*)	6500	15300	2.4	20 (40)	G 100 LC 300< I	G 95 LC 300< I
R-P(TP*)	8500	23900	2.8	25 (50)	G 95 LC 300< I	G 90 LC 300< I
S-P(TP*)	7300	14800	2.0	21 (42)	G 93 LC 300< I	G 90 LC 300< I
R-P(TTP*)	4800	5600	1.2	12 (36)	G 110 N* 250 N 278 I	G 107 N* 246 N 276 I
S-P(TTP*)	4800	5600	1.2	12 (36)	G 120 N* 230 N 270 I	G 115 N* 225 N 268 I
R-P(T*)	3200	4400	1.4	13 (13)	NA ^d	NA ^d
S-P(T*)	3200	4100	1.3	13 (13)	NA ^d	NA ^d
R-P(TT*)	8100	14000	1.7	24 (48)	G 150 LC 300< I	G 145 LC 300< I
S-P(TT*)	7900	12000	1.5	24 (48)	G 150 LC 300< I	G 147 LC 300< I
R-P(TTT*)	4300	5100	1.1	10 (30)	G 120 N* 190 I	G 115 N* 185 I
S-P(TTT*)	4600	5300	1.1	11 (33)	G 120 N* 190 I	G 115 N* 185 I

^a DP (degree of polymerization) stands for the quantity of the repeating unit.

^b The values in the parentheses are averaged number of aromatic rings in the main chain.

^c G; glassy, N*; chiral nematic, N; nematic, LC; LC phase which could not be assigned, I; isotropic.

^d no LC phase was observed.

Liquid Crystalline Properties. Most of these polymers showed enantiotropic main-chain liquid crystallinity at high temperatures and across a wide range of elevated temperatures. Polarized optical micrography (POM) revealed the presence of an enantiotropic LC phase in all of the polymers except for the **R**- and **S**-**P(T*)**. Figure 1 shows the optical textures of the LC phase of **R-P(TTP*)** and **R-P(TTT*)**. The **R-P(TTP*)** exhibited an oily streak texture (a) and a fingerprint texture (b) at approximately 200 and 150 °C, respectively, during the cooling process; both of these textures can be assigned to the chiral nematic (N*) phase. Meanwhile, The **R-P(TTT*)** (Figure 1c) exhibited a focal conic texture with a unique red color at approximately 156 °C during the cooling process, which is also attributed to the N* phase. The **S-P(TTP*)** and **S-P(TTT*)** showed optical textures similar to those of the corresponding **R** polymers. The other polymers showed no distinct optical textures attributable to the N* phase. Table 1 shows the transition temperatures of the polymers determined by POM. All polymers except the **P(TTP*)**s and **P(TTT*)**s were found to possess high clearing points (over 300 °C), which may be due to the higher molecular weight of those polymers.

The author performed XRD measurements of the **P(TTP*)** and **P(TTT*)** with liquid crystallinity. The polymers were annealed at their corresponding liquid crystal temperatures for 1 h (i.e., the **P(TTP*)** at 230 °C and the **P(TTT*)** at 150 °C) and were then cooled to room temperature and used for XRD measurements. The XRD measurements were performed under X-ray irradiation (40 kV, 300 mA, 12 kW) for 6 h at room temperature. The results are shown in Figures 2a and b. The **P(TTP*)** showed a sharp reflection at 20.0 Å (4.4° in 2θ) and a broad one at 4.4 Å (20.1° in 2θ , respectively). The small reflection of 8.8 Å (10.0° in 2θ) may be an overtone of the reflection of 4.4 Å. Similarly, the **P(TTT*)** showed a sharp reflection at 23.2 Å (3.8° in 2θ) and a broad one approximately 4.6–3.8 Å (19.3–23.5° in 2θ). These XRD patterns are characteristic of N*-LC phases. As shown in Figures 2c and d, the reflections in the small angle region, 20.0 Å for the **P(TTP*)** and 23.2 Å for the **P(TTT*)**, correspond to the interchain distances. These distances are smaller than two times the side chain lengths (13.0 Å and 13.5 Å) that are evaluated from the molecular mechanics calculations. This result indicates that the side chains of the neighboring main chains

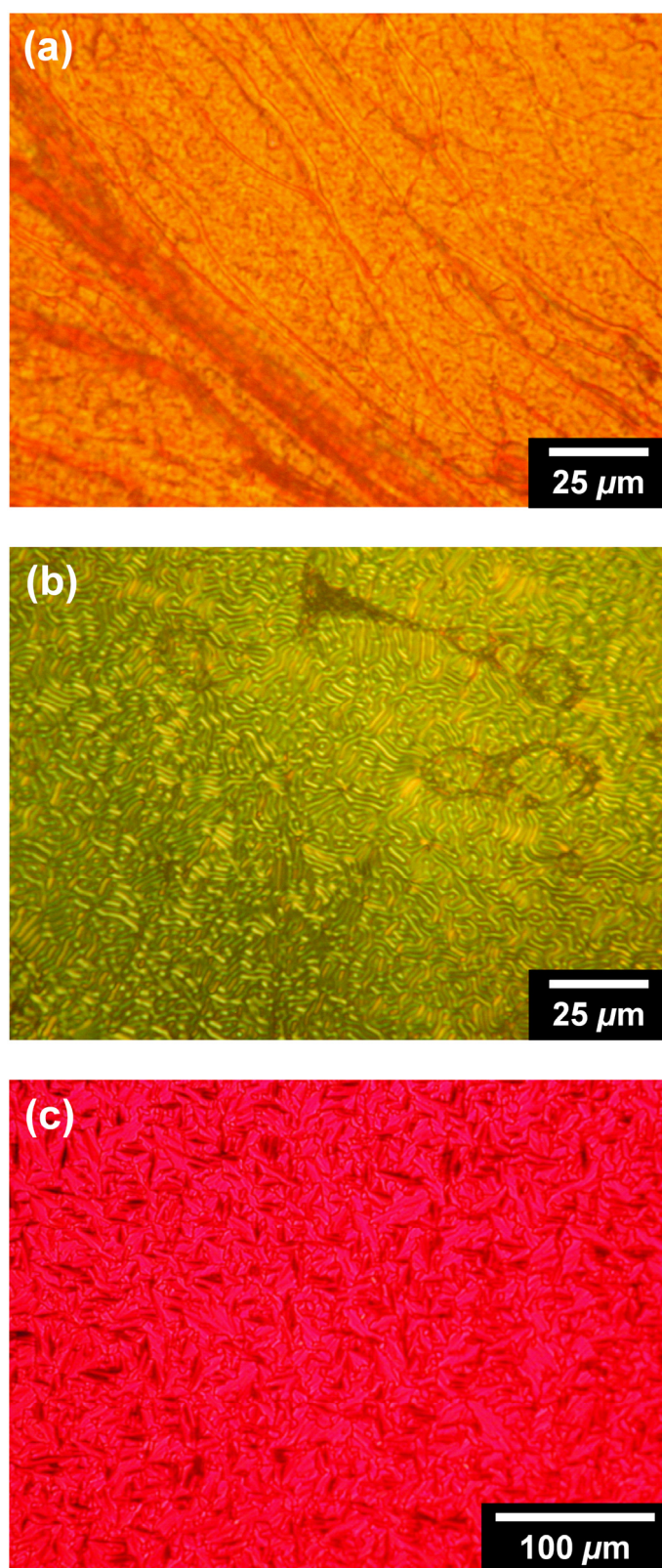


Figure 1. Polarized optical micrographs of *R-P(TTP*)* at (a) 200 °C and (b) 150 °C and of (c) *R-P(TTT*)* at 156 °C during the cooling process.

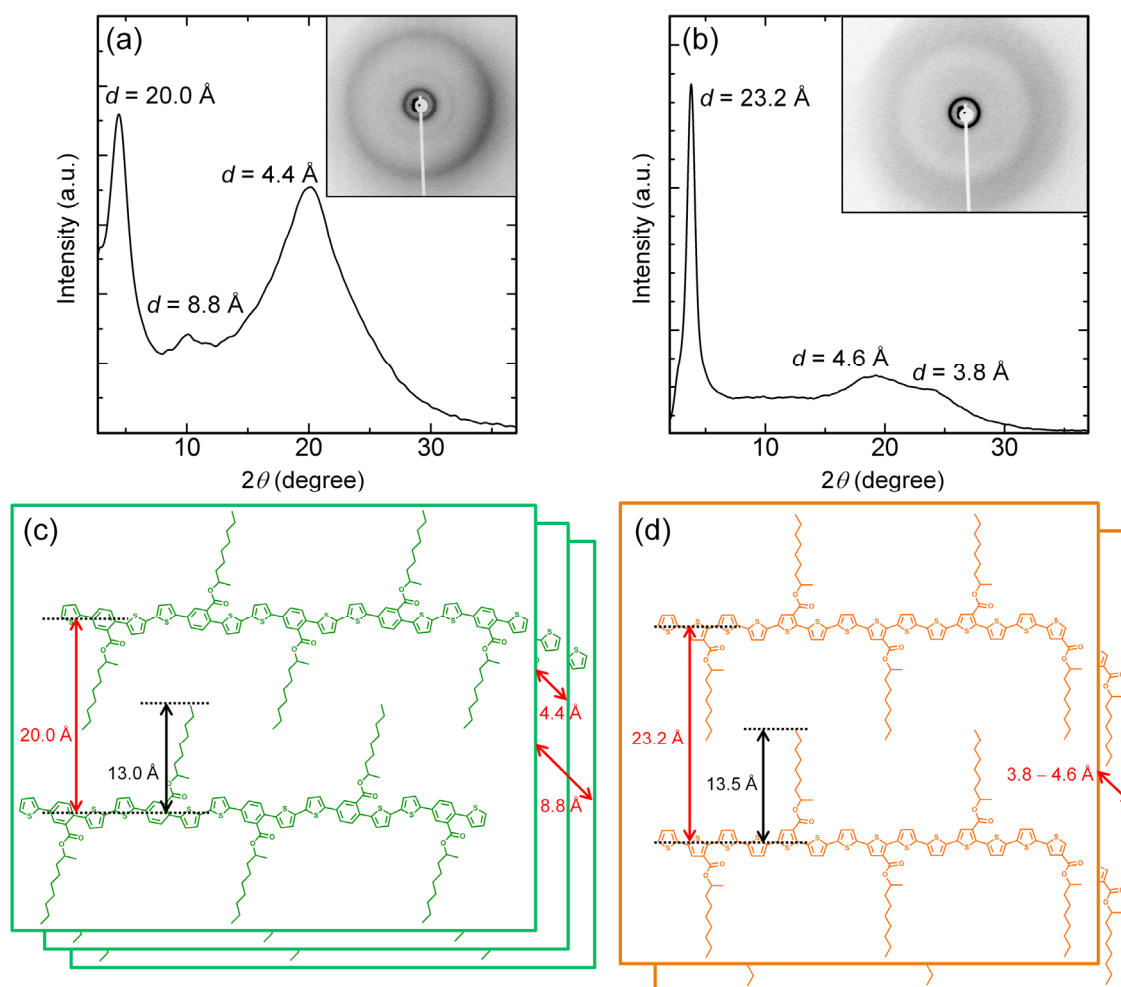


Figure 2. XRD patterns of the annealed (a) *R*-P(TTP*) and (b) *S*-P(TTT*). *R*-P(TTP*) and *S*-P(TTT*) were annealed at 230 and 150 °C for 1 h, respectively. The XRD pattern of *R*-P(TTP*) shows a sharp reflection at 20.0 Å (4.4° in 2θ) and two broad reflections at 8.8 and 4.4 Å (10.0° and 20.1° in 2θ , respectively). The XRD pattern of *S*-P(TTT*) shows a sharp reflection at 23.2 Å (3.8° in 2θ) and a broad one approximately 4.6–3.8 Å (19.3–23.5° in 2θ). The lengths of the alkyl side chains with some conformations were estimated by molecular mechanics calculations. The insets show the Laue patterns of the polymers. The assignments of the XRD reflections for *R*-P(TTP*) and *S*-P(TTT*) are shown in c and d, respectively.

are interdigitated with one another. The degree of interdigitation is larger in the **P(TTP*)** than in the **P(TTT*)**, probably because the bending skeleton of the main chain in **P(TTP*)** is more suitable for the interdigitation of the side chains than the linear skeleton of the main chain in **(TTT*)**.

However, the reflections (4.4 Å and 4.6–3.8 Å) in the wide angle region corresponded to the distance between the polymer layers (Figures 2c and d). In particular, the reflection at 4.4 Å for the **P(TTP*)** was very intense, implying a high periodicity of the polymer layers consistent with the observation of the overtone reflection at 8.8 Å

Optical Properties. The optical properties of the polymers are summarized in Table 2. Figure 3 shows the UV–vis absorption spectra of the *R* polymers both in chloroform (a, 1.0×10^{-4} M) and as a cast film (b). The polymer concentrations are expressed as the repeating unit concentration. The absorption band corresponding to the π – π^* transition is red-shifted by increasing the number of thiophene rings in the repeating units. Despite having similar backbones, which consisted of one thiophene and one phenylene ring, the absorption maxima (λ_{max}) for the **P(TP*)**s were approximately 15 nm longer than those for the **P(PT*)**s. The difference in steric hindrance between phenylene and thiophene rings containing the chiral substituent should be larger than in the unsubstituted rings; moreover, thiophene forms a more planar main chain than phenylene. Therefore, **P(TP*)**s, in which thiophene is the unsubstituted ring, should be more planar than **P(PT*)**s, in which phenylene is the unsubstituted ring, which extends the π -conjugation system. Table 2 shows that the absorption and fluorescence bands of the polymer films are red-shifted by 7–76 nm compared with those in solution, likely due to a more coplanar conformation and an increase in the π – π overlap of the solid state.^{57,58} The degree of the red shift was larger in polymers bearing higher coplanar repeating units. Namely, the polymers consisting of thienylene had larger red shifts than those made of phenylene, and the polymers of non-substituted arylenes (phenylene, thienylene) had more remarkable red shifts than those made of substituted arylenes.

Table 2. Optical Properties of the Polymers.

polymer	$\lambda_{\max}$ (nm)		$\Delta\lambda_{\max}^a$ (nm)	$\log \varepsilon$	$\text{Em}_{\max}$ (nm)		$\Delta\text{Em}_{\max}^a$ (nm)	Φ^b
	in CHCl_3	film			in CHCl_3	film		
<i>R</i>-P(PPT*)	365	376	11	4.33	469	479	10	0.26
<i>S</i>-P(PPT*)	365	380	15	4.42	471	478	7	0.25
<i>R</i>-P(PT*)	375	385	10	4.25	480	491	11	0.24
<i>S</i>-P(PT*)	369	383	14	4.19	480	493	13	0.18
<i>R</i>-P(TP*)	389	411	22	4.29	492	532	40	0.26
<i>S</i>-P(TP*)	390	412	22	4.24	494	520	26	0.24
<i>R</i>-P(TTP*)	420	443	23	4.45	509	557	48	0.23
<i>S</i>-P(TTP*)	418	449	31	4.47	507	551	44	0.23
<i>R</i>-P(T*)	400	407	7	3.69	539	546	7	0.04
<i>S</i>-P(T*)	396	407	11	3.68	537	550	13	0.03
<i>R</i>-P(TT*)	468	533	65	4.17	574	632	58	0.05 ^c
<i>S</i>-P(TT*)	470	544	74	4.22	575	633	58	0.05 ^c
<i>R</i>-P(TTT*)	474	526	52	4.34	570	643	73	0.05 ^c
<i>S</i>-P(TTT*)	474	550	76	4.36	571	640	69	0.05 ^c

^a Difference of wavelength in absorption or fluorescence band between in solution and film.

^b Fluorescence quantum yields, Φ , were evaluated by using quinine sulfate in 1.0 M sulfuric acid as a standard sample.

^c The quantum yields of **P(TT*)** and **P(TTT*)** could not be exactly evaluated because their fluorescence wavelength regions were out of the range covered by quinine sulfate. Therefore, these values were estimated based on their fluorescence intensities.

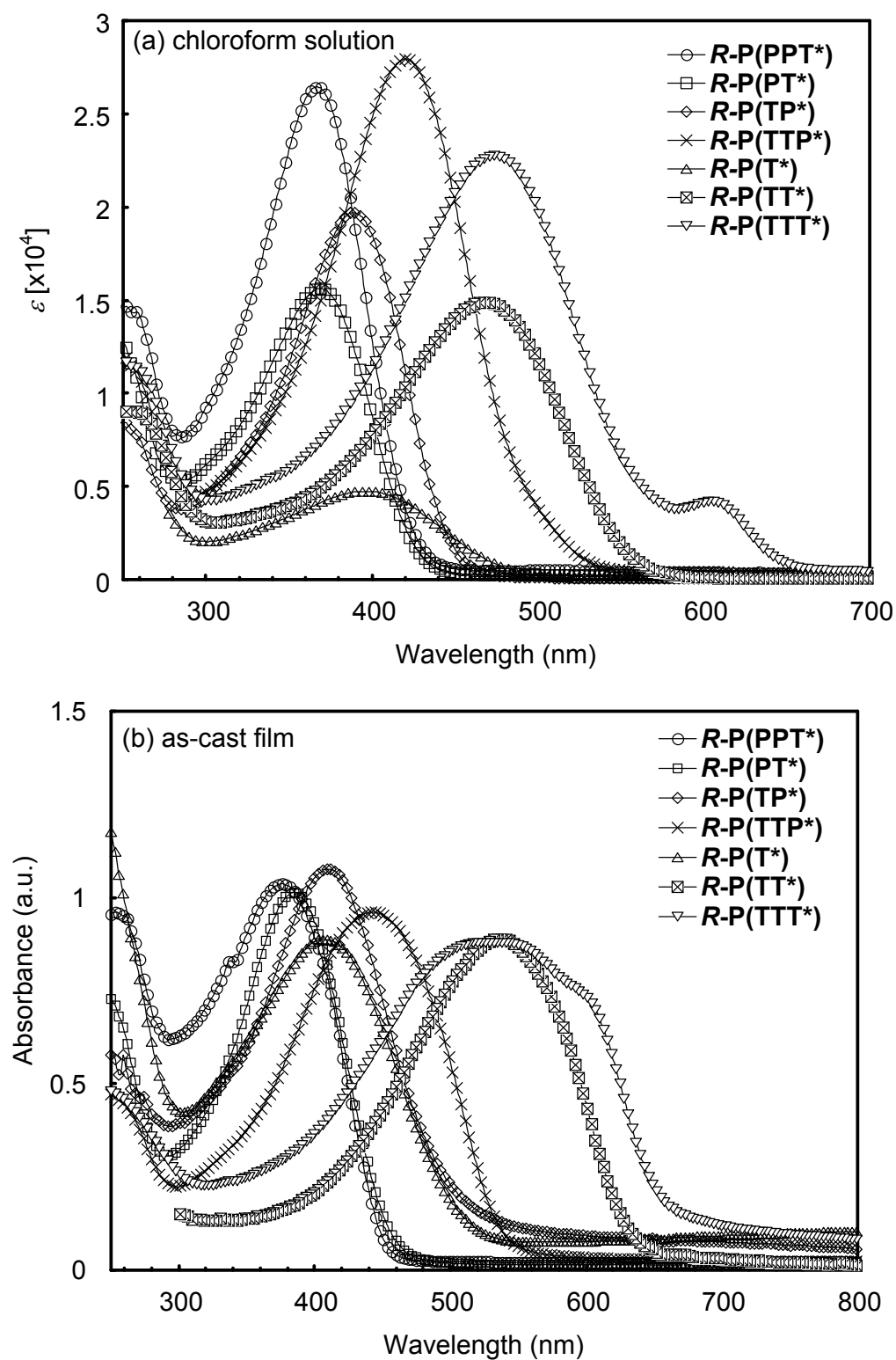


Figure 3. The UV-vis absorption spectra of the polymers in (a) chloroform ($c = 1.0 \times 10^{-4}$ M) and (b) the as-cast film.

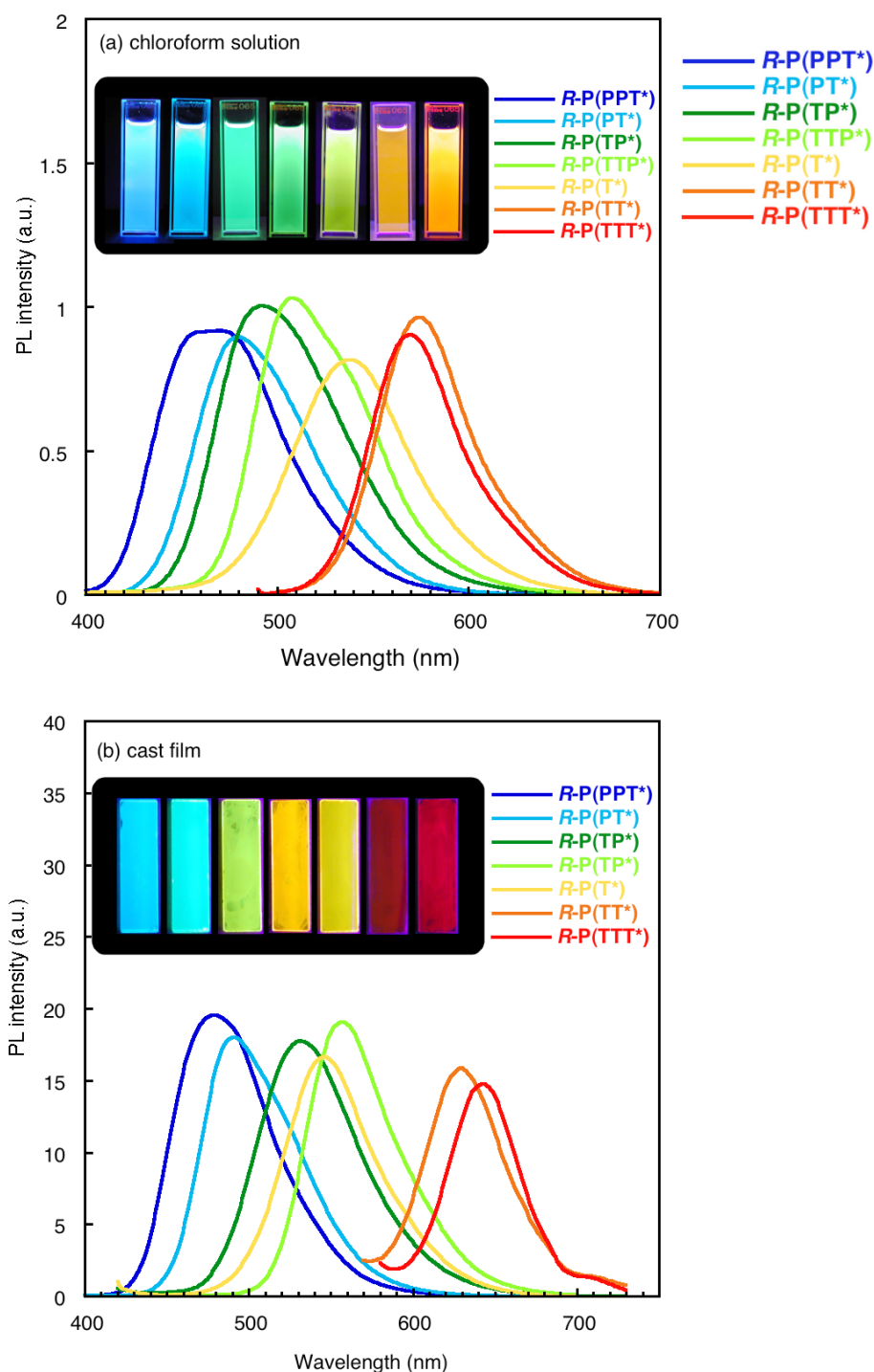
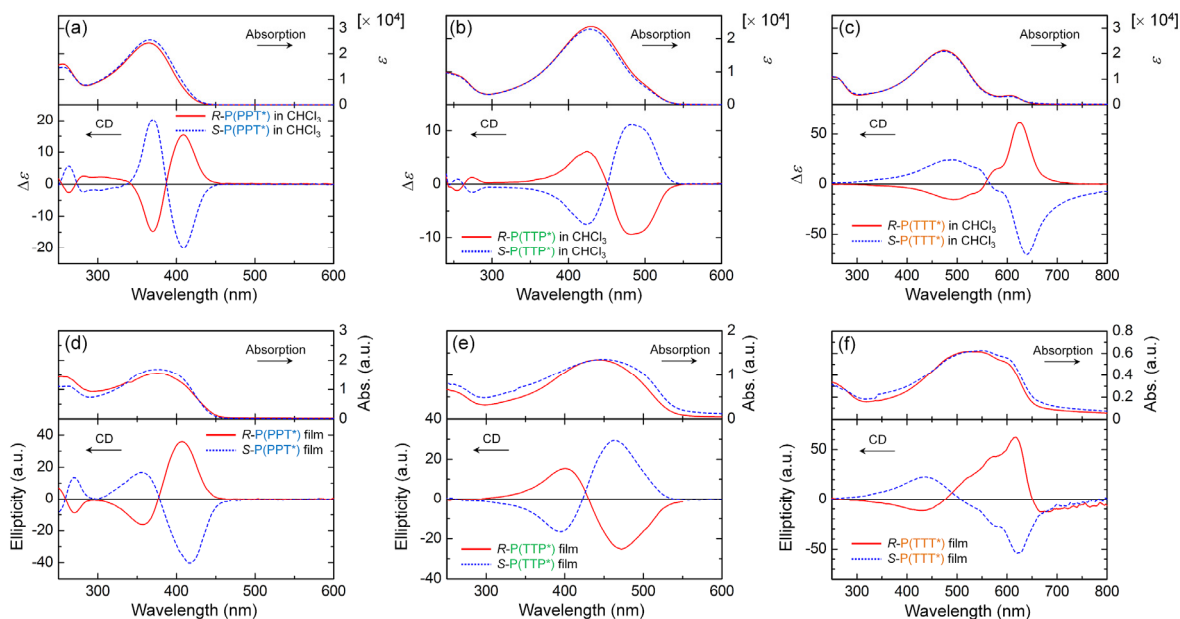


Figure 4. The normalized fluorescence spectra of the polymers in (a) chloroform ($c = 1.0 \times 10^{-4}$ M) and (b) as-cast films. The insets show photos of the polymers in chloroform and as-cast films upon irradiation with 365 nm UV light. From left to right: $R-P(PPT^*)$, $R-P(PT^*)$, $R-P(TP^*)$, $R-P(TTP^*)$, $R-P(T^*)$, $R-P(TT^*)$ and $R-P(TTT^*)$.

Figure 4 shows the normalized fluorescence spectra of the *R* polymers in chloroform (a, 1.0×10^{-4} M) and as films (b). The insets show photos of the polymers in a chloroform solution (a) and as a cast film (b) irradiated with 365 nm UV light. The polymers showed RGB-colored fluorescence both in solution and as a film. In the fluorescence spectra, the polymers showed a red shift similar to that in the absorption spectra. Table 2 lists the fluorescence quantum yields of the polymers evaluated using quinine sulfate in 1.0 M sulfuric acid as a standard and excitation at 366 nm. The polymers containing a phenylene ring in their backbones possessed higher quantum yields (over 0.2) than those consisting of only thiophene rings. The quantum yields of the **P(TT*)**s and **P(TTT*)**s could not be exactly evaluated because their fluorescence wavelengths were outside the range of measurement when using quinine sulfate as the standard. However, on the basis of the fluorescence intensities of the **P(TT*)**s and **P(TTT*)**s in chloroform, their quantum yields were estimated to be 0.05, which were slightly higher than those of the **P(T*)**s.

Circular Dichroism. The circular dichroism (CD) spectra of the **P(PPT*)**s, **P(TTP*)**s, and **P(TTT*)**s in chloroform ($c = 1.0 \times 10^{-4}$ M) are shown in Figure 5a–c. The Cotton effects are observed in the π – π^* transition bands of the conjugated main chains. The **R-P(PPT*)** demonstrated a bisignate Cotton effect that appeared in the π – π^* transition band of the conjugated main chain consisting of biphenylthienyl moieties, with first positive and then negative components at longer (420 nm) and shorter (370 nm) wavelengths, respectively. At the same time, the **S-P(PPT*)** demonstrated a completely reversed CD behavior, which was first negative and then positive (Figure 5a). This behavior implies that a strong exciton coupling occurs in the main chains, leading to the formation of an interchain π -stacked structure.⁵⁹ The **P(TTP*)**s and **P(TTT*)**s also exhibited bisignate Cotton effects, in which the signals for the *R* and *S* configurations were mirror images (Figures 5b and c). The **P(TTP*)**s gave CD signals opposite to those of the **P(PPT*)**s and **P(TTT*)**s; for example, the **R-P(TTP*)** exhibited first negative and then positive signals, whereas the **R-P(PPT*)** and **R-P(TTT*)** exhibited first positive and then negative signals. The bisignate Cotton effect observed for the polymers with three aromatic rings in the repeating unit suggests that

Figure 5. The UV–vis absorption (upper) and CD (lower) spectra of the polymers in



chloroform ($c = 1.0 \times 10^{-4}$ M) for (a) **P(PPT*)s**, (b) **P(TTP*)s**, and (c) **P(TTT*)s** and the as-cast films of (d) **P(PPT*)s**, (e) **P(TTP*)s**, and (f) **P(TTT*)s**. The solid and dotted lines indicate the spectra of polymers with (*R*)- and (*S*)-configurations, respectively.

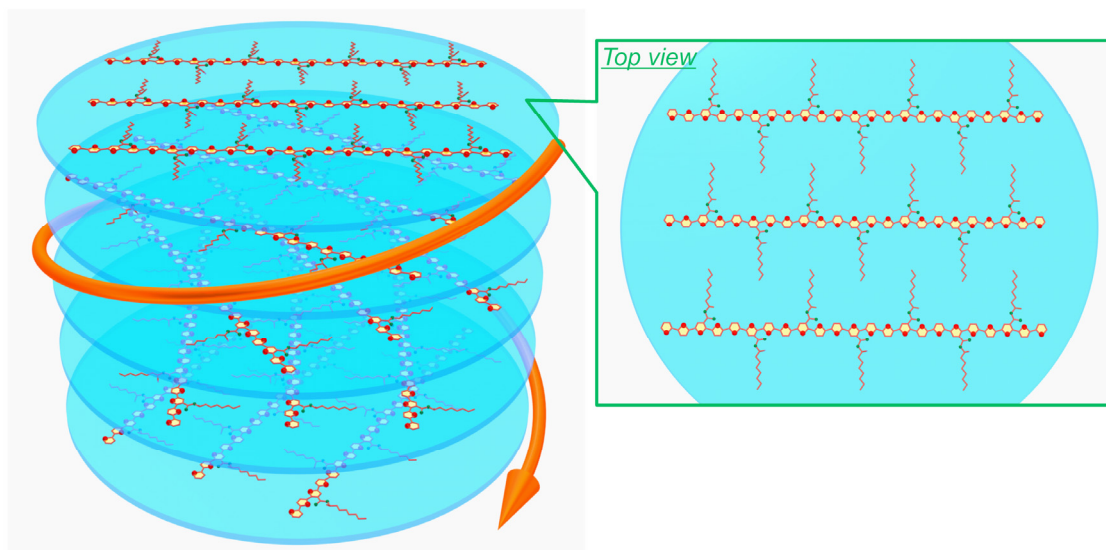


Figure 6. The schematic representation of the interchain helically π -stacked structure of **P(TTT*)** assembly.

the polymers are stacked with twisting through π – π interactions, resulting in a helically π -stacked assembly. Figure 6 shows a schematic representation of the helically π -stacked structure of the polymer assembly.

According to the exciton coupling theory,⁵⁹ the **R-P(TTP*)** that shows a negative bisignate Cotton effect has a left-handed helical sense (*M*-helicity), whereas both the **R-P(PPT*)** and **R-P(TTT*)** showing a positive bisignate Cotton effect have a right-handed helical sense (*P*-helicity). These two groups of polymers have helical π -stacking structures with helical senses that are opposite to one another. It is likely that the difference in linkage between the chiral substituent and the arylene ring may cause the difference in the helical sense of the π -stacking structure, although the chiral substituent has the same configuration; that is, the chiral substituents of the **R-P(TTP*)**s are linked to the phenylene ring, whereas those of the **R-P(PPT*)**s and **R-P(TTT*)**s are linked to the thiophene rings. However, the actual mechanism for the difference in helical sense of the π -stacking structure is still unclear and needs to be elucidated by further investigations.

Next, the author measured the UV–vis and CD spectra of the polymers, the **P(PPT*)**s, **P(TTP*)**s, and **P(TTT*)**s, by changing the concentrations of the chloroform solutions, 1.0×10^{-3} M, 1.0×10^{-4} M, and 1.0×10^{-5} M, with respect to the repeating unit. The results are shown in Figure 7. The feature of the CD spectra and the dissymmetry factor (g_{abs}) are not notably affected by the change in the polymer concentration, indicating that the polymer assembly with a helically π -stacked structure exists even in dilute concentrations down to 10^{-5} M. Subsequently, the author examined the temperature dependence of the UV–vis and CD spectra of the polymers **P(PPT*)**s, **P(TTP*)**s, and **P(TTT*)**s in chloroform by changing temperatures for the measurements, where the concentrations of the polymers were fixed at 1.0×10^{-4} M with respect to the repeating unit. The results are shown in Figure 8. The Cotton effects in CD spectra decreased in intensity with increasing the temperature and finally disappeared at 70 °C for the **P(PPT*)**s and **P(TTP*)**s and at 80 °C for the **P(TTT*)**s. Additionally, the absorption bands of the polymers shifted toward shorter wavelengths with increasing temperature, resulting in isosbestic points at 390–470 nm. These results imply that, although the polymer assembly with helically π -stacked structure exists even

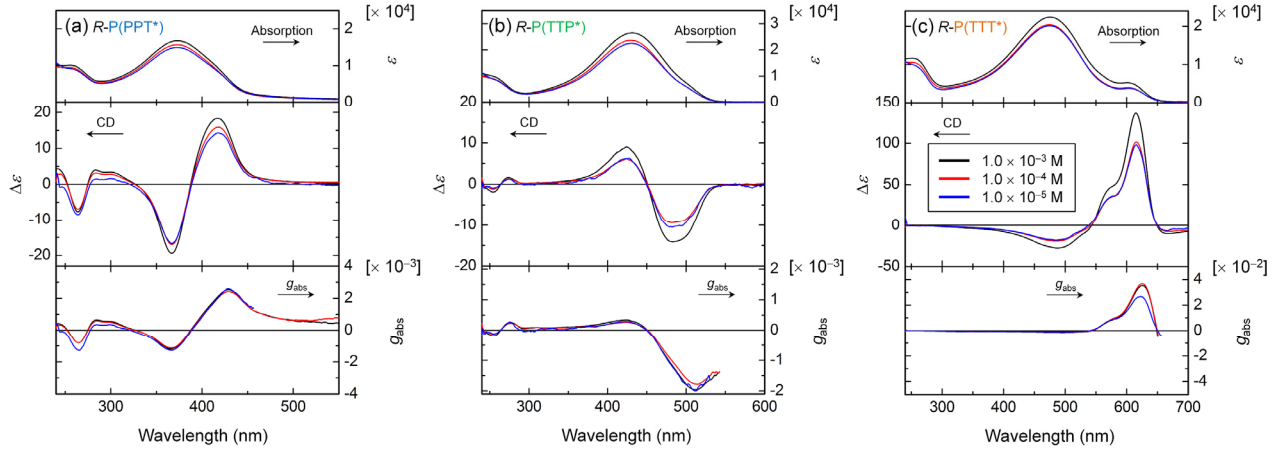


Figure 7. Concentration dependence of UV-vis absorption (upper), CD (middle) and dissymmetry factor (g_{abs} , lower) spectra of R -P(PPT*) (a), R -P(TTP*) (b) and R -P(TTT*) (c) in chloroform. Measurements were carried out under various concentrations of the polymers, $c = 1.0 \times 10^{-3}$, 1.0×10^{-4} and 1.0×10^{-5} M.

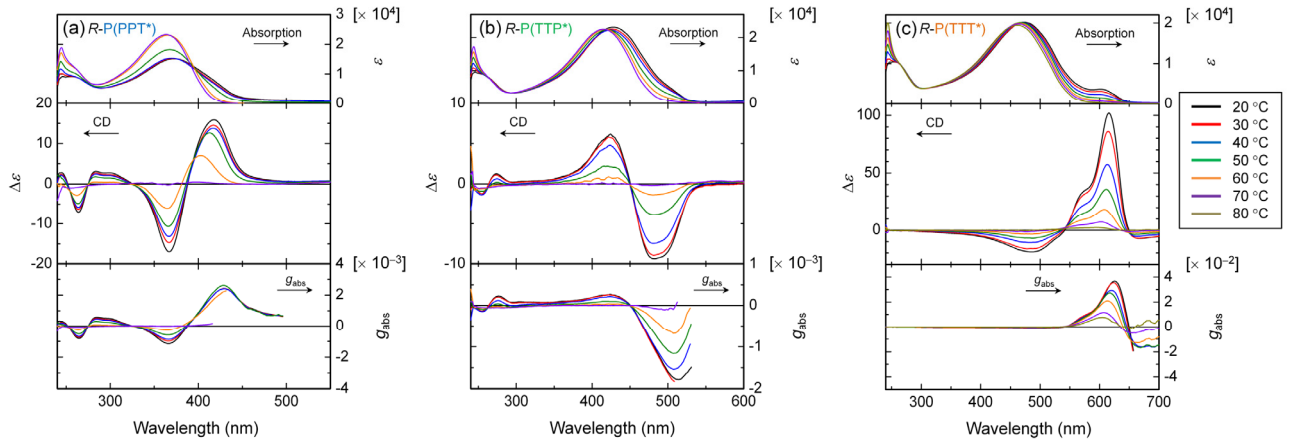


Figure 8. Temperature dependence of UV-vis absorption (upper), CD (middle) and g_{abs} (lower) spectra of (a) R -P(PPT*), (b) R -P(TTP*), and (c) R -P(TTT*) in chloroform (1.0×10^{-4} M). Measurements were performed at temperatures ranging from 20 to 80 °C. The quartz cell was sealed to prevent the solvent from evaporating.

in dilute solution at room temperature, it dissociates into single polymers at higher temperatures (70–80 °C). The appearance of the isosbestic point indicates the equilibrium between the assembled state and the dissociated one.

The polymers consisting of one or two aromatic rings in the repeating unit, such as the **P(T*)**s, **P(PT*)**s, **P(TP*)**s, and **P(TT*)**s, were next examined by measuring the CD spectra at room temperature in chloroform ($c = 1.0 \times 10^{-4}$ M). Although the **P(T*)**s, **P(PT*)**s, and **P(TT*)**s exhibited monosignate Cotton effects and the **P(TP*)**s showed a slightly split Cotton effect, the CD intensities of the Cotton effects in both cases were extremely small. Moreover, the CD intensities ($\Delta\epsilon$) were approximately 1 or 2 orders of magnitude smaller than those of the **P(PPT*)**s, **P(TTP*)**s, and **P(TTT*)**s (see g_{abs} values in Table 3). The monosignate Cotton effect most likely occurs because the chirality of the side chain is slightly transferred to the main chain via through bond interactions. These results suggest that the polymers with one or two aromatic rings in the repeating unit do not form helically π -stacked structure based on the polymer assembly in chloroform, in contrast to the case of the polymers consisting of three aromatic rings in the unit cell. The polymers with one or two aromatic rings in the repeating unit are well soluble in chloroform and do not form associated species, such as a polymer assembly. Conversely, the polymers with three aromatic rings in the repeating unit are less soluble in chloroform and therefore more easily form an associated species, such as a polymer assembly with a helically π -stacked structure. The presence of two non-substituted aromatic rings enhances the attraction between the polymer chains due to the π – π interaction, and the position of the chiral substituent on the aromatic ring (thienylene or phenylene ring) determines the helical sense in the π -stacking of the polymers by minimizing the steric hindrance of chiral substituents.

The dissymmetry factors in absorption, defined as $g_{\text{abs}} = 2(\epsilon_{\text{L}} - \epsilon_{\text{R}})/(\epsilon_{\text{L}} + \epsilon_{\text{R}}) = \Delta\epsilon/\epsilon$,⁶⁰ represent the degree of circular polarization in absorption and are summarized in Table 3. The **P(PPT*)**s, **P(TTP*)**s, and **P(TTT*)**s had values of g_{abs} on the order of 10^{-3} at λ_{max} , while the rest of the polymers had values of $10^{-4} \sim 10^{-5}$ that were 1 or 2 orders of magnitude lower, as mentioned above. It is interesting to note that the **P(T*)**s, which are *regiorandom* polythiophenes with chiral alkoxy carbonyl side chains, exhibited a small Cotton effect with monosignate features in solution, while even

regioregular polythiophenes with chiral alkyl or alkoxy side chains do not exhibit the Cotton effect in solution.^{39,61–63} These results suggest that the key ways to induce chirality in the conjugated backbone are by attaching the chiral center (i) through an ester group and (ii) as close to the backbone as possible.

Table 3. Dissymmetry Factors (g_{abs}) Evaluated from CD Spectra of the Polymers.^a

polymer	g_{abs} (wavelength/nm) ^b
<i>R</i> -P(PPT*)	-6.1×10^{-4} (370), $+2.5 \times 10^{-3}$ (410)
<i>S</i> -P(PPT*)	$+8.0 \times 10^{-4}$ (370), -2.4×10^{-3} (410)
<i>R</i> -P(PT*)	$+8.0 \times 10^{-5}$ (350), -6.7×10^{-5} (391)
<i>S</i> -P(PT*)	-7.8×10^{-5} (342), $+2.5 \times 10^{-5}$ (398)
<i>R</i> -P(TP*)	$+1.8 \times 10^{-5}$ (361)
<i>S</i> -P(TP*)	-1.4×10^{-5} (366)
<i>R</i> -P(TTP*)	$+1.8 \times 10^{-4}$ (421), -1.3×10^{-3} (485)
<i>S</i> -P(TTP*)	-1.8×10^{-4} (420), $+1.4 \times 10^{-3}$ (478)
<i>R</i> -P(T*)	$+3.9 \times 10^{-4}$ (342)
<i>S</i> -P(T*)	-4.5×10^{-4} (371)
<i>R</i> -P(TT*)	$+2.7 \times 10^{-5}$ (437)
<i>S</i> -P(TT*)	-2.5×10^{-5} (435)
<i>R</i> -P(TTT*)	-7.7×10^{-4} (492), $+2.5 \times 10^{-2}$ (628)
<i>S</i> -P(TTT*)	$+1.2 \times 10^{-3}$ (492), -6.0×10^{-2} (628)

^a Measured in chloroform.

^b Wavelength at which g_{abs} was evaluated.

The *R* and *S* polymer thin films also demonstrated a mirrored Cotton effect in the region of the π – π^* transition (Figure 5d–f). The linear polarization of these films was carefully determined prior to measuring the CD spectra and was found to be negligible. Furthermore, the thin films of the corresponding achiral (racemic) polymers demonstrated no Cotton effect. These facts indicate that the CD spectra observed for the polymer thin films are not artifacts.⁶⁰ At the same time, the CD intensity of the film is enhanced by approximately 2–10 times that of the solution. These results are attributed to a strengthening of the helical π -stacking between the polymer main chains in solid states, such as films.

Effects of Chemical Doping on Chiral Optical Properties. It is intriguing to elucidate how the chiral optical properties of the polymers are affected by oxidation through chemical doping. The author performed chemical doping by focusing on the polymers, such as the **P(PPT*)s**, **P(TTP*)s**, and **P(TTT*)s**, that exhibited Cotton effects in their CD spectra. Several kinds of electron-accepting [iodine (I_2) and iodine monobromide (IBr)] or proton-donating [concentrated sulfuric acid (conc. H_2SO_4) and nitric acid (HNO_3)] compounds were examined as chemical dopants. As a result, only IBr acted as a dopant to **P(TTP*)s** and **P(TTT*)s** but not to **P(PPT*)s**. The spectroscopic changes of the polymers are shown in Figures 9 and 10. Exposing the spin-cast films of the **P(PPT*)s** to IBr gas did not change the UV-vis or CD spectra, indicating that chemical doping did not occur. This behavior is because **P(PPT*)s** have a lower HOMO level and are less oxidative (electron donating) to the dopant.

However, exposing the spin-cast films of the **P(TTP*)s** to IBr gas for one second resulted in a decrease in the intensity of the absorption band at 456 nm and the appearance of a new band at 612 nm in the UV-vis spectra (Figure 9a), indicating an increase in the effective conjugation length of the doped main chain with a quinoid structure formed upon the doping. Additionally, a new broad band appeared approximately 2500 nm upon doping (Figure 9a). The band may be assigned to a polaron and/or a bipolaron band in the doped main chain. The chemical doping also decreased the intensity of the Cotton effect and caused a slight red shift in the CD spectra as well as a decrease in the g value (Figure 10a). This result implies that the interchain helically π -stacked structure of the polymer is destructed upon chemical doping, probably because the dopants interpenetrate the helically stacked polymer chains.

The exposure of the spin-cast films of the **P(TTT*)s** to IBr gas for one second resulted in similar changes as observed in the case of the **P(TTP*)s**. Namely, upon doping, the absorption band of the main chain at 540 nm decreased in intensity, and a new band of the doped main chain appeared at 724 nm. Additionally, the broad band attributable to a polaron and/or a bipolaron band in the doped main chain appeared approximately 2500 nm (Figure 9b). The change in CD spectrum was similar to the case of the **P(TTP*)s**. The Cotton effect observed in the nondoped main chain

decreased in intensity, which was associated with a slight red shift and resulted in a decrease in the g value (Figure 10b). This result indicates that the chirality due to the interchain helical π -stacking structure is decreased by the interpenetration of the dopants into the helical π -stacked polymer main chains.

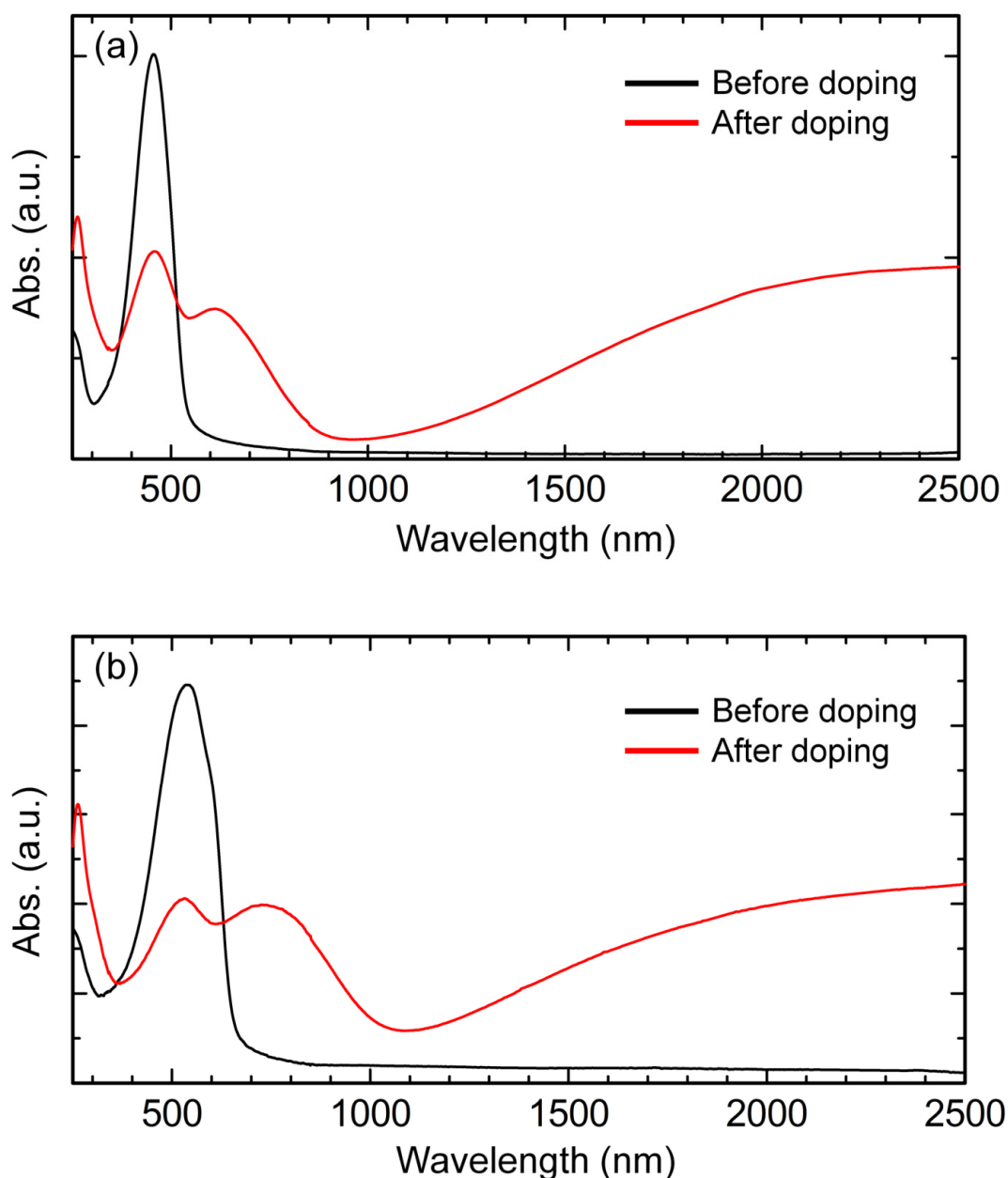


Figure 9. UV-vis spectra of cast films of (a) **R-P(TTP*)** and (b) **R-P(TTT*)** before and after chemical doping with IBr.

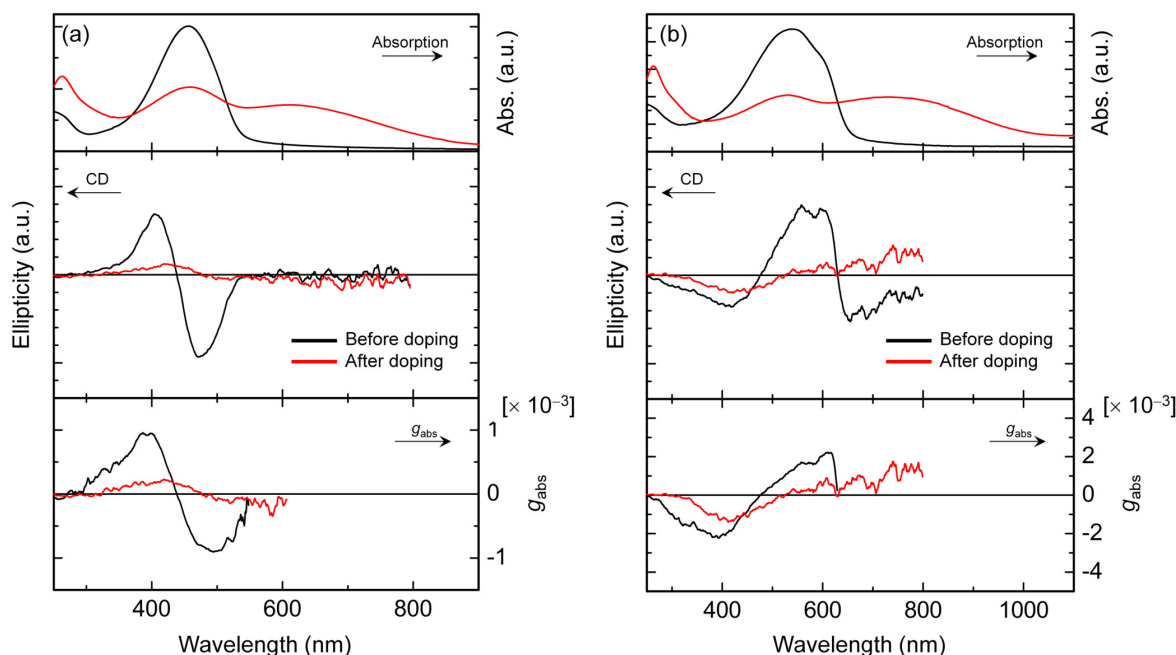


Figure 10. UV-vis (upper), CD (middle), and g_{abs} (lower) spectra of cast films of (a) **R-P(TTP*)** and (b) **R-P(TTT*)** before and after chemical doping with IBBr.

Circularly Polarized Fluorescence. Figure 11a shows the circularly polarized fluorescence (CPF) spectra of the **P(PPT*)**s, **P(TTP*)**s, and **P(TTT*)**s in chloroform (1.0×10^{-4} M), which exhibit circular polarization in their fluorescence bands. The CPF signals for the polymers with *R* and *S* configurations appear in opposite directions, resulting in almost mirror images in solution and cast films; for example, the **R-P(TTP*)** exhibits a positive signal, whereas the **S-P(TTP*)** exhibits a negative signal.

The fluorescence dissymmetry factors, g_{lum} , of the polymers in chloroform are listed in Table 4. The factor is defined as $g_{\text{lum}} = 2(I_L - I_R)/(I_L + I_R) = \Delta I/I$, where I_L and I_R denote the intensities of the left- and right-handed polarized emissions, respectively.⁶⁰ The g_{lum} values of the polymer solutions are approximately 10^{-3} , which agree with the g_{abs} in solution.

Figure 11b shows the CPF spectra of the polymer films. Any artifacts are negligible for these polymers, as indicated by the lack of CPF signal from the films of the corresponding achiral polymers. The g_{lum} values of the polymer films for the **P(TTP*)**s and **P(TTT*)**s increased relative to the corresponding solution by approximately 1 order of magnitude, whereas the g_{lum} values for the **P(PPT*)**s only

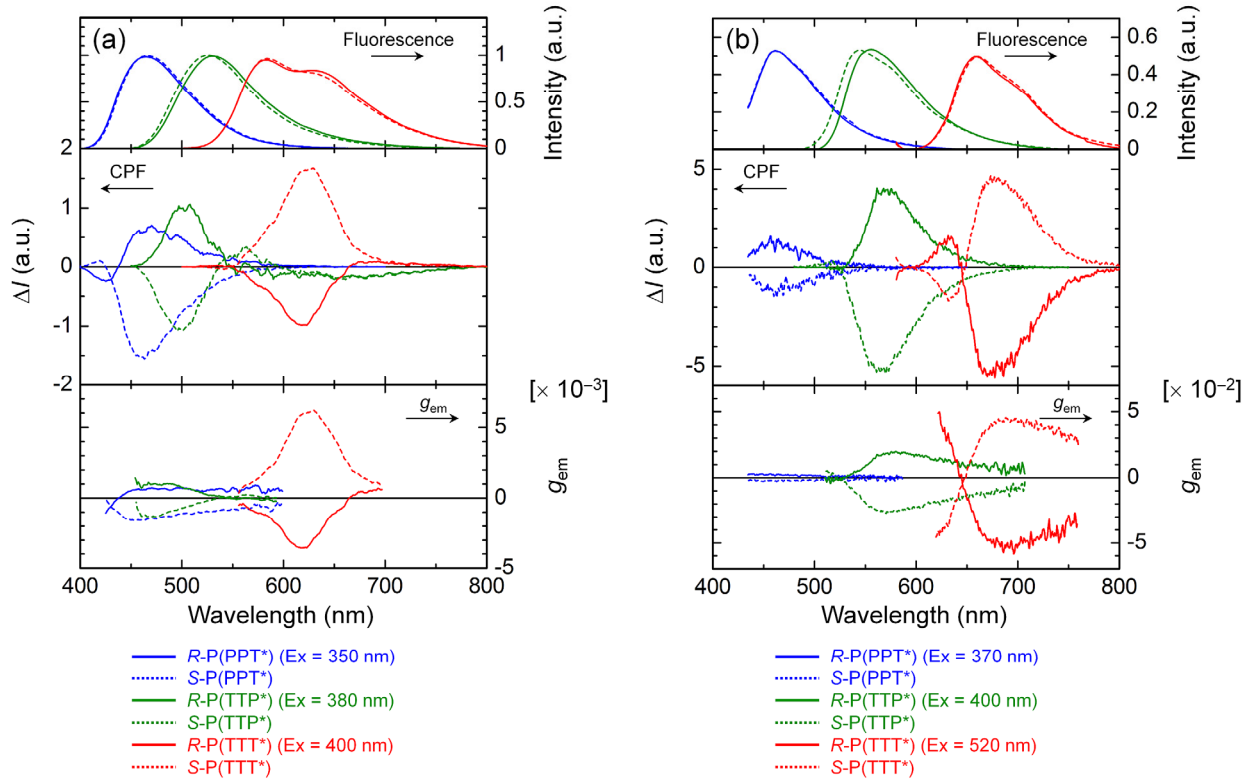


Figure 11. The fluorescence (upper), CPF (middle), and g_{lum} (lower) spectra of the polymers in (a) chloroform ($c = 1.0 \times 10^{-4}$ M) and (b) as-cast films.

Table 4. Dissymmetry Factors (g_{lum}) Evaluated from CPF Spectra of the Polymers.

polymer	g_{lum} (wavelength/nm) ^a		
	in CHCl ₃	film	annealed film
R-P(PPT*)	$+0.72 \times 10^{-3}$ (447)	$+3.1 \times 10^{-3}$ (457)	-6.9×10^{-3} (456)
S-P(PPT*)	-1.5×10^{-3} (455)	-2.9×10^{-3} (463)	$+1.1 \times 10^{-2}$ (454)
R-P(TTP*)	$+1.1 \times 10^{-3}$ (500)	$+1.8 \times 10^{-2}$ (568)	$+2.9 \times 10^{-1}$ (558)
S-P(TTP*)	-2.2×10^{-3} (502)	-2.6×10^{-2} (565)	-1.1×10^{-2} (534)
R-P(TTT*)	-4.0×10^{-3} (623)	-4.8×10^{-2} (680)	$+0.96 \times 10^{-1}$ (666)
S-P(TTT*)	$+3.0 \times 10^{-3}$ (627)	$+4.1 \times 10^{-2}$ (680)	-1.5×10^{-1} (666)

^a wavelength at which g_{lum} was evaluated.

increased by approximately 2–3 times relative to the corresponding solution. This increase may be attributed to the strong π – π interactions between polymer backbones in the solid state, as mentioned above. The **P(TTP*)**s and **P(TTT*)**s, which have a bithiophene moiety in the repeating unit, possessed larger g_{lum} values than the **P(PPT*)**s, which have biphenyl moieties instead. This difference may be explained by the difference in coplanarity between bithiophene and biphenyl. Incorporating bithiophene into the polymer backbone leads to a higher degree of coplanarity and stronger π – π interactions, which results in larger g_{lum} relative to the **P(PPT*)**s (see also Figure 12).

The polymer films were annealed for 30 min at 150 °C, which falls in the LC temperature range, and were then subjected to CPF measurement. Figure 13 shows the CPF and g_{lum} spectra of the as-cast and annealed films for the **P(TTT*)**s.

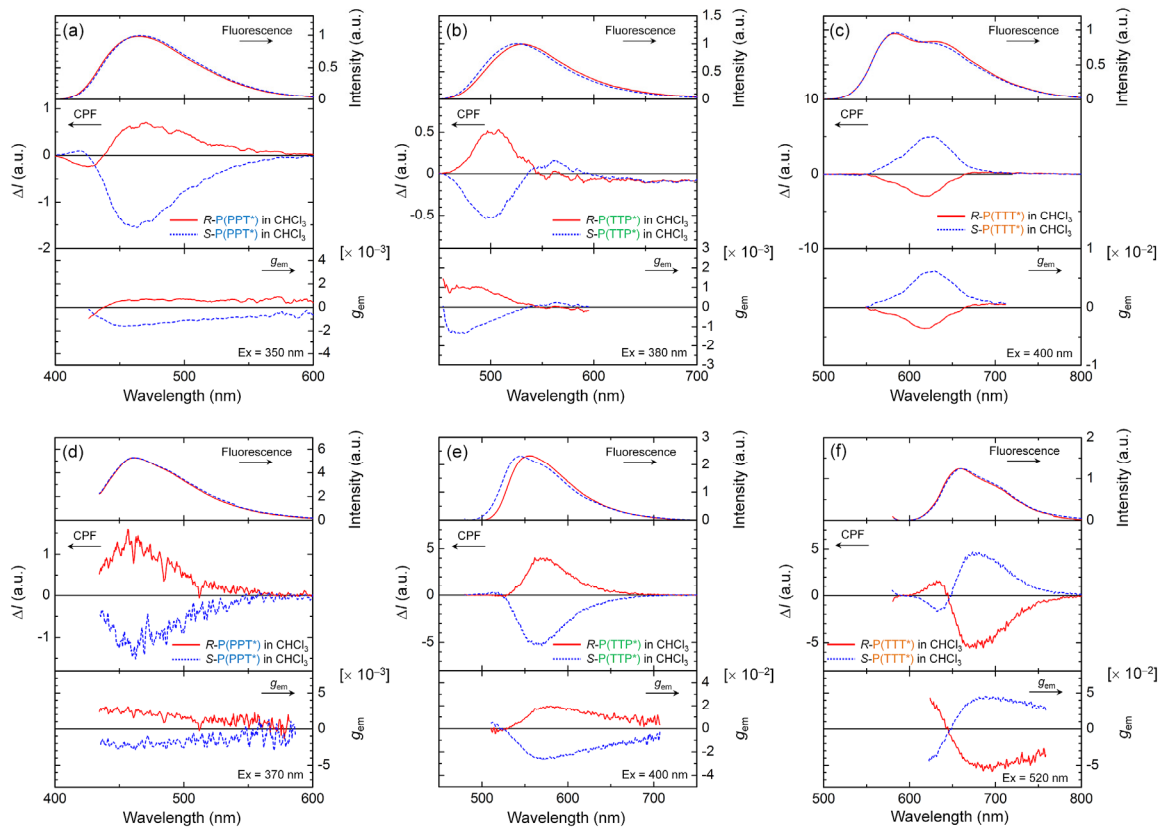


Figure 12. Fluorescence (upper), CPF (middle) and dissymmetry factor (g_{em} , lower) spectra of the polymers in chloroform ($c = 1.0 \times 10^{-4}$ M) and the cast films, **P(PPT*)**s (a: solution, d: film), **P(TTP*)**s (b: solution, e: film) and **P(TTT*)**s (c: solution, f: film). The solid and dotted lines indicate the spectra of polymers with (R)- and (S)-configurations, respectively.

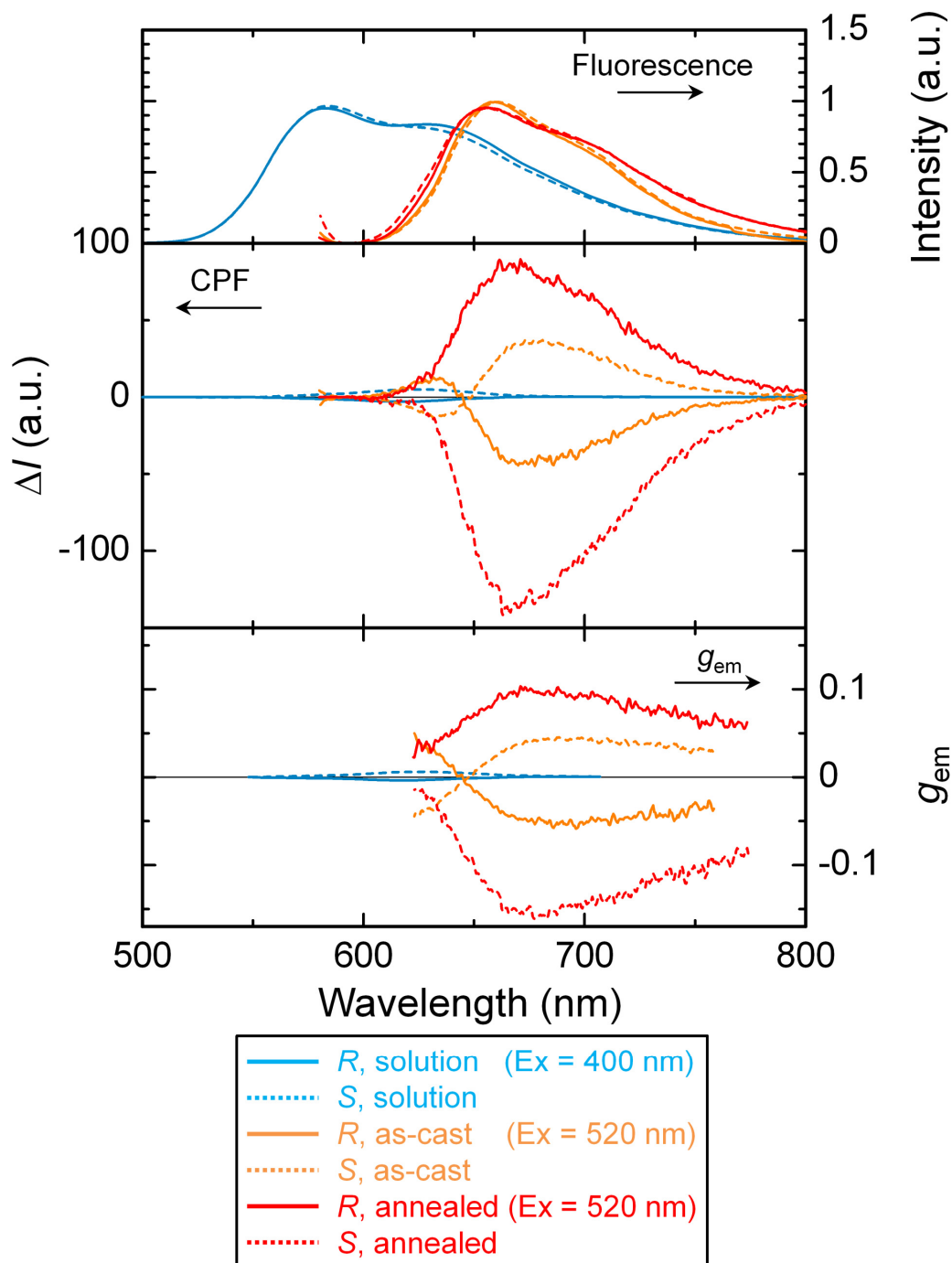


Figure 13. Fluorescence (upper), CPF (middle), and g_{lum} (lower) spectra of **P(TTT*)** in chloroform ($c = 1.0 \times 10^{-4}$ M), the as-cast films, and the annealed films.

The g_{lum} values for the annealed polymer films are listed in Table 4. After annealing, the absolute g_{lum} values increased by at least 1 order of magnitude and produced g_{lum} values as high as 10^{-1} , which is similar to those of chiral polyfluorenes.^{45,46} These g_{lum} values are very high, despite the *regiorandom* structure of the polymers. This value may be due to the helical π -stacking during annealing at the LC temperature. Interestingly, the CPF signals inverted after annealing the **P(TTT*)**s; that is, the g_{lum} of the as-cast **S-P(TTT*)** film showed a positive signal of $+4.1 \times 10^{-2}$ at 680 nm that became a negative signal of -1.5×10^{-1} at 666 nm after annealing. Annealing in the LC phase encourages the self-assembly of the polymer backbone and the formation of macroscopic π - π stacks, which leads to high absolute g_{lum} values.^{45,46} Annealing may also lead to the helical packing of the polymer backbones⁴² in the chiral nematic phase, which may cause the inversion of the g_{lum} signal for the **P(PPT*)**s and **P(TTT*)**s. However, the **P(TTP*)**s showed no inversion of the g_{lum} signal. In the **P(TTP*)**s, the chiral substituent is linked to phenylene, whereas it is linked to thiophene in the **P(PPT*)**s and **P(TTT*)**s, as indicated above. Although the structural changes in the polymer thin films caused by annealing have not yet been understood, any differences in the chemical structure may be related to the inversion of the g_{lum} signals caused by annealing. The hierarchical arrangement of higher-order structures by chiral liquid crystallinity, such as the self-ordering of the polymer aggregates in the chiral nematic phase by annealing at the LC temperature, is a promising way for highly enhancing the dissymmetry factor up to 10^{-1} in the CPF of the chiral conjugated polymers.

RGB and White Fluorescence. Finally, the author mixed solutions of the **P(PPT*)**s, **P(TTP*)**s, and **P(TTT*)**s, which exhibit blue, green, and orange fluorescence, respectively. The actual ratio of **P(PPT*)**, **P(TTP*)**, and **P(TTT*)** employed in the mixture was 1:1:5 (5.0×10^{-5} M/ 5.0×10^{-5} M/ 2.5×10^{-4} M) based on inverse quantum yields of 1/0.26, 1/0.23 and 1/0.05, respectively. Figure 14 shows the CPF spectra of the polymer mixtures. System 1 is the mixture of **(R)-P(PPT*)**, **(R)-P(TTP*)**, and **(S)-P(TTT*)**, which displays a positive g_{lum} , and system 2 is the mixture of **(S)-P(PPT*)**, **(S)-P(TTP*)**, and **(R)-P(TTT*)**, which displays a negative g_{lum} . These mixtures

displayed mirrored CPF spectra from 400–700 nm and a g_{lum} on the order of 10^{-3} , demonstrating circularly polarized white fluorescence. Figure 15a shows a photo of the polymer mixture in chloroform, which emits white light.

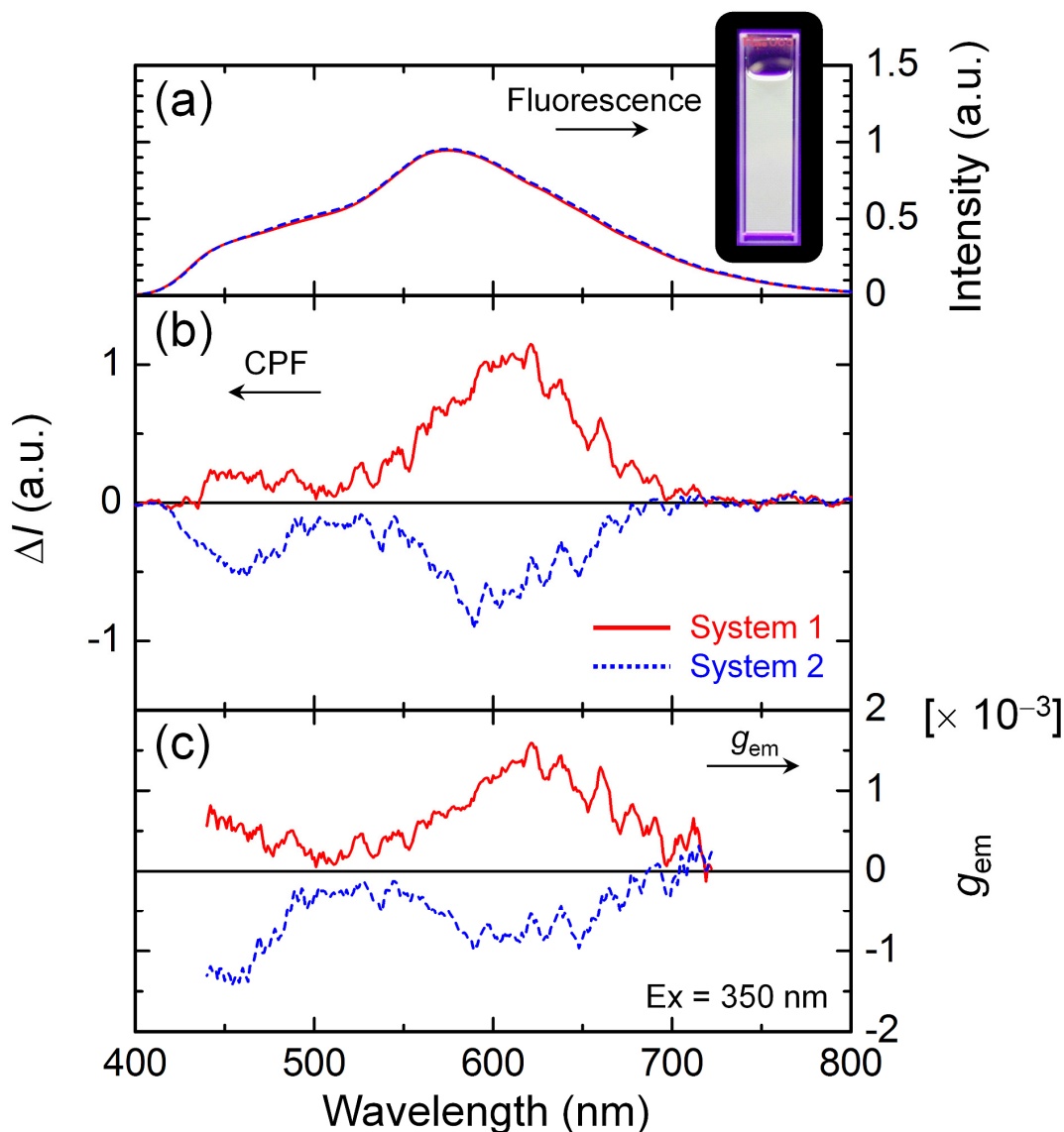


Figure 14. (a) Fluorescence, (b) CPF, and (c) g_{lum} spectra of the polymer mixtures in chloroform [P(PPT*), 5.0×10^{-5} M; P(TTP*), 5.0×10^{-5} M; P(TTT*), 2.5×10^{-4} M], where system 1 is the mixture of *R*-P(PPT*), *R*-P(TTP*), and *S*-P(TTT*), and system 2 is a mixture of *S*-P(PPT*), *S*-P(TTP*), and *R*-P(TTT*). The inset shows a photo of system 1 in chloroform, irradiated with 365 nm UV light.

However, the cast films prepared using the above mixtures showed red, not white, fluorescence due to polymer aggregation, which allows either an energy transfer from the excited states of the **P(PPT*)** and **P(TTP*)** to that of the **P(TTT*)** or the reabsorption of the fluorescent emissions of the **P(PPT*)** and **P(TTP*)** by the **P(TTT*)**. To suppress both energy transfer and reabsorption, the interchain distances in the polymers need to be increased. Therefore, the polymer mixture in system 1 was dispersed in an excess of polystyrene by dissolving both solutions in chloroform and then casting them onto a quartz substrate. This cast film sufficiently separated the polymers from each other in terms of their interchain distances to create a so-called “pseudodilute solution” state.

Figure 15b depicts the white fluorescence of the film on a quartz substrate. The white fluorescence is circularly polarized emissions. The g_{lum} values increased by a factor of 1.5–5.8 compared with the corresponding values in solution but remained on the order of 10^{-3} because the polymers are dispersed in an excess of polystyrene to avoid aggregation by decreasing the interchain interactions, which results in conditions similar to those observed in the solutions.

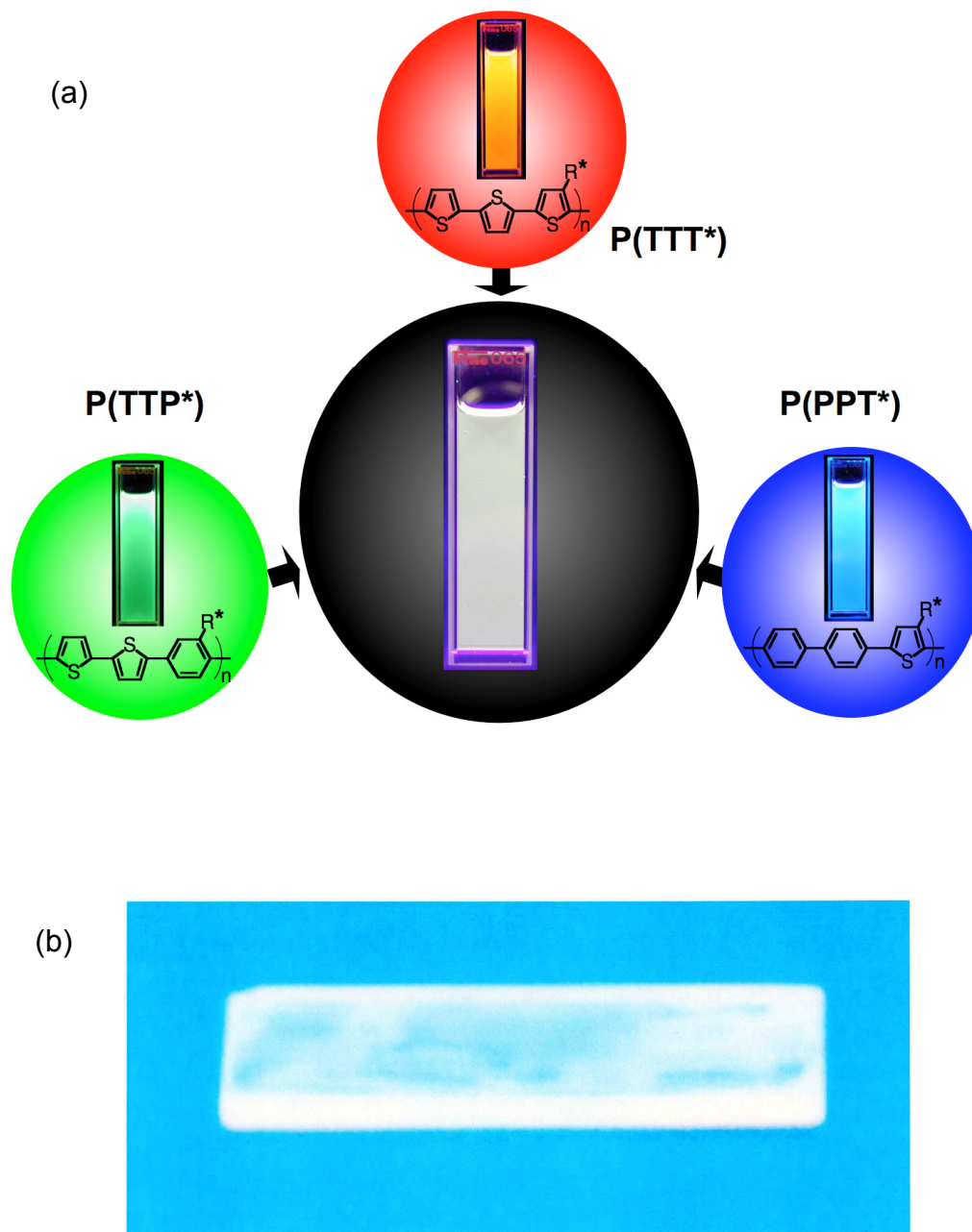


Figure 15. (a) RGB and white fluorescence of system 1, the mixture of ***R*-P(PPT*)**, ***R*-P(TTP*)**, and ***S*-P(TTT*)**, in chloroform and (b) white fluorescence of the cast film of system 1 on a quartz substrate. The film was prepared by dissolving the mixture and an excess of polystyrene in chloroform followed by casting onto the quartz substrate. UV light at 365 nm was used for excitation.

Conclusions

The author has synthesized various types of thiophene-based LC conjugated copolymers containing a chiral nonyloxy carbonyl group in the side chain. The polymers with three aromatic rings in the repeating unit showed bisignate Cotton effects in the CD spectra of solutions and films and formed a polymer assembly with an interchain helically π -stacked structure. The concentration and temperature dependence of the absorption and CD spectra indicated that the polymer assembly exists even at dilute concentrations at room temperature but dissociates into single polymers at high temperatures. These polymers exhibited RGB-colored fluorescence with quantum yields from 0.04–0.26 and also showed CPF both in solution and as a film. The films showed enhanced CPF signals because of the strengthening of the helical π -stacking in solid states. The annealed films demonstrated very high CPF with g_{lum} values up to 10^{-1} , which were due to the large interchain interactions achieved during self-ordering in the N*-LC phase. The author found that the hierarchical arrangement of the higher-order structure by chiral liquid crystallinity is promising for the evolution of CPF with a very high dissymmetry factor in the chiral conjugated polymers. Furthermore, when some of the polymers were mixed in the appropriate ratio, CPF was observed across most of the visible region, indicating circularly polarized white luminescence. These results suggest that the polymers synthesized here may be useful as advanced materials for creating unique optical devices, such as circularly polarized electroluminescence in next-generation polymer electronics.

Experimental Section

1. Measurements. All compounds were completely characterized by using elemental analysis (except polymers), ^1H NMR, ^{13}C NMR, and mass (except polymers) spectroscopies. ^1H NMR and ^{13}C NMR spectra were measured in CDCl_3 as a deuterated solvent by using Bruker AM500 FT-NMR spectrometer. High-resolution mass spectra (HRMS) were obtained by using Thermo Fisher Scientific EXACTIVE (ESI and APCI) and JEOL JMS-HX110A (FAB). Optical purities of chiral compounds were evaluated with the specific rotation measured by JASCO P-2300 polarimeter. Molecular weights of the polymers were evaluated through gel permeation chromatography (GPC) calibrated by polystyrene standard at 40 °C. Tetrahydrofuran (THF) was used as an eluent and the flow rate was 1.0 mL/min. A Shodex A-80M column and a JASCO HPLC 870 UV detector were used for the measurement. Polarizing optical micrography was performed by Nikon ECLIPS E 400 POL polarizing microscope equipped with Linkam TM 600PM heating/cooling stage. Phase transition temperatures were determined by using Perkin-Elmer differential scanning calorimeter (DSC 7) apparatus at the rate of 10 °C/min in both heating and cooling processes. Measurements of absorption and fluorescence spectra of the polymers were carried out with HITACHI U-3500 spectrometer, JASCO V-570 UV/VIS/NIR spectrophotometer, and JASCO FP-750 spectrometer, respectively. Circular dichroism spectra were measured with JASCO J-820 spectropolarimeter. Circularly polarized fluorescence measurements were carried out by JASCO CPL200.

2. Materials. All chemicals were used as purchased. *N, N'*-dimethylformamide (DMF), THF, dichloromethane, and hexane were distilled prior to use.

3. Synthesis. All syntheses were carried out under argon atmosphere.

2,5-Dibromo-3-thiophenecarboxylic Acid (1). To a stirred mixture of *N*-bromosuccinimide (NBS) (13.9 g, 78 mmol) and 50 mL of DMF, a solution of 3-thiophenecarboxylic acid (5 g, 39 mmol) in 20 mL of DMF was added dropwise at room temperature, during which time the flask had been covered with aluminum foil. The mixture was stirred at 50 °C overnight and then poured into 800 mL of saturated

aqueous solution of sodium bicarbonate. The resulting precipitate was collected by filtration and washed with ethanol. The crude product was recrystallized from ethanol and water to give 9.9 g of white needle (yield = 89%). Anal. calcd for $C_5H_2Br_2O_2S$: C, 21.00; H, 0.71. Found: C, 21.17; H, 0.82. 1H NMR ($CDCl_3$, d from TMS, ppm): 7.40 (s, 1H, ThH). ^{13}C NMR ($CDCl_3$, d from TMS, ppm): 111.7, 121.4, 130.7, 131.7, 165.3. HRMS (ESI) calcd for $C_5H_2Br_2O_2S$ [$M - H^+$]: 284.8049. Found: 284.8052.

(R)-(-)-2-Nonyl 2,5-Dibromothiophene-3-carboxylate (R-2). To a solution of **1** (8.1 g, 28 mmol), (*S*)-(+)-2-nonanol (4.1 g, 28 mmol) and triphenylphosphine (TPP) (7.5 g, 28 mmol) in 35 mL of THF was added dropwise a solution of diethyl azodicarboxylate (DEAD) (40% in toluene; 12.4 g, 28 mmol) in 35 mL of THF. The solution was stirred for 10 h at room temperature, and then diethyl ether and water were added. The organic layer was washed twice with water and dried over magnesium sulfate. After removing the solvent by evaporation, the resulting crude product was purified by column chromatography (silica gel, hexane/ethyl acetate = 10) to afford 9.2 g of colorless oil (yield = 79%). Anal. calcd for $C_{14}H_{20}Br_2O_2S$: C, 40.80; H, 4.89; Br, 38.77; S, 7.78. Found: C, 40.66; H, 4.83; Br, 38.55; S, 7.88. 1H NMR ($CDCl_3$, d from TMS, ppm): 0.88 (t, $J = 6.8$ Hz, 3H, CH_2CH_3), 1.28–1.40 (m, 13H, CH_2 , $COOCHCH_3$), 1.52–1.75 (dm, 2H, $COOCHCH_2$), 5.09 (sext, $J = 6.4$ Hz, 1H, $OCH(CH_3)CH_2$), 7.33 (s, 1H, ThH). ^{13}C NMR ($CDCl_3$, d from TMS, ppm): 14.1, 20.0, 22.6, 25.4, 29.2, 29.4, 31.8, 35.9, 72.6, 111.2, 118.8, 131.8, 132.4, 160.5. HRMS (APCI) calcd for $C_{14}H_{20}Br_2O_2S$ [$M + H^+$]: 412.9603. Found: 412.9596. $[\alpha]_D^{25} -21.67^\circ$ (c 1.05, $CHCl_3$).

(S)-(+)-2-Nonyl 2,5-Dibromothiophene-3-carboxylate (S-2). The same procedure with **R-2** was employed by using **1**, (*R*)-(-)-2-nonanol, TPP and DEAD (yield = 75%). Anal. calcd for $C_{14}H_{20}Br_2O_2S$: C, 40.80; H, 4.89; Br, 38.77; S, 7.78. Found: C, 40.85; H, 4.76; Br, 37.50; S, 7.76. 1H NMR ($CDCl_3$, d from TMS, ppm): 0.88 (t, $J = 6.8$ Hz, 3H, CH_2CH_3), 1.28–1.40 (m, 13H, CH_2 , $COOCHCH_3$), 1.53–1.75 (dm, 2H, $COOCHCH_2$), 5.09 (sext, $J = 6.4$ Hz, 1H, $OCH(CH_3)CH_2$), 7.33 (s, 1H, ThH). ^{13}C NMR ($CDCl_3$, d from TMS, ppm): 14.1, 20.0, 22.6, 25.4, 29.2, 29.4, 31.8, 35.9, 72.6, 111.2, 118.8, 131.8, 132.4, 160.5. HRMS (APCI) calcd for $C_{14}H_{20}Br_2O_2S$ [$M + H^+$]: 412.9603. Found: 412.9596. $[\alpha]_D^{23} +21.64^\circ$ (c 1.02, $CHCl_3$).

(R)-(-)-2-Nonyl 2,5-Dibromobenzoate (R-3). The same procedure with **R-2** was employed by using 2,5-dibromobenzoic acid and (S)-(+)-2-nonanol as reagents and hexane/chloroform (= 1) as the eluent for column chromatography to afford a colorless oil (yield = 94%). Anal. calcd for $C_{16}H_{22}Br_2O_2$: C, 47.32; H, 5.46; Br, 39.35. Found: C, 47.59; H, 5.53; Br, 39.34. 1H NMR ($CDCl_3$, δ from TMS, ppm): 0.88 (t, J = 6.8 Hz, 3H, CH_2CH_3), 1.28–1.43 (m, 13H, CH_2 , $COOCHCH_3$), 1.56–1.79 (dm, 2H, $COOCHCH_2$), 5.17 (sext, J = 6.4 Hz, 1H, $OCH(CH_3)CH_2$), 7.42 (dd, J = 2.4/8.4 Hz, 1H, PhH), 7.50 (d, J = 8.4 Hz, 1H, PhH), 7.84 (d, J = 2.4 Hz, 1H, PhH). ^{13}C NMR ($CDCl_3$, δ from TMS, ppm): 14.1, 19.9, 22.6, 25.4, 29.2, 29.4, 31.8, 35.9, 73.5, 120.1, 121.0, 133.8, 134.7, 135.1, 135.6, 164.6. HRMS (APCI) calcd for $C_{16}H_{22}Br_2O_2$ [$M + H^+$]: 407.0040. Found: 407.0032. $[\alpha]_D^{24}$ -20.83° (c 0.98, $CHCl_3$).

(S)-(+)-2-Nonyl 2,5-Dibromobenzoate (S-3). The same procedure with **R-2** was employed by using 2,5-dibromobenzoic acid and (R)-(-)-2-nonanol as reagents and hexane/chloroform (= 1) as the eluent for column chromatography (yield = 95%). Anal. calcd for $C_{16}H_{22}Br_2O_2$: C, 47.32; H, 5.46; Br, 39.35. Found: C, 47.49; H, 5.32; Br, 39.15. 1H NMR ($CDCl_3$, δ from TMS, ppm): 0.88 (t, J = 6.8 Hz, 3H, CH_2CH_3), 1.28–1.43 (m, 13H, CH_2 , $COOCHCH_3$), 1.56–1.79 (dm, 2H, $COOCHCH_2$), 5.17 (sext, J = 6.4 Hz, 1H, $OCH(CH_3)CH_2$), 7.42 (dd, J = 2.4/8.4 Hz, 1H, PhH), 7.50 (d, J = 8.4 Hz, 1H, PhH), 7.84 (d, J = 2.4 Hz, 1H, PhH). ^{13}C NMR ($CDCl_3$, δ from TMS, ppm): 14.1, 19.9, 22.6, 25.4, 29.2, 29.4, 31.8, 35.9, 73.5, 120.1, 121.0, 133.8, 134.7, 135.1, 135.6, 164.6. HRMS (APCI) calcd for $C_{16}H_{22}Br_2O_2$ [$M + H^+$]: 407.0040. Found: 407.0033. $[\alpha]_D^{25}$ $+20.87^\circ$ (c 1.03, $CHCl_3$).

1,4-Phenylenediboronic Acid Bis(1,3-propanediol) Cyclic Ester (4). A solution of 1,4-phenylenediboronic acid (5 g, 30 mmol) and 1,3-propanediol (4.6 g, 60 mmol) in 300 mL of dichloromethane was stirred for 24 h at room temperature. The crude product obtained by evaporating the solvent was recrystallized from ethanol to give 6.8 g of white crystal (yield = 92%). Anal. calcd for $C_{12}H_{16}B_2O_4$: C, 58.62; H, 6.56. Found: C, 58.59; H, 6.67. 1H NMR ($CDCl_3$, δ from TMS, ppm): 2.05 (quint, J = 5.4 Hz, 4H, $CH_2CH_2CH_2$), 4.16 (t, J = 5.4 Hz, 8H, OCH_2CH_2), 7.73 (s, 4H, PhH). ^{13}C NMR ($CDCl_3$, δ from TMS, ppm): 27.4, 61.9, 132.5. HRMS (ESI) calcd for $C_{12}H_{16}B_2O_4$ [$M + H^+$]: 247.1307. Found: 247.1302.

5,5'-Bis(trimethylstannyl)-2,2'-bithiophene (5).⁵² To a solution of 2,2'-bithiophene (3.3 g, 20 mmol) and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) (5.8 g, 50 mmol) in 50 mL of THF, *n*-BuLi (1.6 M in hexane; 31.2 mL, 50 mmol) was added dropwise at $-78\text{ }^{\circ}\text{C}$. The solution was stirred for 1 h at $-78\text{ }^{\circ}\text{C}$. Then, a solution of trimethyltin chloride (10 g, 50 mmol) in 20 mL of THF was added dropwise. The reaction mixture was stirred for 3 h at room temperature and was quenched by an addition of aqueous solution of ammonium chloride and diethyl ether. The organic layer was washed with aqueous solution of copper sulfate and dried over magnesium sulfate. The solvent was removed by evaporation and the resulting residue was recrystallized from methanol to afford 4.92 g of yellow needle (yield = 50%). Anal. calcd for $\text{C}_{14}\text{H}_{22}\text{S}_2\text{Sn}_2$: C, 34.19; H, 4.51. Found: C, 34.57; H, 4.62. ^1H NMR (CDCl_3 , δ from TMS, ppm): 0.34 (s, 18H, SnCH_3), 7.07 (d, $J = 3.4\text{ Hz}$, 2H, Th*H*), 7.26 (d, $J = 3.3\text{ Hz}$, 2H, Th*H*). ^{13}C NMR (CDCl_3 , δ from TMS, ppm): -8.2 , 124.8, 135.8, 137.5, 143.0. HRMS (FAB) calcd for $\text{C}_{14}\text{H}_{22}\text{S}_2\text{Sn}_2\text{ [M}^+]$: 493.9201. Found: 493.9209.

2,5-Bis(trimethylstannyl)thiophene (6).⁵³ To a solution of thiophene (1.0 g, 12 mmol) and TMEDA (2.9 g, 25 mmol) in 15 mL of hexane, *n*-BuLi (1.6 M in hexane; 15.6 mL, 25 mmol) was added dropwise at $-78\text{ }^{\circ}\text{C}$. The solution was once allowed to warm up to room temperature and stirred for 1 h. Then the solution was cooled down to $-78\text{ }^{\circ}\text{C}$ again and a solution of trimethyltin chloride (5 g, 25 mmol) in 15 mL of hexane was added dropwise. The reaction mixture was stirred for 3 h at room temperature and was quenched by an addition of aqueous solution of ammonium chloride. The organic layer was washed with aqueous solution of copper sulfate and dried over magnesium sulfate. The solvent was removed by evaporation and the resulting residue was recrystallized from hexane to afford 2.7 g of pale yellow needle (yield = 54%). Anal. calcd for $\text{C}_{10}\text{H}_{20}\text{SSn}_2$: C, 29.31; H, 4.92. Found: C, 29.34; H, 4.92. ^1H NMR (CDCl_3 , δ from TMS, ppm): 0.37 (s, 18H, SnCH_3), 7.37 (s, 2H, Th*H*). ^{13}C NMR (CDCl_3 , δ from TMS, ppm): -8.2 , 135.9, 143.1.

R-P(PPT*). A mixture of **R-2** (0.41 g, 1 mmol), 4,4'-biphenyldiboronic acid bis(neopentyl glycol) cyclic ester (**7**) (0.38 g, 1 mmol), tetrakis(triphenylphosphine) palladium(0) [$\text{Pd}(\text{PPh}_3)_4$] (17 mg, 0.015 mmol), sodium bicarbonate (1.1 g, 13 mmol), 100 mL of THF and 70 mL of water was vigorously stirred under reflux for 3 days.

Chloroform was added and the collected organic layer was concentrated. The resulting residue was dissolved in the minimum amount of THF and poured into an excess amount of methanol. The precipitated product was filtered and dried under vacuum to give 0.39 g of yellow powder (yield = 96%). ^1H NMR (CDCl_3 , δ from TMS, ppm): 0.86 (br, 3H, CH_2CH_3), 1.24 (br, 15H, CH_2 , COOCHCH_3), 5.05 (br, 1H, $\text{OCH}(\text{CH}_3)\text{CH}_2$), 6.64–7.79 (m, 9H, overlapped, ThH and PhH). ^{13}C NMR (CDCl_3 , δ from TMS, ppm): 14.1, 19.9, 22.6, 25.3, 29.2, 29.5, 31.8, 35.9, 71.7, 126.1, 126.2, 126.4, 127.3, 127.5, 129.7, 130.3, 132.6, 162.7.

S-P(PPT*). Using **S-2** and **7** as reagents employed the same procedure as **R-P(PPT*)** (yield = 95%). ^1H NMR (CDCl_3 , δ from TMS, ppm): 0.86 (br, 3H, CH_2CH_3), 1.24 (br, 15H, CH_2 , COOCHCH_3), 5.05 (br, 1H, $\text{OCH}(\text{CH}_3)\text{CH}_2$), 6.64–7.79 (m, 9H, overlapped, ThH and PhH). ^{13}C NMR (CDCl_3 , δ from TMS, ppm): 14.1, 19.9, 22.6, 25.3, 29.2, 29.5, 31.8, 35.9, 71.7, 126.1, 126.2, 126.4, 127.3, 127.5, 129.7, 130.3, 132.6, 162.7.

R-P(PT*). Using **R-2** and **4** as reagents employed the same procedure as **R-P(PPT*)** (yield = 99%). ^1H NMR (CDCl_3 , δ from TMS, ppm): 0.77 (3H, CH_2CH_3), 1.0–1.8 (15H, CH_2 , COOCHCH_3), 5.1 (1H, $\text{OCH}(\text{CH}_3)\text{CH}_2$), 7.4–7.9 (5H, overlapped, ThH and PhH). ^{13}C NMR (CDCl_3 , δ from TMS, ppm): 14.1, 20.0, 22.6, 25.3, 29.1, 30.2, 31.0, 35.9, 72.3, 110–140, 161.8.

S-P(PT*). Using **S-2** and **4** as reagents employed the same procedure as **R-P(PPT*)** (yield = 99%). ^1H NMR (CDCl_3 , δ from TMS, ppm): 0.77 (3H, CH_2CH_3), 1.0–1.8 (15H, CH_2 , COOCHCH_3), 5.1 (1H, $\text{OCH}(\text{CH}_3)\text{CH}_2$), 7.4–7.9 (5H, overlapped, ThH and PhH). ^{13}C NMR (CDCl_3 , δ from TMS, ppm): 14.1, 20.0, 22.6, 25.3, 29.1, 30.2, 31.0, 35.9, 72.3, 110–140, 161.8.

R-P(TP*). Tris(dibenzylideneacetone)dipalladium(0) [$\text{Pd}_2(\text{dba})_3$] (18 mg, 0.02 mmol), and tri-2-furylphosphine (TFP) (19 mg, 0.08 mmol) were dissolved in 3 mL of THF and stirred for 30 min at room temperature. Then, a solution of **R-3** (0.41 g, 1 mmol) in 3 mL of THF was added to the solution and stirred for 1 h at 50 °C. Addition of a solution of **6** (0.41 g, 1 mmol) in 3 mL of THF was followed and the resulting mixture was allowed to stir for 7 days at 60 °C. The mixture was poured into 500 mL of methanol containing small amount of hydrochloric acid and vigorously stirred for 3 h. After filtration the precipitate was dissolved in minimum amount of THF and

reprecipitated in 500 mL of methanol. The resulting precipitate was filtered and dried under vacuum to give 0.25 g of light brown powder (yield = 76%). ^1H NMR (CDCl_3 , d from TMS, ppm): 0.85 (3H, CH_2CH_3), 1.1–1.8 (15H, CH_2 , COOCHCH_3), 5.02 (1H, $\text{OCH}(\text{CH}_3)\text{CH}_2$), 7.05 (1H, ThH), 7.40 (1H, ThH), 7.53 (1H, PhH), 7.71 (1H, PhH), 7.95 (1H, PhH). ^{13}C NMR (CDCl_3 , d from TMS, ppm): 14.1, 19.5, 22.6, 25.3, 29.2, 29.5, 31.8, 35.8, 72.8, 124.2, 125.2, 126.3, 126.9, 127.5, 127.8, 131.6, 132.3, 133.3, 133.9, 142.1, 143.1, 168.2.

S-P(TP*). Using **S-3** and **6** as reagents employed the same procedure as **R-P(TP*)** (yield = 80%). ^1H NMR (CDCl_3 , d from TMS, ppm): 0.85 (3H, CH_2CH_3), 1.1–1.8 (15H, CH_2 , COOCHCH_3), 5.07 (1H, $\text{OCH}(\text{CH}_3)\text{CH}_2$), 7.05 (1H, ThH), 7.40 (1H, ThH), 7.53 (1H, PhH), 7.70 (1H, PhH), 7.96 (1H, PhH). ^{13}C NMR (CDCl_3 , d from TMS, ppm): 14.1, 19.5, 22.7, 25.3, 29.2, 29.5, 31.8, 35.8, 72.8, 124.2, 125.1, 126.3, 126.9, 127.5, 127.8, 131.5, 132.3, 133.3, 133.7, 142.0, 143.0, 168.2.

R-P(TTP*). Using **R-3** and **5** as reagents employed the same procedure as **R-P(TP*)** (yield = 73%). ^1H NMR (CDCl_3 , d from TMS, ppm): 0.77 (3H, CH_2CH_3), 1.0–1.8 (15H, CH_2 , COOCHCH_3), 4.99 (1H, $\text{OCH}(\text{CH}_3)\text{CH}_2$), 6.90 (1H, ThH), 7.05 (1H, ThH), 7.09 (1H, ThH), 7.23 (1H, ThH), 7.41 (1H, PhH), 7.56 (1H, PhH), 7.83 (1H, PhH). ^{13}C NMR (CDCl_3 , d from TMS, ppm): 14.1, 19.5, 22.7, 25.2, 29.2, 29.5, 31.8, 35.7, 72.9, 123.9, 124.0, 124.1, 124.7, 124.9, 126.2, 127.3, 127.6, 131.4, 132.2, 133.2, 133.6, 133.7, 134.1–141.2, 168.2.

S-P(TTP*). Using **S-3** and **5** as reagents employed the same procedure as **R-P(TP*)** (yield = 83%). ^1H NMR (CDCl_3 , d from TMS, ppm): 0.77 (3H, CH_2CH_3), 1.0–1.8 (15H, CH_2 , COOCHCH_3), 4.99 (1H, $\text{OCH}(\text{CH}_3)\text{CH}_2$), 6.90 (1H, ThH), 7.04 (1H, ThH), 7.09 (1H, ThH), 7.24 (1H, ThH), 7.41 (1H, PhH), 7.60 (1H, PhH), 7.83 (1H, PhH). ^{13}C NMR (CDCl_3 , d from TMS, ppm): 14.1, 19.5, 22.7, 25.2, 29.2, 29.5, 31.8, 35.7, 72.9, 123.9, 124.1, 124.7, 124.9, 126.2, 127.4, 127.6, 131.4, 132.2, 133.2, 133.6, 133.7, 134.1–140.9, 168.2.

R-P(TT*). Using **R-2** and **6** as reagents employed the same procedure as **R-P(TP*)** (yield = 98%). ^1H NMR (CDCl_3 , d from TMS, ppm): 0.87 (3H, CH_2CH_3), 1.1–1.8 (15H, CH_2 , COOCHCH_3), 5.13 (1H, $\text{OCH}(\text{CH}_3)\text{CH}_2$), 7.12 (1H, ThH), 7.48–7.58 (2H,

ThH). ^{13}C NMR (CDCl_3 , d from TMS, ppm): 14.1, 20.0, 22.7, 25.5, 29.2, 29.5, 31.8, 36.0, 72.2, 124.5, 125.2, 126.7, 129.5, 130.4, 133.5, 134.7, 135.5, 135.9, 141.0, 162.4.

S-P(TT*). Using **S-2** and **6** as reagents employed the same procedure as **R-P(TP*)** (yield = 92%). ^1H NMR (CDCl_3 , d from TMS, ppm): 0.87 (3H, CH_2CH_3), 1.1–1.8 (15H, CH_2 , COOCHCH_3), 5.14 (1H, $\text{OCH}(\text{CH}_3)\text{CH}_2$), 7.11 (1H, ThH), 7.48–7.52 (2H, ThH). ^{13}C NMR (CDCl_3 , d from TMS, ppm): 14.1, 20.0, 22.7, 25.5, 29.2, 29.5, 31.8, 36.0, 72.2, 124.5, 125.2, 126.6, 129.5, 130.3, 133.5, 134.6, 135.5, 135.9, 141.2, 162.3.

R-P(TTT*). Using **R-2** and **5** as reagents employed the same procedure as **R-P(TP*)**. Reaction time was 45 min (yield = 81%). ^1H NMR (CDCl_3 , d from TMS, ppm): 0.79 (3H, CH_2CH_3), 1.1–1.8 (15H, CH_2 , COOCHCH_3), 4.98 (1H, $\text{OCH}(\text{CH}_3)\text{CH}_2$), 6.9–7.5 (5H, ThH). ^{13}C NMR (CDCl_3 , d from TMS, ppm): 13.1, 18.9, 21.6, 24.4, 28.2, 28.7, 30.8, 34.9, 71.1, 123.4, 124.5, 126.0, 127.0, 128.0, 128.3, 131.8, 134.2, 134.7, 139.1, 142.2, 147.7, 160.5, 161.4, 185.2.

S-P(TTT*). Using **S-2** and **5** as reagents employed the same procedure as **R-P(TP*)**. Reaction time was 45 min (yield = 77%). ^1H NMR (CDCl_3 , d from TMS, ppm): 0.79 (3H, CH_2CH_3), 1.1–1.8 (15H, CH_2 , COOCHCH_3), 4.99 (1H, $\text{OCH}(\text{CH}_3)\text{CH}_2$), 6.9–7.5 (5H, ThH). ^{13}C NMR (CDCl_3 , d from TMS, ppm): 13.1, 18.9, 21.6, 24.4, 28.2, 28.7, 30.8, 34.9, 71.1, 123.4, 124.5, 126.0, 127.0, 128.0, 128.3, 131.8, 134.2, 134.7, 139.1, 142.2, 147.7, 160.5, 161.4, 185.2.

R-P(T*). A mixture of bis(1,5-cyclooctadiene)nickel(0) [$\text{Ni}(\text{cod})_2$] (0.66 g, 2.4 mmol), 2,2'-bipyridine (bpy) (0.38 g, 2.4 mmol) and 5 mL of DMF was stirred for 1 h at room temperature, and then, a solution of **R-2** (0.82 g, 2 mmol) in 3 mL of DMF was added in one portion. The reaction mixture was stirred vigorously for 2 days at 70 °C. The mixture was poured into 500 mL of methanol containing a small amount of hydrochloric acid and vigorously stirred for 3 h. After filtration the precipitate was dissolved in the minimum amount of THF and reprecipitated in 500 mL of methanol. The resulting sticky precipitate was dissolved in benzene and lyophilized to give 0.15 g of brown oil (yield = 30%). ^1H NMR (CDCl_3 , d from TMS, ppm): 0.78 (3H, CH_2CH_3), 1.0–1.8 (15H, CH_2 , COOCHCH_3), 4.99 (1H, $\text{OCH}(\text{CH}_3)\text{CH}_2$), 7.5–7.8 (1H, ThH). ^{13}C NMR (CDCl_3 , d from TMS, ppm): 14.0, 19.9, 22.6, 25.3, 29.2, 29.5, 31.8, 35.9, 71.8, 125.7, 126.3, 127.6, 128.3, 130.2, 132.6, 142.0, 149.1, 162.9.

***S*-P(T^{*})**. Using ***S*-2** as reagent employed the same procedure as ***R*-P(T^{*})** (yield = 35%).
¹H NMR (CDCl₃, *d* from TMS, ppm): 0.78 (3H, CH₂CH₃), 1.0–1.8 (15H, CH₂, COOCHCH₃), 4.99 (1H, OCH(CH₃)CH₂), 7.5–7.8 (1H, ThH). ¹³C NMR (CDCl₃, *d* from TMS, ppm): 14.0, 19.9, 22.6, 25.3, 29.2, 29.5, 31.8, 35.9, 71.8, 125.7, 126.3, 127.6, 128.3, 130.2, 132.6, 142.0, 149.1, 162.9.

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Chapter 1

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Chapter 2

Chirality Transfer via Self-Assembly of Interchain Helicity between Aromatic Conjugated Polymers through Interchain π - π Interaction

Introduction

Helical conjugated polymers (HCPs) have attracted current interest because the semiconducting properties of conjugated polymers (CPs) can achieve chirality and helicity to afford the peculiar optoelectronic functionalities, such as induced solenoid magnetism,¹ circularly polarized luminescence (CPL),²⁻⁵ and nonlinear second harmonic optics,⁶ and therefore they are regarded as next-generation plastic materials. Several approaches for producing HCPs have recently been reported. One of the most simple and straightforward methods is to introduce a chiral moiety into the side chain of the polymer. Various types of HCPs based on polyacetylene [PA],⁷⁸ poly(*para*-phenylene) [PPP],⁹ poly(*meta*-phenylene) [PMP],¹⁰ polypyrrole,¹¹ polythiophene [PT],¹¹ and polyfluorene [PF]^{5, 12} derivatives, all of which bear chiral substituents in their side chains, have been synthesized. Among them, the CPs with a linear main chain are known to form helically associated species through supramolecular assemblies and to exhibit chiroptical properties.

On the other hand, the induction of chirality into the CPs is also a promising way to produce HCPs. In this case, CPs can obtain chirality and helicity through the intermolecular interactions such as electrostatic, acid-base, hydrogen bonding, van der Waals, and π - π interactions, between the CPs and chiral molecules. Hence it is possible to control the helical sense by chirality of the additives, which is applied for the chiral sensor.⁷

A polymer nanosphere is an nanometer-scale spherical aggregate of polymers. When dispersing in solution, the nanosphere can be considered as an intermediate state between solution and film because the polymer nanoparticles are uniformly dispersed in the solvent, similar to the solution state, and also aggregate with each other, similar to the film state. Such bilateral character of the nanosphere causes the polymer to exhibit

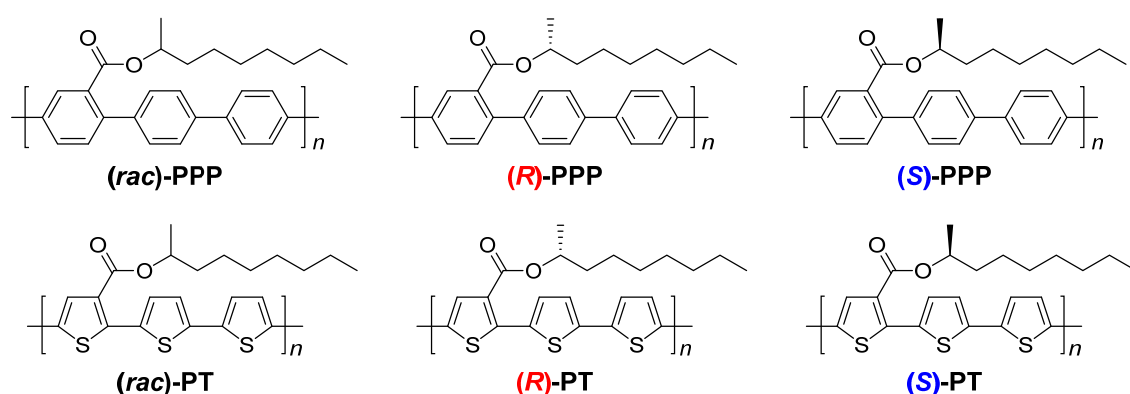
high processability and fluidity as well as aggregation effects. Moreover, each polymer nanosphere can freely move and rotate in solution and hence no linear dichroism is observed even if the nanosphere is linearly polarized. This feature is suitable for chiroptical measurements because an artifact corresponding to the linear polarization can be excluded from the circular dichroism (CD) and CPL spectra of the nanosphere solution.

Herein, the author reports the synthesis of three-ring type aromatic conjugated polymers (ACPs) with chiral side chains and the chirality-transferring behavior from chiral ACPs to achiral ones via self-assembly of interchain helicity. When aggregating into polymer nanosphere, the soluble parts of the three-ring type ACPs self-assemble the interchain helical π -stacking to exhibit circular polarization in both absorption and luminescence, although the chloroform solutions show no circular polarization. Furthermore, by aggregating chiral and achiral ACPs into a polymer nanosphere, these polymers cooperatively self-assembled the interchain helicity with one-handed helical sense, which indicates the chirality transfer between ACPs.

Results and Discussion

Synthesis of PPPs and PTs. The author synthesized poly(*para*-terphenylene) derivatives bearing either racemic or optically-active (2-nonyloxy)carbonyl side chains, which were designated as (*rac*)-, (*R*)-, and (*S*)-**PPPs**, respectively. In addition, poly(terthiophene) derivatives were also synthesized by introducing the same side chain series, designated as (*rac*)-, (*R*)-, and (*S*)-**PTs**, respectively. The chemical structures of these three-ring type ACPs are depicted in Scheme 1 and the synthetic routes are shown in Scheme 2 and Experimental Section. All the synthesized polymers were purified through the 2-step Soxhlet extraction, which removed oligomers and impurities in the 1st step by refluxing acetone for 5–7 days and then collected the soluble parts of the polymers in 2nd step by refluxing chloroform for 4–7 days. The obtained polymers were soluble in organic solvents such as tetrahydrofuran (THF) and chloroform, but insoluble in polar solvents such as water and methanol. Average molecular weights of the soluble polymers are summarized in Table 1. The number-average molecular weights (M_n) were 16.3–17.5 kDa for **PPPs** and 4.1–5.0 kDa for **PTs**. As a result, the

degree of polymerization (DP) of **PPPs** was about 4 times larger than that of **PTs** (see Table 1). This is because **PTs** are less soluble in organic solvents than **PPPs** due to the strong π - π interaction between the planar polythiophene backbones and hence only low-molecular-weight **PTs** can dissolve in chloroform. This is supported by the fact that the yields of the **PT** soluble parts were lower than 15 % because most of the synthesized **PTs** were insoluble in chloroform, whereas those of the **PPP** soluble parts were higher than 70 %.



Scheme 1. Chemical structures of three-ring type aromatic conjugated polymers bearing either racemic or chiral side chains.

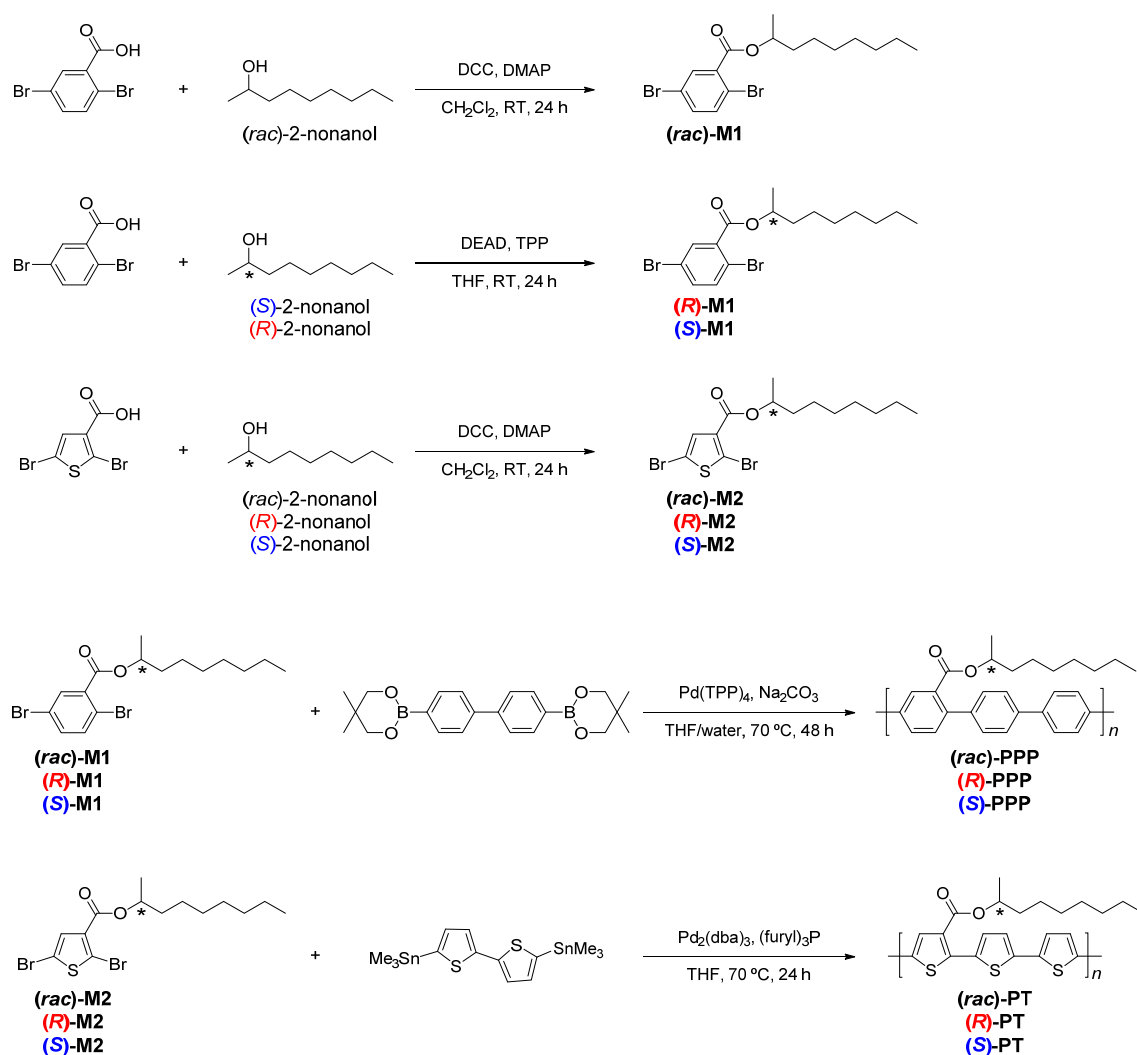
Table 1. Average molecular weights of polymers.

Polymer	M_n^a	M_w^a	M_w/M_n	DP ^b
(rac)-PPP	17,500	190,800	10.9	44
(R)-PPP	17,100	165,600	9.7	43
(S)-PPP	16,300	167,500	10.3	41
(rac)-PT	4,100	9,300	2.3	10
(R)-PT	4,700	10,000	2.1	11
(S)-PT	5,000	10,900	2.2	12

^a Number- (M_n) and weight-average (M_w) molecular weights evaluated with polystyrene standard.

^b Degree of polymerization estimated by using M_n .

Chapter 2



Scheme 2. Synthetic routes of all monomers and polymers.

Chiroptical properties of PPPs and PTs in chloroform solution. Figure 1 shows the UV–vis absorption, circular dichroism (CD), photoluminescence (PL), and circularly polarized luminescence (CPL) spectra of **PPP**s and **PT**s in chloroform solution. The optical properties are summarized in Table 2. All the polymers exhibited an absorption band and a luminescent band corresponding to the π – π^* and π^* – π transitions of their π -conjugated backbones, respectively. Therefore blue- and orange-colored emissions were observed in the chloroform solutions of **PPP**s and **PT**s, respectively, under UV irradiation ($\lambda = 365 \text{ nm}$). However no Cotton effect was observed in both absorption

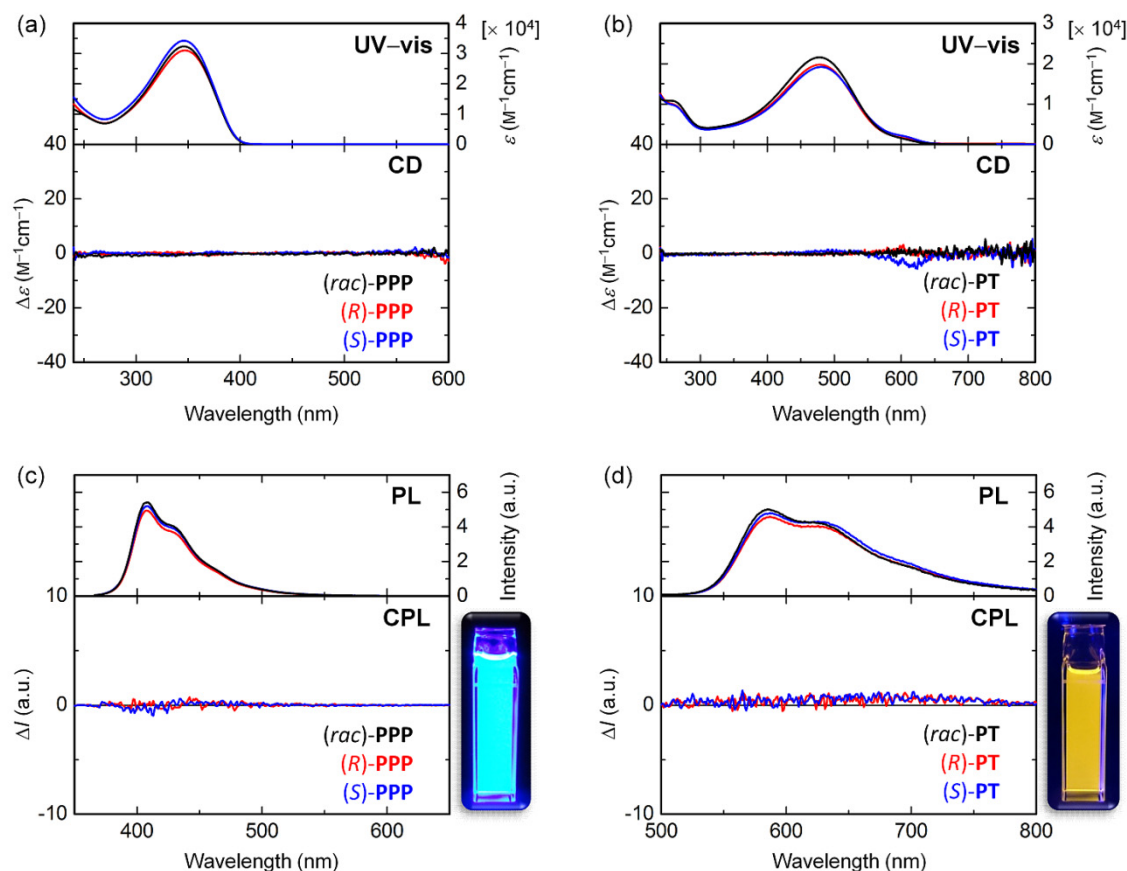


Figure 1. UV-vis absorption (upper) and CD (lower) spectra of (a) **PPPs** and (b) **PTs** in chloroform solution ($c = 2 \times 10^{-5}$ M). PL (upper) and CPL (lower) spectra of (c) **PPPs** and (d) **PTs** in chloroform solution ($c = 2 \times 10^{-5}$ M). Excitation wavelength: 352 nm for (rac)- and (R)-**PPPs**; 350 nm for (S)-**PPP**; 467 nm for **PTs**. Insets show the photos of the chloroform solutions of (R)-**PPP** and (R)-**PT**, respectively, under UV irradiation ($\lambda = 365$ nm).

and luminescent bands of all the polymers, as shown in CD and CPL spectra. These results indicate that the π -conjugated backbones of the chiral polymers showed no CD despite the presence of chiral side chains containing asymmetric centers and that the chiral polymers have neither intrachain helicity nor interchain helicity, similarly to the achiral polymers. Previously the author demonstrated that even in chloroform solution, three-ring type ACPs with optically-active (2-nonyloxy)carbonyl side chains showed bisignate Cotton effects in the absorption bands of their π -conjugated backbones.¹³ Because the bisignate Cotton effects decreased in intensity with increasing

Table 2. Optical properties of polymers in chloroform solution.^a

Polymer	UV-vis absorption		Photoluminescence		
	$\lambda_{\max}$ (nm)	ε (M ⁻¹ cm ⁻¹)	Em _{max} ^b (nm)	Ex ^c (nm)	Φ ^d (%)
(<i>rac</i>)- PPP	346	3.24×10^4	409	352	77.7
(<i>R</i>)- PPP	347	3.11×10^4	407	352	71.9
(<i>S</i>)- PPP	346	3.00×10^4	408	350	70.0
(<i>rac</i>)- PT	478	2.16×10^4	585	467	24.5
(<i>R</i>)- PT	478	1.98×10^4	587	467	19.4
(<i>S</i>)- PT	480	1.92×10^4	587	467	17.1

^a The concentrations of polymer solutions were kept at 2×10^{-5} M.

^b Peak emission wavelength.

^c Excitation wavelength.

^d Fluorescence quantum yield evaluated by using an integral sphere.

temperature and finally disappeared, it was argued that the Cotton effects resulted from the interchain helically π -stacked structure in the polymer aggregates. It is worthy to note that these polymers used for the chiroptical measurements were collected without Soxhlet extraction process. Meanwhile, in this study, only the soluble parts of **PPPs** and **PTs** were used. Thus, it can be argued that all the polymers exist as isolated chains in chloroform solution without forming polymer aggregates, resulting in no Cotton effect in both absorption and luminescence.

Chiroptical properties of nanosphere solutions of PPPs and PTs in water. On the above hypothesis the author investigated the chiroptical properties of **PPPs** and **PTs** in the aggregated state. Polymer nanospheres dispersed in aqueous solution were used as the aggregated polymer samples for the chiroptical measurements instead of solid films so as to remove the influence of CD artifacts. The polymer nanosphere solution was prepared by adding a THF solution of a polymer dropwise into water under

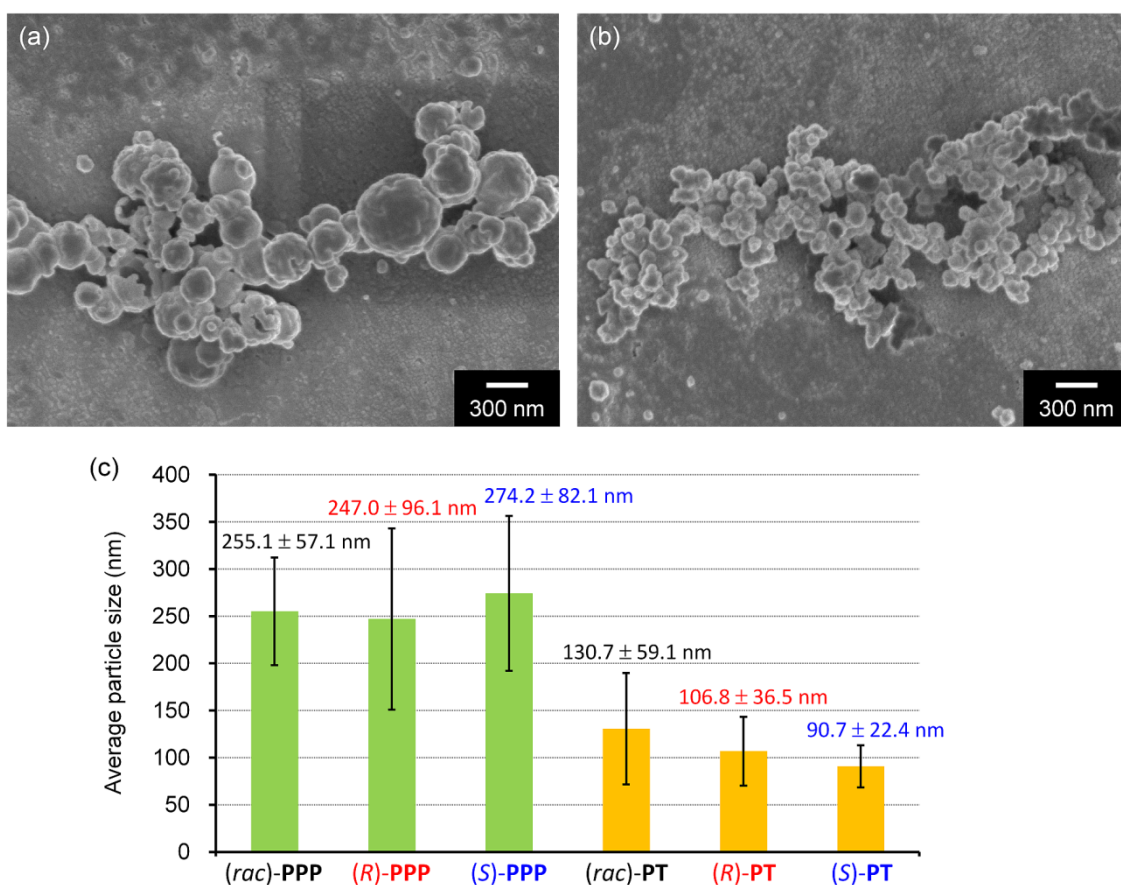


Figure 2. SEM images of (a) (R)-PPP and (b) (R)-PT nanospheres cast on a sample plate. (c) Average particle sizes of the polymer nanospheres evaluated by DLS measurements.

ultrasonication, and then slowly evaporating THF at 25 °C. The formation of polymer nanospheres was confirmed by scanning electron microscopy (SEM) and dynamic light scattering (DLS). Figure 2 depicts the SEM images of (R)-PPP and (R)-PT nanospheres and the average particle sizes of all polymer nanospheres evaluated by the DLS results (see also Figure 3). Table 3 also summarizes the average particle sizes. As shown in the SEM images, both of PPPs and PTs formed the spherical aggregates. The average particle size of PPPs and PTs were estimated to be 250–280 nm and 90–130 nm in diameter, respectively. Both of the SEM and DLS results indicate that PPPs formed larger nanospheres than PTs. The difference in particle size between PPPs and PTs may arise from the difference in DP of the polymers, i.e., the main chain length.

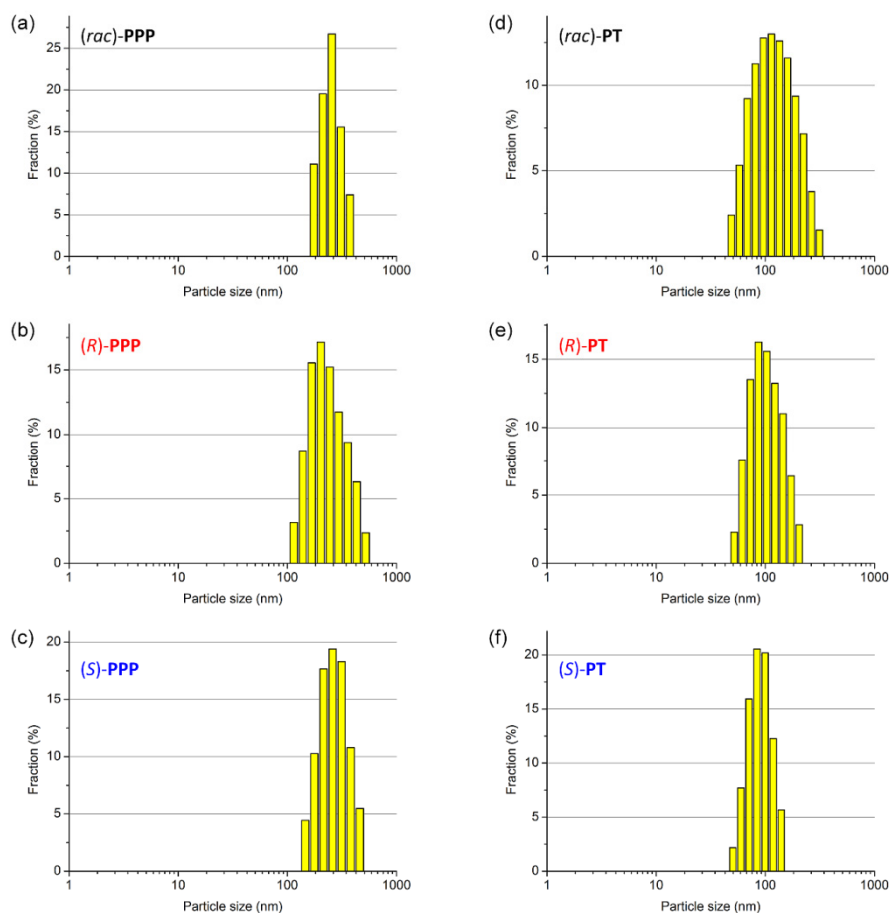


Figure 3. DLS results of the polymer nanospheres dispersed in water.

Figures 4a and b show UV-vis absorption and CD spectra of **PPP** and **PT** nanospheres in water. It was obviously observed that the (*R*)- and (*S*)-polymers respectively exhibited the negative and positive bisignate Cotton effects in the absorption regions of their π -conjugated backbones, whereas (*rac*)-polymers did not. This indicates that the chiral polymers self-assemble into the interchain helically π -stacked structure, i.e., the interchain helicity in the polymer aggregates. According to the exciton coupling theory,¹⁴ positive and negative bisignate Cotton effects in CD spectra indicate right- (*P*-helicity) and left-handed (*M*-helicity) screw structure, respectively. Thus, the interchain π -stacked structures of (*R*)-**PPP** and (*R*)-**PT** have left-handedness with *M*-helicity, whereas those of (*S*)-**PPP** and (*S*)-**PT** have right-handedness with *P*-helicity. Furthermore (*R*)- and (*S*)-**PPP** nanospheres showed negative and positive monosignate Cotton effects at around 408 nm in CPL spectra

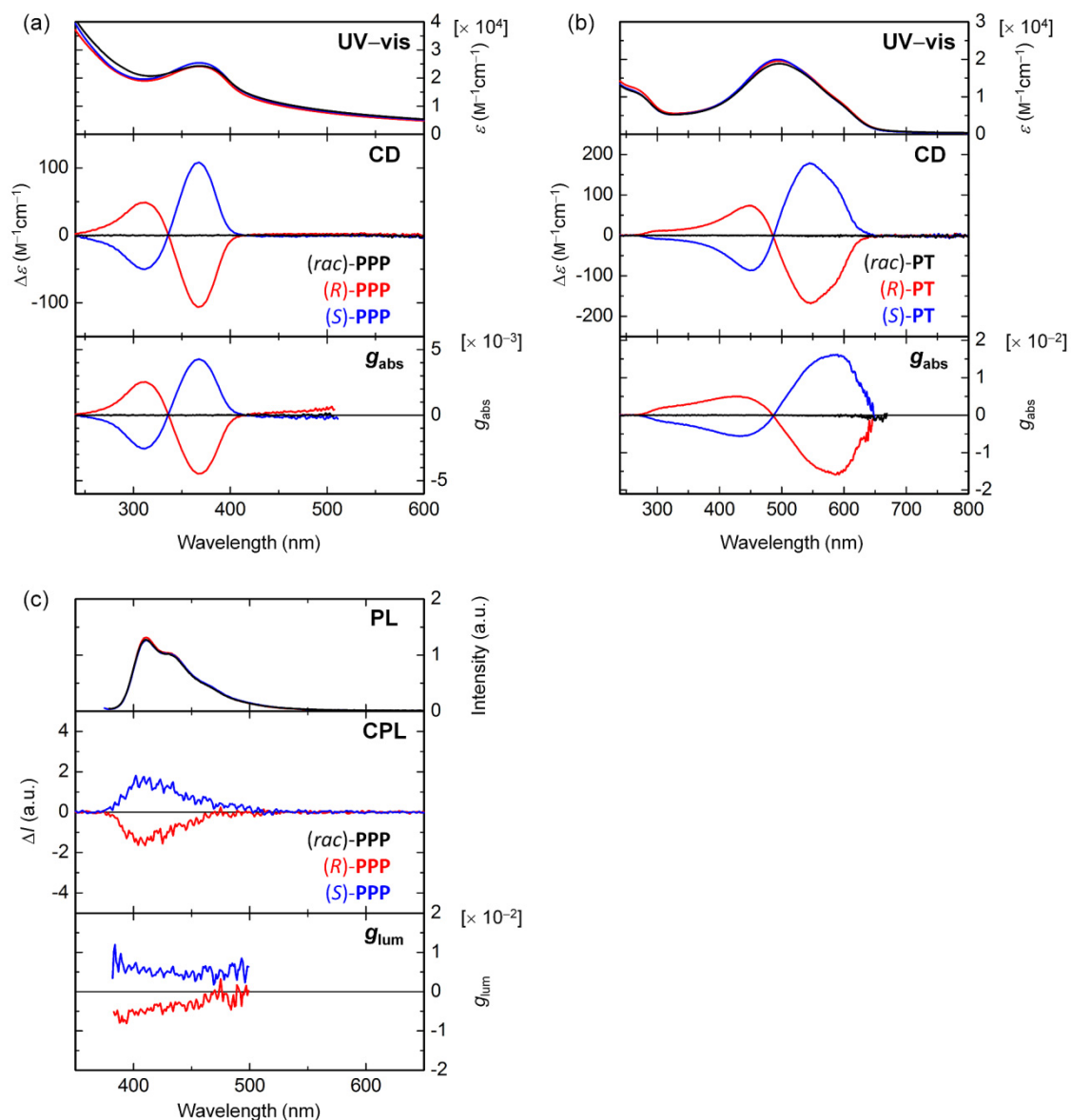


Figure 4. UV-vis absorption and CD spectra and dissymmetry factors in absorption (g_{abs}) of (a) **PPP** and (b) **PT** nanospheres dispersed in water. (c) PL and CPL spectra and dissymmetry factors in luminescence (g_{lum}) of **PPP** nanospheres dispersed in water. All the concentrations were kept at ca. 1.33×10^{-5} M.

Table 3. Optical properties and average particle sizes of polymer nanospheres in water.^a

Polymer	UV-vis absorption		CD			Photoluminescence		CPL		Average particle size (nm)
	$\lambda_{\max}$ (nm)	ε (M ⁻¹ cm ⁻¹)	$\lambda_{\max}$ (nm)	$\Delta\varepsilon$ (M ⁻¹ cm ⁻¹)	g_{abs}^b	Em _{max} ^c (nm) [Ex ^d (nm)]	Φ^e (%)	Em _{max} ^c (nm) [Ex ^d (nm)]	g_{lum}^b	
(<i>rac</i>)- PPP	368	2.43×10^4	- ^f	- ^f	- ^f	411 [366]	54.6	- ^f	- ^f	255.1 ± 57.1
(R)- PPP	368	2.42×10^4	313	+48.9	$+2.54 \times 10^{-3}$	411 [364]	49.9	408 [300]	-5.13×10^{-3}	247.0 ± 96.1
			367	-106.3	-4.47×10^{-3}					
(S)- PPP	369	2.54×10^4	311	-50.3	-2.57×10^{-3}	411 [364]	50.4	406 [300]	$+5.36 \times 10^{-3}$	274.2 ± 82.1
			368	+108.2	$+4.28 \times 10^{-3}$					
(<i>rac</i>)- PT	496	1.88×10^4	- ^f	- ^f	- ^f	- ^g	- ^g	- ^g	- ^g	130.7 ± 59.1
(R)- PT	495	1.96×10^4	448	+73.7	$+4.58 \times 10^{-3}$	- ^g	- ^g	- ^g	- ^g	106.8 ± 36.5
			547	-168.5	-1.29×10^{-2}					
(S)- PT	494	2.00×10^4	449	-86.7	-5.22×10^{-3}	- ^g	- ^g	- ^g	- ^g	90.7 ± 22.4
			545	+178.7	$+1.32 \times 10^{-2}$					

^a The concentrations of polymer nanospheres in water were ca. 1.33×10^{-5} M.^b Dissymmetry factors in absorption (g_{abs}) and luminescence (g_{lum}).^c Peak emission wavelength.^d Excitation wavelength.^e Fluorescence quantum yield evaluated by using an integral sphere.^f No Cotton effect was observed.^g No emission was observed.

(Figure 4c), indicating the emission of right- and left-handed circularly polarized light, respectively. As a result, it was demonstrated that the polymer π -conjugated backbones obtained circular polarization in both of the ground and excited states through the self-assembly of the interchain helicity. Note that **PT** nanospheres did not fluoresce, which may be due to a so-called "concentration quenching in fluorescence" phenomenon in the aggregated state. In addition, the polarizable environment consisted of the surrounding water solvent may further decay the energy in the excited state of **PTs**, resulting in the fluorescence quenching. These are also the reasons why the fluorescent quantum yields of **PPPs** decreased from 70–78 % to 50–55 % with forming the polymer nanospheres. The chiroptical properties of the polymer nanospheres are also summarized in Table 3.

In both of the CD and CPL spectra, the Cotton effects of the (*R*)- and (*S*)-polymers are mirror images of each other in sign, implying that the helical sense of the interchain helicity depends on chirality of the asymmetric centers in their side chains. This prospect is in good agreement with the result that (*rac*)-polymers in the aggregated state showed no Cotton effect in both absorption and luminescence, and hence do not have the interchain helicity.

Consequently, by comparing the isolated chain state and the aggregated state, the author successfully demonstrated that the circular polarization of three-ring type ACPs in absorption and luminescence arises from the interchain helically π -stacked structure in polymer aggregates and that the interchain helicity was self-assembled according to chirality of their side chains.

Chirality transfer through π - π interaction. As mentioned above, three-ring type ACPs in the aggregated state showed circular polarization due to the interchain helically π -stacked structure, although the polymers in the isolated chain state did not. Hence it is expected that, when mixing chiral and achiral ACPs into a polymer aggregate, chirality may transfer from the chiral ACP to the achiral one through the π - π interaction between their π -conjugated main chains. So the author chiroptically investigated the polymer mixtures in the aggregated state. Hereafter the mixtures of (*rac*)-**PPP** with chiral **PTs** and (*rac*)-**PT** with chiral **PPPs** are called as System 1 and 2, respectively.

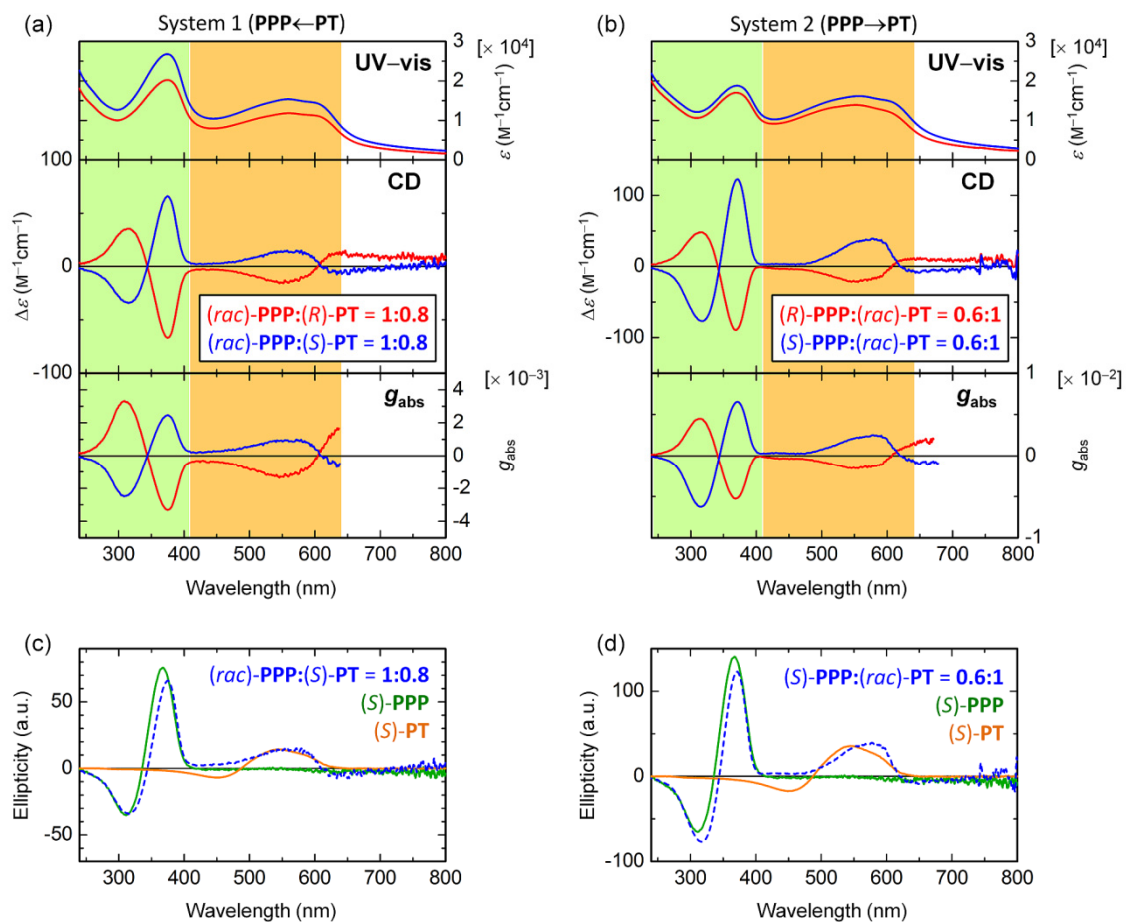


Figure 5. UV–vis absorption and CD spectra and dissymmetry factors in absorption (g_{abs}) of mixed polymer nanospheres of (a) System 1 consisting of (*rac*)-**PPP** and chiral **PT**s and (b) System 2 consisting of chiral **PPPs** and (*rac*)-**PT**. CD spectrum comparison of (c) (*S*)-System 1 or (d) (*S*)-System 2 with (*S*)-**PPP** and (*S*)-**PT**.

In addition, the representation such as "(*R*)-System 1" is used to express the enantiomer of chiral polymers. Herein, the polymer nanosphere in aqueous solution was adopted as the aggregated polymer sample for the optical measurements. The chiroptical properties were evaluated by using only CD spectra because the mixed polymer nanospheres showed no fluorescence.

Figures 5a and b show UV–vis absorption and CD spectra of System 1 and 2 in water. Both absorption spectra exhibited two absorption bands corresponding to **PPP** (green zone) and **PT** (orange zone) π -conjugated backbones. The induced CD bands were observed in the absorption region of (*rac*)-polymers, that is, (*rac*)-**PPP** of System

1 and (*rac*)-**PT** of System 2. The signs of induced CD depended on the chiral polymers, and therefore the Cotton effects of (*R*)-System 1 and (*S*)-System 1 showed mirror image of each other in sign, as well as those of (*R*)-System 2 and (*S*)-System 2. Interestingly, the both CD spectra of (*S*)-System 1 and 2 coincided with the sum of the CD spectra of (*S*)-**PPP** and (*S*)-**PT**, as shown in Figures 5c and d. In the aggregated state, (*S*)-**PPP** and (*S*)-**PT** exhibit a positive bisignate Cotton effect (Figures 4a and b) and form the interchain π -stacked structure with *P*-helicity. Thus, in (*S*)-Systems, all the polymers have the interchain π -stacked structure with *P*-helicity regardless of the presence or absence of chiral side chains. (*R*)-Systems also showed the same result. Consequently, it is argued that chirality in side chains of the chiral polymers transfer into (*rac*)-polymers through interchain π - π interaction, and that both **PPP** and **PT** have the interchain π -stacked structure with same helical sense.

3. Conclusion

The author synthesized poly(*para*-terphenylene) and poly(terthiophene) derivatives, **PPPs** and **PTs**, by introducing the racemic or optically-active (2-nonyloxy)carbonyl side chains and then collected the soluble parts by Soxhlet extraction. By investigating the chiroptical properties, the author found that **PPPs** and **PTs** existed as isolated chains in chloroform solution and showed no circular polarization in both absorption and luminescence regardless of the presence or absence of chiral side chains. Meanwhile, it was also found that **PPPs** and **PTs** with optically-active side chains self-assembled into the interchain helically π -stacked structure in the aggregated state such as polymer nanospheres and furthermore that the chiral **PPPs** fluoresced the circularly polarized light. Thus it is clarified that the circular polarization of **PPPs** and **PTs** in absorption and luminescence arises from the interchain helicity in polymer aggregates. Subsequently the author successfully demonstrated that chirality transferred from the chiral polymer to the achiral polymer through the interchain π - π interaction by mixing these polymers into a polymer nanosphere. The mixed system consisting of (*rac*)-**PPP** and chiral **PT** showed a CD spectrum that coincided with the sum of the CD spectra of chiral **PPP** and chiral **PT** in the aggregated state. This indicates that not only **PT** but also **PPP** have the interchain

π -stacked structure with same helical sense according to the side chain chirality of chiral **PT**. The same result was obtained in the mixed system of chiral **PPP** and (*rac*)-**PT**. As a result, it was successfully demonstrated that the interchain π - π interaction can play an important role in the appearance of circular polarization on ACP main chain and the chiral transfer between ACPs.

Experimental Section

1. Measurements. NMR spectra were obtained with JEOL AL-400, JEOL EX-400, and JEOL JNM-ECA600. Chemical shifts are represented in parts per million downfield from tetramethylsilane (TMS) or (trimethylsilyl)propionic-2,2,3,3- d_4 acid sodium salt (TSP- d_4) as internal standards. Elemental analyses were performed by Yanako CHN Corders (MT-3, MT-5 and MT-6), JSL JM-10, Mitsubishi chemical analytech AQF-100, and Dionex ICS-1500. High-resolution mass spectra (HRMS) were obtained by using Thermo Fisher Scientific EXACTIVE (APCI).

Gel permeation chromatography (GPC) result was obtained with a system consisting of a JASCO CO-2065 Plus column oven and a JASCO UV-2070 Plus detector, where the instrument was calibrated by polystyrene standard at 40 °C. Tetrahydrofuran (THF) was used as an eluent and the flow rate was 1.0 mL/min.

Ultraviolet-visible (UV-vis) absorption spectra were measured with JASCO V-570 UV/VIS/NIR spectrophotometer. Photoluminescence (PL) spectra were measured with JASCO FP-6500 spectrofluorometer. Circular dichroism (CD) spectra were measured with JASCO J-820 spectropolarimeter. Circularly polarized luminescence (CPL) spectra were measured with JASCO CPL-200S spectrometer. All optical measurements were performed using a quartz cell. Dynamic light scattering (DLS) measurements were performed using Otsuka Electronics ELSZ-2Plus zeta-potential/particle-size analyzer. Scanning electron microscopy (SEM) was performed with JEOL JSM-7500F. The samples were coated with Pt-Pd alloy using JEOL JFC-1600 ion coater before measurements of SEM. Ultrasonication was carried out with BRANSONIC 2510J-MT ultrasonic cleaner (100 W, 42 kHz).

2. Materials. All the chemicals were commercially available and used as received. 4,4'-biphenyldiboronic acid bis(neopentyl glycol) cyclic ester was purchased from Alfa Aesar. Tri-2-furylphosphine [(2-furyl) $_3$ P] was purchased from Lancaster. All other chemicals were purchased from Merck KGaA, Sigma-Aldrich Japan K. K., Tokyo Chemical Industry Co., Ltd., Wako Pure Chemical Industries, Ltd., and Nacalai Tesque. Solvents were dried and distilled before use.

3. Synthesis. All syntheses were carried out under argon atmosphere. 2,5-Dibromo-3-thiophene-carboxylic acid, 5,5'-bis(trimethylstannyl)-2,2'-bithiophene, (*R*)-**M1**, and (*S*)-**M1** were synthesized according to our previous report.¹³

(*rac*)-2-Nonyl 2,5-Dibromobenzoate [(*rac*)-M1**].** A solution of 2,5-dibromobenzoic acid (1.68 g, 6.01 mmol), (*rac*)-2-nonanol (0.96 g, 6.67 mmol), *N,N'*-dicyclohexylcarbodiimide (DCC, 1.36 g, 6.61 mmol), and 4-(dimethylamino)pyridine (DMAP, 0.81 g, 6.61 mmol) in dichloromethane (CH₂Cl₂, 50 mL) was stirred for 36 h at room temperature. The precipitate was removed by filtration and then the filtrate was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel; hexane/ethyl acetate = 15:1) to give (*rac*)-**M1** as colorless oil (1.68 g, 68.8 %): ¹H NMR (400 MHz, CDCl₃, TMS): δ = 0.88 (t, 3H, *J* = 6.8 Hz, (CH₂)₆CH₃), 1.28–1.44 (m, 13H, CH₂, COOCHCH₃), 1.57–1.79 (dm, 2H, COOCHCH₂), 5.17 (sext, 1H, *J* = 6.4 Hz, COOCH), 7.42 (dd, 1H, *J* = 8.4 and 2.8 Hz, Ar-*H*), 7.50 (d, 1H, *J* = 8.4 Hz, Ar-*H*), 7.84 ppm (d, 1H, *J* = 2.8 Hz, Ar-*H*); ¹³C NMR (100 MHz, CDCl₃, TMS): δ = 14.1, 19.9, 22.6, 25.4, 29.2, 29.4, 31.8, 35.9, 73.5, 120.1, 121.0, 133.8, 134.7, 135.1, 135.6, 164.7 ppm; Anal calcd for C₁₆H₂₂Br₂O₂: C 47.32, H 5.46, Br 39.35, Found: C 47.40, H 5.50, Br 39.22; HRMS (APCI) calcd for C₁₆H₂₂Br₂O₂ [M + H⁺]: 407.0039, Found: 407.0031.

(*rac*)-2-Nonyl 2,5-Dibromothiophene-3-carboxylate [(*rac*)-M2**].** A solution of 2,5-dibromo-3-thiophenecarboxylic acid (1.72 g, 6.00 mmol), (*rac*)-2-nonanol (0.96 g, 6.66 mmol), DCC (1.36 g, 6.61 mmol), and DMAP (0.81 g, 6.61 mmol) in CH₂Cl₂ (50 mL) was stirred for 36 h at room temperature. The precipitate was removed by filtration and then the filtrate was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel; hexane/ethyl acetate = 15:1) to give (*rac*)-**M2** as colorless oil (2.07 g, 83.5 %): ¹H NMR (400 MHz, CDCl₃, TMS): δ = 0.88 (t, 3H, *J* = 7.2 Hz, (CH₂)₆CH₃), 1.28–1.40 (m, 13H, CH₂, COOCHCH₃), 1.53–1.75 (dm, 2H, COOCHCH₂), 5.09 (sext, 1H, *J* = 6.4 Hz, COOCH), 7.33 ppm (s, 1H, Ar-*H*); ¹³C NMR (100 MHz, CDCl₃, TMS): δ = 14.1, 20.0, 22.6, 25.4, 29.2, 29.4, 31.8, 35.9, 72.6, 111.2, 118.8, 131.8, 132.4, 160.5 ppm; Anal calcd for C₁₄H₂₀Br₂O₂S: C 40.80, H 4.89, Br 38.77, S 7.78, Found: C 40.86, H 4.95, Br 38.86, S 7.69; HRMS (APCI) calcd for C₁₄H₂₀Br₂O₂S [M + H⁺]: 412.9603, Found: 412.9595.

(R)-2-Nonyl 2,5-Dibromothiophene-3-carboxylate [(R)-M2]. The same procedure with (*rac*)-M2 was employed by using 2,5-dibromo-3-thiophenecarboxylic acid (1.72 g, 6.00 mmol), (*R*)-2-nonanol (0.95 g, 6.62 mmol), DCC (1.36 g, 6.60 mmol), and DMAP (0.81 g, 6.62 mmol) as reagents and hexane/ethyl acetate (15:1) as the eluent for column chromatography to give colorless oil (2.12 g, 85.8 %): ^1H NMR (400 MHz, CDCl_3 , TMS): δ = 0.88 (t, 3H, J = 6.8 Hz, $(\text{CH}_2)_6\text{CH}_3$), 1.28–1.40 (m, 13H, CH_2 , COOCHCH_3), 1.52–1.75 (dm, 2H, COOCHCH_2), 5.09 (sext, 1H, J = 6.2 Hz, COOCH), 7.33 ppm (s, 1H, Ar-*H*); ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ = 14.1, 20.0, 22.6, 25.4, 29.2, 29.4, 31.8, 35.9, 72.6, 111.2, 118.8, 131.8, 132.4, 160.5 ppm; Anal calcd for $\text{C}_{14}\text{H}_{20}\text{Br}_2\text{O}_2\text{S}$: C 40.80, H 4.89, Br 38.77, S 7.78, Found: C 40.94, H 5.03, Br 38.64, S 7.88; HRMS (APCI) calcd for $\text{C}_{14}\text{H}_{20}\text{Br}_2\text{O}_2\text{S}$ [$\text{M} + \text{H}^+$]: 412.9603, Found: 412.9599; $[\alpha]_D^{25}$ -21.46° (*c* 1.03, CHCl_3).

(S)-2-Nonyl 2,5-Dibromothiophene-3-carboxylate [(S)-M2]. The same procedure with (*rac*)-M2 was employed by using 2,5-dibromo-3-thiophenecarboxylic acid (1.72 g, 6.00 mmol), (*S*)-2-nonanol (0.96 g, 6.65 mmol), DCC (1.36 g, 6.62 mmol), and DMAP (0.81 g, 6.62 mmol) as reagents and hexane/ethyl acetate (15:1) as the eluent for column chromatography to give colorless oil (2.11 g, 85.4 %): ^1H NMR (400 MHz, CDCl_3 , TMS): δ = 0.88 (t, 3H, J = 6.6 Hz, $(\text{CH}_2)_6\text{CH}_3$), 1.28–1.40 (m, 13H, CH_2 , COOCHCH_3), 1.53–1.75 (dm, 2H, COOCHCH_2), 5.09 (sext, 1H, J = 6.2 Hz, COOCH), 7.33 ppm (s, 1H, Ar-*H*); ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ = 14.1, 20.0, 22.6, 25.4, 29.2, 29.4, 31.8, 35.9, 72.6, 111.2, 118.8, 131.8, 132.4, 160.5 ppm; Anal calcd for $\text{C}_{14}\text{H}_{20}\text{Br}_2\text{O}_2\text{S}$: C 40.80, H 4.89, Br 38.77, S 7.78, Found: C 40.86, H 4.93, Br 38.88, S 7.83; HRMS (APCI) calcd for $\text{C}_{14}\text{H}_{20}\text{Br}_2\text{O}_2\text{S}$ [$\text{M} + \text{H}^+$]: 412.9603, Found: 412.9600; $[\alpha]_D^{25}$ $+21.58^\circ$ (*c* 1.15, CHCl_3).

(rac)-Poly(*para*-terphenylene) derivative [(rac)-PPP]. To a solution of (*rac*)-M1 (1.21 g, 2.99 mmol), 4,4'-biphenyldiboronic acid bis(neopentyl glycol) cyclic ester (1.13 g, 2.99 mmol), and tetrakis(triphenylphosphine)palladium(0) [$\text{Pd}(\text{PPh}_3)_4$, 105.7 mg, 91.5 μmol] in THF (60 mL) was added a solution of sodium carbonate (Na_2CO_3 , 2.55 g, 24.0 mmol) in water (15 mL), and then the mixture was stirred for 48 h at 70 $^\circ\text{C}$. The reaction mixture was poured into methanol (500 mL) and vigorously stirred for 1 h. The resulting precipitate was collected by filtration, washed by water, and dissolved in

chloroform (200 mL). The solution was mixed with THF (50 mL) and a solution of NaCN (0.14 g) in water/methanol (1:4, 8 mL), and then stirred for 30 min at 60 °C. After filtration, the filtrate was concentrated under reduced pressure and reprecipitated by stirring in acetone (450 mL) for 12 h. The precipitated polymer was collected by filtration and washed by 1st Soxhlet extraction (acetone, 7 days). Finally the soluble part was extracted by 2nd Soxhlet extraction (chloroform, 4 days), reprecipitated by stirring in methanol (450 mL) for 3 h, and collected by filtration to give a white solid (1.10 g, 92.7 %): ^1H NMR (600 MHz, CDCl_3 , TMS): δ = 0.85 (br, $(\text{CH}_2)_6\text{CH}_3$), 1.11–1.78 (m, $\text{COOCH}(\text{CH}_3)(\text{CH}_2)_6\text{CH}_3$), 5.00–5.23 (br, COOCH), 7.05–8.12 ppm (m, Ar-*H*); ^{13}C NMR (150 MHz, CDCl_3 , TMS): δ = 14.1, 19.5, 22.7, 25.3, 29.2, 29.5, 31.9, 35.8, 72.4, 126.7–139.4, 168.7 ppm; Anal calcd for $(\text{C}_{28}\text{H}_{30}\text{O}_2)_n$: C 84.38, H 7.59, Found: C 82.46, H 7.44.

(*R*)-Poly(*para*-terphenylene) derivative [(*R*)-PPP]. The same procedure with (*rac*)-PPP was employed by using (*R*)-**M1** (0.406 g, 1.00 mmol), 4,4'-biphenyl-diboronic acid bis(neopentyl glycol) cyclic ester (0.378 g, 1.00 mmol), $\text{Pd}(\text{PPh}_3)_4$ (36.9 mg, 31.9 μmol), and Na_2CO_3 (0.849 g, 8.01 mmol) as reagents to give a white solid (0.291 g, 72.9 %): ^1H NMR (600 MHz, CDCl_3 , TMS): δ = 0.86 (br, $(\text{CH}_2)_6\text{CH}_3$), 1.12–1.79 (m, $\text{COOCH}(\text{CH}_3)(\text{CH}_2)_6\text{CH}_3$), 5.01–5.22 (br, COOCH), 7.08–8.34 ppm (m, Ar-*H*); ^{13}C NMR (150 MHz, CDCl_3 , TMS): δ = 14.1, 19.4, 22.7, 25.3, 29.2, 29.5, 31.9, 35.8, 72.4, 126.7–139.5, 168.8 ppm; Anal calcd for $(\text{C}_{28}\text{H}_{30}\text{O}_2)_n$: C 84.38, H 7.59, Found: C 82.60, H 7.75.

(*S*)-Poly(*para*-terphenylene) derivative [(*S*)-PPP]. The same procedure with (*rac*)-PPP was employed by using (*S*)-**M1** (0.406 g, 1.00 mmol), 4,4'-biphenyl-diboronic acid bis(neopentyl glycol) cyclic ester (0.378 g, 1.00 mmol), $\text{Pd}(\text{PPh}_3)_4$ (35.5 mg, 30.7 μmol), and Na_2CO_3 (0.849 g, 8.01 mmol) as reagents to give a white solid (0.294 g, 73.8 %): ^1H NMR (400 MHz, CDCl_3 , TMS): δ = 0.85 (br, $(\text{CH}_2)_6\text{CH}_3$), 1.12–1.79 (m, $\text{COOCH}(\text{CH}_3)(\text{CH}_2)_6\text{CH}_3$), 5.01–5.20 (br, COOCH), 7.08–8.33 ppm (m, Ar-*H*); ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ = 14.1, 19.5, 22.7, 25.2, 29.2, 29.5, 31.9, 35.8, 72.4, 126.8–139.2, 168.7 ppm; Anal calcd for $(\text{C}_{28}\text{H}_{30}\text{O}_2)_n$: C 84.38, H 7.59, Found: C 83.22, H 7.59.

(rac)-Poly(terthiophene) derivative [(rac)-PT]. A solution of (2-furyl)₃P (56.0 mg, 0.241 mmol) and tris(dibenzylideneacetone)dipalladium [Pd₂(dba)₃, 55.4 mg, 60.5 μ mol] in THF (20 mL) was stirred for 30 min at room temperature, followed by addition of (rac)-**M2** (1.24 g, 3.00 mmol) dissolved in THF (5 mL) and further stirring for 1 h at 50 °C. The solution was mixed with a solution of 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (1.48 g, 3.00 mmol) in THF (15 mL) and then stirred for 24 h at 70 °C. The reaction mixture was poured into methanol/HCl (10:1, 500 mL) and then vigorously stirred for 1 h. The resulting precipitate was collected by filtration, dissolved in chloroform (2 $\times$ 30 mL), and reprecipitated by stirring in acetone (500 mL) overnight. The precipitated polymer was collected by filtration and washed by 1st Soxhlet extraction (acetone, 5 days). Finally the soluble part was extracted by 2nd Soxhlet extraction (chloroform, 7 days) and dried under vacuum to give a dark green solid (0.133 g, 10.6 %): ¹H NMR (600 MHz, CDCl₃, TMS): δ = 0.88 (br, 3H, (CH₂)₆CH₃), 1.29–1.50 (m, 13H, CH₂, COOCHCH₃), 1.60–1.73 (d, 2H, COOCHCH₂), 5.13 (br, 1H, COOCH), 7.06 (br, 3H, Ar-H), 7.39–7.46 ppm (br, 2H, Ar-H); ¹³C NMR (150 MHz, CDCl₃, TMS): δ = 14.1, 20.1, 22.7, 25.5, 29.3, 29.6, 31.9, 36.1, 72.2, 124.2–142.0, 162.5 ppm; Anal calcd for (C₂₂H₂₄O₂S₃)_n: C 63.42, H 5.81, S 23.09, Found: C 59.88, H 5.31, S 20.53.

(R)-Poly(terthiophene) derivative [(R)-PT]. The same procedure with (rac)-PT was employed by using (R)-**M2** (1.24 g, 3.01 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (1.48 g, 3.01 mmol), Pd₂(dba)₃ (55.2 mg, 60.3 μ mol), and (2-furyl)₃P (56.4 mg, 0.243 mmol) as reagents to give a dark green solid (0.181 g, 14.5 %): ¹H NMR (400 MHz, CDCl₃, TMS): δ = 0.87 (br, 3H, (CH₂)₆CH₃), 1.29–1.48 (m, 13H, CH₂, COOCHCH₃), 1.60–1.72 (d, 2H, COOCHCH₂), 5.13 (br, 1H, COOCH), 7.08 (br, 3H, Ar-H), 7.40–7.48 ppm (br, 2H, Ar-H); ¹³C NMR (100 MHz, CDCl₃, TMS): δ = 14.1, 20.1, 22.7, 25.5, 29.3, 29.6, 31.9, 36.1, 72.2, 124.2–142.0, 162.5 ppm; Anal calcd for (C₂₂H₂₄O₂S₃)_n: C 63.42, H 5.81, S 23.09, Found: C 61.83, H 5.69, S 21.66.

(S)-Poly(terthiophene) derivative [(S)-PT]. The same procedure with (rac)-PT was employed by using (S)-**M2** (1.24 g, 3.00 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (1.48 g, 3.00 mmol), Pd₂(dba)₃ (55.1 mg, 60.2 μ mol), and (2-furyl)₃P (56.2 mg, 0.242 mmol) as reagents to give a dark green solid (0.163 g, 13.0 %): ¹H NMR

(400 MHz, CDCl₃, TMS): δ = 0.87 (br, 3H, (CH₂)₆CH₃), 1.29–1.49 (m, 13H, CH₂, COOCHCH₃), 1.60–1.72 (d, 2H, COOCHCH₂), 5.13 (br, 1H, COOCH), 7.09 (br, 3H, Ar-H), 7.40–7.48 ppm (br, 2H, Ar-H); ¹³C NMR (100 MHz, CDCl₃, TMS): δ = 14.1, 20.1, 22.7, 25.5, 29.3, 29.6, 31.9, 36.1, 72.2, 124.2–142.0, 162.5 ppm; Anal calcd for (C₂₂H₂₄O₂S₃)_n: C 63.42, H 5.81, S 23.09, Found: C 62.03, H 5.61, S 21.63.

4. Sample preparation

4.1. Preparation of nanospheres consisting of a single polymer

A THF solution of a polymer (2 mL, $c = 4 \times 10^{-5}$ M) was added dropwise into water (6 mL) under ultrasonication. The dropping speed was kept at 1.1 mL/min. Then the mixed solution was put in a thermostat chamber (25 °C) for 48 h to evaporate THF. The resulting nanosphere solution ($c = \text{ca. } 1.33 \times 10^{-5}$ M) was used for the optical measurements and DLS. Furthermore the nanosphere solution was dried at room temperature on a sample stage to give a solid sample for the SEM measurement.

4.2. Preparation of nanospheres consisting of a mixture of chiral and achiral polymers

A THF solution (3 mL) including an achiral polymer ($c = 4 \times 10^{-5}$ M) and a chiral polymer (the concentration varied to adjust the polymer mixing ratio) was added dropwise into water (6 mL) under ultrasonication and stirring. The dropping speed was kept at 1.1 mL/min. Then the mixed solution was put in a thermostat chamber (25 °C) for 48 h to evaporate THF. The resulting nanosphere solution ($c = \text{ca. } 2.0 \times 10^{-5}$ M) was used for the optical measurements and DLS. Furthermore the nanosphere solution was dried at room temperature on a sample stage to give a solid sample for the SEM measurement.

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Chapter 3

Circularly Polarized Blue Luminescent Spherulites Consisting of Hierarchically Assembled Ionic Conjugated Polymers with a Helically π -Stacked Structure

Introduction

It is well known that the spherulite is a spherical semicrystalline material with a radiated structure in which both crystalline and amorphous regions coexist.^{1,2} The polymer spherulite is composed of a highly ordered lamellar structure, which results in higher density, hardness, and mechanical strength values than those of the amorphous polymer.² The lamellar regions of the spherulite also exhibit birefringence because of their aligned polymeric structure; this property produces a variety of colored patterns and even a characteristic so-called Maltese Cross when illuminated under polarized light in an optical microscope.^{2,3} Thus, polymer spherulites are fascinating particles and are superior to randomly aggregated particles because of their potentially profound mechanical and optical properties. Although spherulites consisting of nonconjugated polymers such as polyethylene and polypropylene have been extensively investigated, those composed of π -conjugated polymers have not yet been examined in depth.

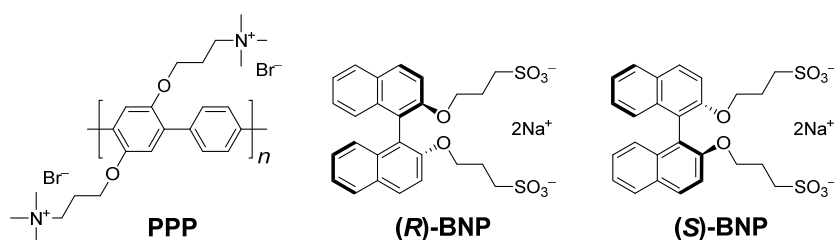
Helical π -conjugated polymers have attracted increasing interest because of their potentially profound electro-optical properties, which might be applied to next-generation plastic electronics.^{4–13} The addition of a chiral compound to the achiral π -conjugated polymer is one of the most promising means of inducing chirality, and possibly helicity, to the polymer.^{6,14–17} The induction of chirality is largely based on intermolecular interactions, e.g., electrostatic, hydrogen bonding, and van der Waals interactions, between the chiral compound and the π -conjugated polymer. Recent studies have indicated that the mixture of an aromatic π -conjugated polymer with an axially chiral binaphthyl derivative generates a polymer assembly with an interchain helically π -stacked structure because of π – π interactions in the film.^{16,17} However, this

type of assembly gives no higher-ordered structure, mainly due to its general stability, which is based on weak intermolecular interactions and is very low. If it were possible to further stabilize the assembly through electrostatic interactions by introducing ionic constituents into both the π -conjugated polymer and the chiral compound, then the reinforced assembly could be used as a building unit for a polymer aggregate with a higher-ordered structure.

In this study, the author reports that cationic π -conjugated polymers form an interchain helically π -stacked assembly with anionic chiral compounds that is stabilized by both electrostatic and π - π interactions to hierarchically self-organize into a spherulite with a circularly polarized blue luminescence. To the best of our knowledge, this is the first example of a chiroptical spherulite that is hierarchically constructed from π -conjugated polymers.

Results and Discussion

Synthesis. A water-soluble poly(*para*-phenylene) derivative (designated as **PPP**) was synthesized by introducing tetraalkylammonium cations at the terminal sites of side chains. A water-soluble and axially chiral binaphthyl derivative (**BNP**) was synthesized by introducing two sulfonate anions at terminal sites of the substituents, which are linked via propoxyl chains to the 2 and 2' positions of the 1,1'-binaphthalene, as shown in Scheme 1 (the synthetic routes of **PPP** and **BNP** are shown in Schemes 2 and 3, respectively). Subsequently, **PPP** and **BNP** were separately dissolved in a mixture of methanol and water (designated as methanol–water hereafter), where the concentrations of the former and the latter are $c = 1.0 \times 10^{-3}$ M (in terms of repeating unit) and $c = 1.0 \times 10^{-3}$ M, respectively. Then, the solutions were mixed with various molar ratios at RT.



Scheme 1. The poly(*para*-phenylene) derivative (**PPP**) and binaphthyl derivatives (**BNPs**) with (*R*)- and (*S*)-configurations.

Chiroptical Properties of PPP, BNP and their Mixture. Figure 1a presents the UV-vis absorption and circular dichroism (CD) spectra of **PPP**, **BNP**, and a mixture of **PPP** and **BNP** (abbreviated as **PPP-BNP**) in methanol-water (50:50 v/v). **PPP** showed an absorption band at 340 nm, which corresponds to the π - π^* transition of the π -conjugated backbone. **BNP** showed an absorption band at 228 nm, which corresponds to the π - π^* transition of the binaphthalene. **BNP** exhibited a bisignate Cotton effect in the absorption band region due to the axial chirality of the binaphthalene (see also Figure 2 and Table 1). **PPP-BNP** showed an additional absorption band at a wavelength (384 nm) that was 44 nm longer than that of **PPP**. This implies that the effective conjugation length of the **PPP** backbone increases, accompanying an increase in the coplanarity of the polymer backbone, which could be due to the formation of an interchain π -stacked structure. Meanwhile, **PPP-BNP** exhibited a CD band in the π - π^* transition region of the π -conjugated backbone (Figure 1a). The strong bisignate Cotton effects observed at 376 and 341 nm imply the presence of an exciton-coupling phenomenon between the main chains.¹⁸ The CD band, as well as the absorption band, increased in intensity with an increasing concentration of **BNP** (Figure 3). These results imply that **PPP** forms an assembly with **BNP** in the mixed solvent of methanol and water and that the assembly has induced chirality of the polymer moiety, which is caused by chirality transfer from the axially chiral compound (**BNP**) to the achiral polymer (**PPP**). That is, the cationic **PPP** polymers are able to come sufficiently close to each other, with the aid of the anionic **BNP**, to yield an interchain helically π -stacked assembly.^{9-12,19-22} Because the aliphatic chiral compound, which bears two anionic sulfonate groups, gives no CD band even when it is mixed with **PPP**, the π - π interaction between the conjugated polymer and the aromatic chiral compound, in addition to the presence of electrostatic interactions between the compounds, is indispensable for the formation of the π -stacked assembly. Notably, the absorption band at 384 nm and the CD band with the bisignate Cotton effect decreased in intensity with increasing temperature, and both absorption features finally disappeared at 75 °C (Figure 1c). This result indicates that the helically π -stacked assembly is gradually destroyed upon heating to give free **PPPs** and **BNPs**. The XRD pattern of the **PPP-BNP** precipitate exhibited a broad reflection at

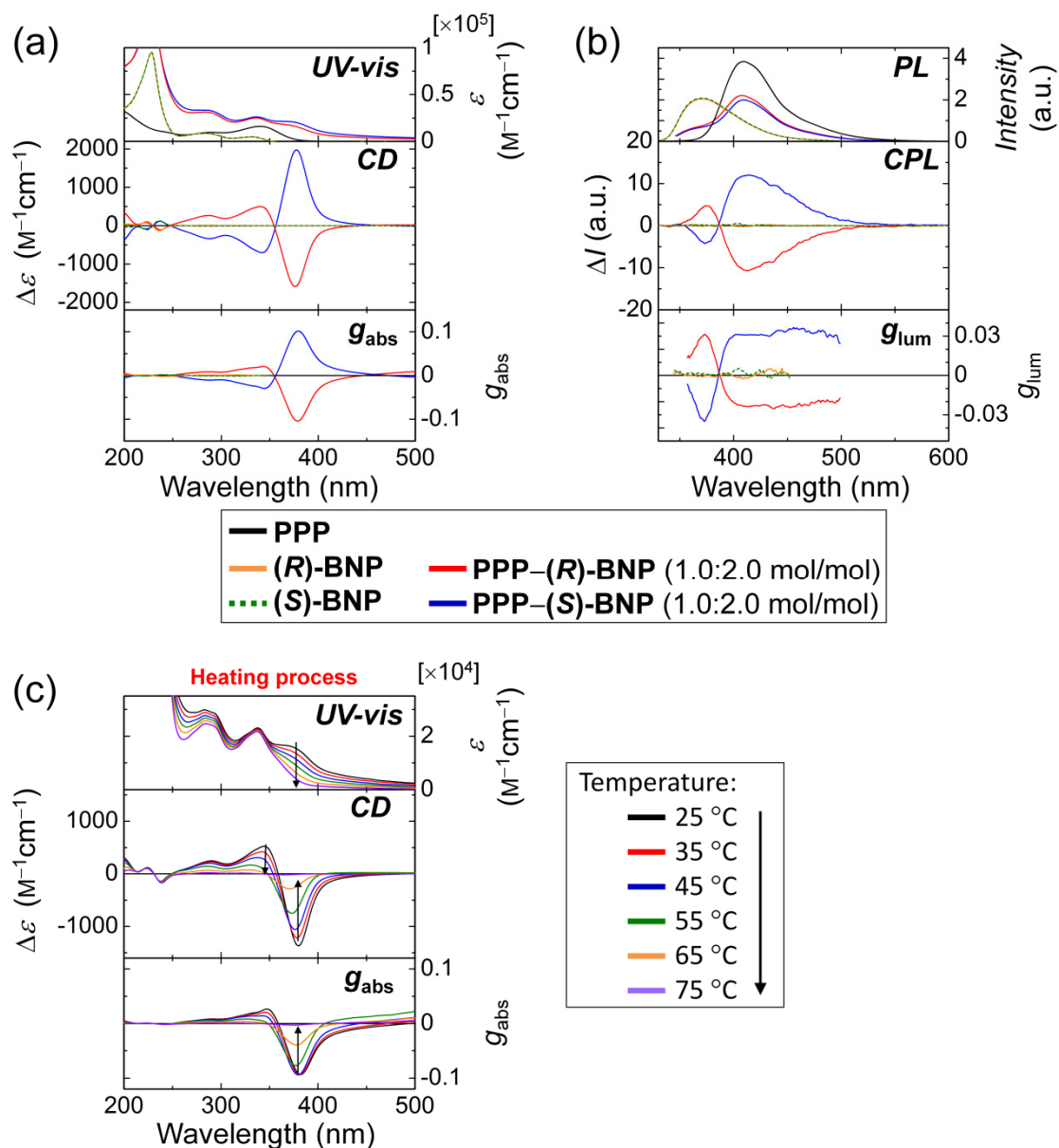


Figure 1. (a) The UV-vis absorption, CD, and g_{abs} spectra and (b) PL, CPL, and g_{lum} spectra of **PPP**, **BNP**, and a mixture (**PPP-BNP**) (1.0:2.0 mol/mol) in methanol-water (50:50 v/v). The concentrations are as follows: **PPP**, 5.8×10^{-5} M (expressed in terms of repeating unit); **BNP**, 2.0×10^{-5} M; **PPP** in the mixture, 2.0×10^{-5} M (expressed in terms of the repeating unit). (c) The UV-vis absorption, CD, and g_{abs} spectra of **PPP-(R)-BNP** (1.0:2.0 mol/mol) in methanol-water (50:50 v/v) at various temperatures during the heating process. The concentration of **PPP** is 2.0×10^{-5} M (expressed in terms of the repeating unit).

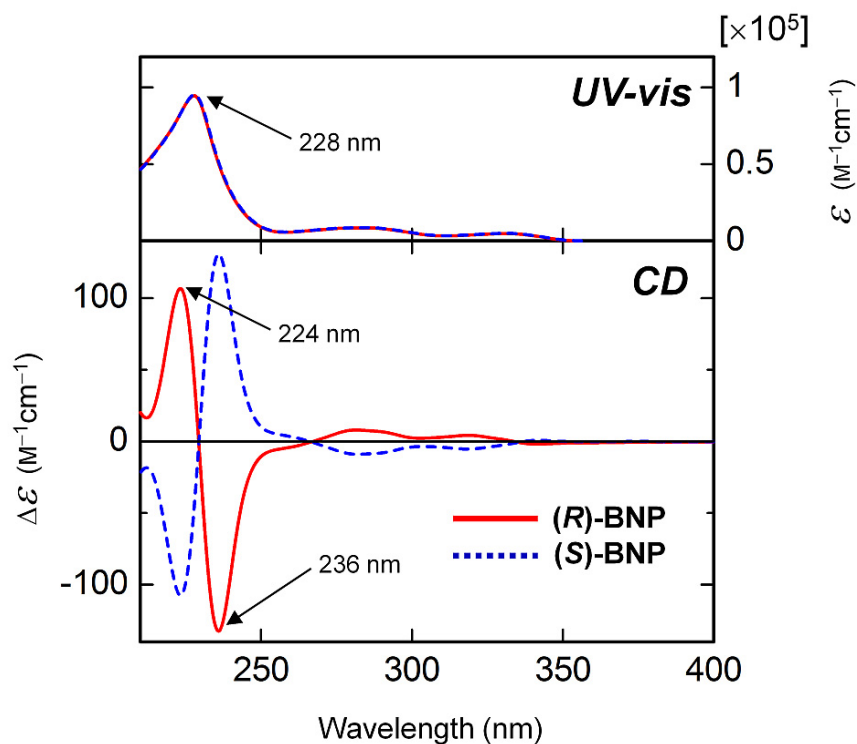


Figure 2. The UV–vis absorption (upper) and CD (lower) spectra of the anionic chiral binaphthyl derivatives (**BNPs**) in methanol–water (50:50 v/v). The concentration of **BNP** is 2.0×10^{-5} M.

Table 1. The chiroptical properties of the anionic chiral binaphthyl derivatives (**BNP**) in methanol–water (50:50 v/v).

Chiral binaphthyl derivative ^a	UV–vis absorption		CD		
	λ_{max} (nm)	ε ($\text{M}^{-1}\text{cm}^{-1}$)	λ (nm)	$\Delta\varepsilon$ ($\text{M}^{-1}\text{cm}^{-1}$)	g_{abs}
(R)-BNP	228	0.95×10^5	224	+105.3	$+1.11 \times 10^{-3}$
			236	–132.5	-1.72×10^{-3}
(S)-BNP	228	0.95×10^5	224	–106.3	-1.11×10^{-3}
			236	+130.8	$+1.66 \times 10^{-3}$

^a Concentration of **BNP** is 2.0×10^{-5} M.

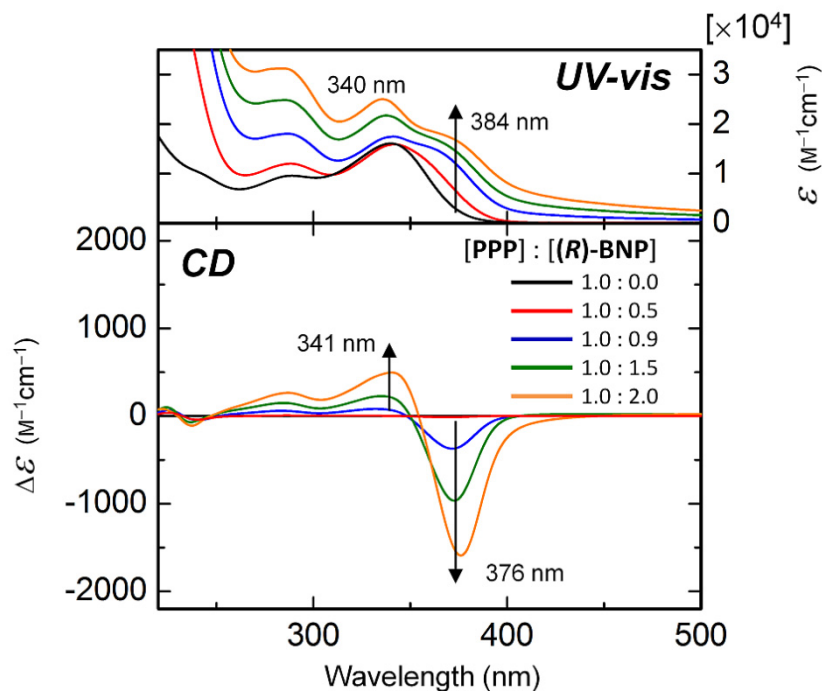


Figure 3. The UV-vis absorption (upper) and CD (lower) spectra of **PPP-(R)-BNP** in methanol-water (50:50 v/v) at various molar ratios. The concentration of **PPP** is held constant at 2.0×10^{-5} M (expressed in terms of the repeating unit).

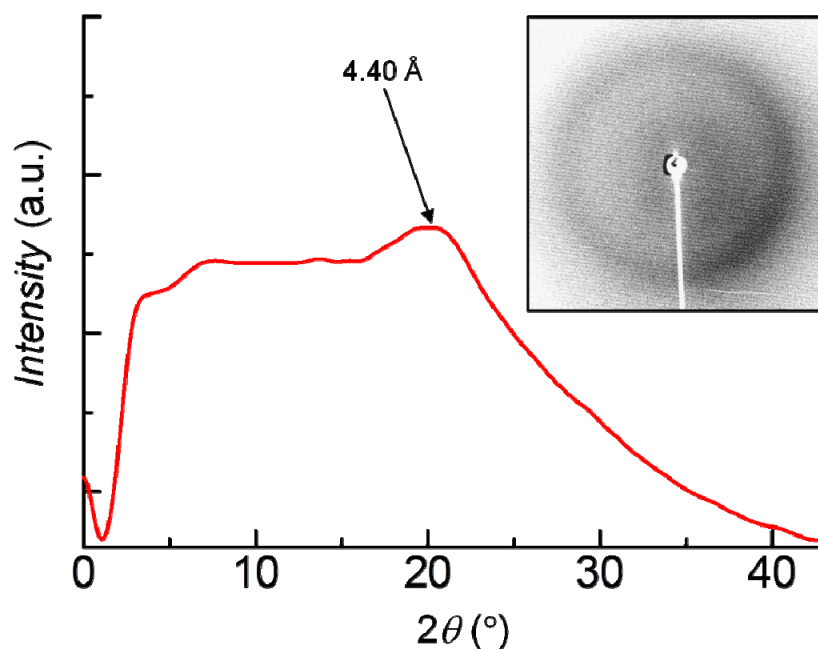


Figure 4. The XRD pattern of the mixed solution precipitate (**PPP-BNP**) (1.0:2.0 mol/mol). The inset shows the Laue pattern of the precipitate.

20.15° in 2θ , which corresponds to a distance of 4.40 Å between the interchain π -stacked polymers (Figure 4).

Figure 1b depicts the photoluminescence (PL) and circularly polarized luminescence (CPL) analyses of **PPP**, **BNP**, and **PPP-BNP** in methanol–water (50:50 v/v). Not only did **PPP** exhibit blue fluorescence, but **PPP-BNP** did as well, although the fluorescence intensity of **PPP-BNP** was weaker than that of **PPP**. This may be due to the presence of a so-called “concentration quenching in fluorescence” phenomenon resulting from the formation of a polymer assembly with an interchain π -stacked structure.^{9,20,21} This is also supported by the fluorescence measurements where the quantum yield of **PPP** was evaluated in the presence or absence of various organic sulfonates including **BNP**. As expected from the PL intensity of **PPP-BNP**, the quantum yield of **PPP** decreased with an increase in concentration of **BNP**. On the other hand, additions of the aliphatic sulfonates, that have no ability to form assemblies with **PPP**, gave no notable change in the quantum yield of **PPP**. These results imply that the fluorescent quenching in **PPP-BNP** is due to the formation of the polymer assembly, that is so-called “concentration quenching in fluorescence,” but not the addition of counterions such as sulfonate anions. In addition, the polymer assemblies of **PPP-BNP** were stable at least for several months, and showed no decrease in PL intensity of **PPP-BNP**. It is intriguing that both **PPP-(R)-BNP** and **PPP-(S)-BNP** exhibited negative and positive monosignate Cotton effects at 414 nm in the CPL spectra. This indicates that the former and the latter have right- and left-handed circularly polarized fluorescence, respectively. Note that the PL and CPL bands at approximately 370 nm arise from the chiral inducer, **BNP**. Meanwhile, luminescence and absorption spectra overlap considerably around 370 nm, and therefore the CPL might be affected by the CD to some extent. For example, CD spectrum of **PPP-(R)-BNP** shows a negative Cotton effect at 376 nm, which implies that the right-handed molar extinction coefficient (ϵ_R) is larger than the left-handed one (ϵ_L) because $\Delta\epsilon = \epsilon_L - \epsilon_R < 0$. As a result, the CPL spectrum shows apparently a positive Cotton effect ($\Delta I = I_L - I_R > 0$) at 370 nm, which can be explained with a self-absorption of right-handed luminescence. However, the negative CPL at 414 nm, corresponding to the emission of a right-handed CPL, cannot be explained with the self-absorption.

Furthermore, there is no overlap between luminescence and absorption spectra at the longer wavelength than 400 nm. Therefore, it can be argued that the CPL at 414 nm is an intrinsic CPL of the polymer, but not an apparent one.

Both Cotton effects in the CD and CPL spectra of **PPP-(R)-BNP** and **PPP-(S)-BNP** show mirror images in sign, implying that the helical sense of the polymer assembly strictly depends on the chirality of the chiral inducer, **BNP**. According to the exciton coupling theory,¹⁸ positive and negative bisignate Cotton effects²³ in CD spectra indicate right- (*P*-helicity) and left-handed (*M*-helicity) screw structures, respectively. Therefore, **PPP-(R)-BNP**, which shows a negative bisignate Cotton effect in the CD spectrum, has a left-handed π -stacked structure with *M*-helicity. This is consistent with the negative monosignate Cotton effect observed in the CPL spectrum, which indicates the emission of circularly polarized light with *M*-helicity. On the other hand, **PPP-(S)-BNP**, which shows a positive bisignate Cotton effect in the CD spectrum and a positive monosignate one in the CPL spectrum, has a right-handed π -stacked structure with *P*-helicity. The circular dichroism strengths in the absorption and luminescence were evaluated with the dissymmetry factors g_{abs} and g_{lum} , respectively.²⁴ The g_{abs} values were -9.8×10^{-2} (at 376 nm) and $+2.1 \times 10^{-2}$ (at 341 nm) for **PPP-(R)-BNP** and $+9.9 \times 10^{-2}$ (at 378 nm) and -2.8×10^{-2} (at 342 nm) for **PPP-(S)-BNP** (Table 2). The g_{lum} values were -2.4×10^{-2} (at 414 nm) for **PPP-(R)-BNP** and $+3.1 \times 10^{-2}$ (at 415 nm) for **PPP-(S)-BNP** (Table 2). The values of g_{abs} and g_{lum} increased with increasing amounts of **BNP** until the molar ratio of $[\text{BNP}]/[\text{PPP}]$ reached 2.0. The observation of dissymmetry factors on the order of 10^{-2} – 10^{-1} in the CD and CPL spectra indicate that the polymer assembly has a considerably strong helicity due to the interchain π -stacked structure.

Table 2. The dissymmetry factors of the absorption (g_{abs}) and luminescence (g_{lum}) of the polymer assemblies (**PPP–BNP**) (1.0:2.0 mol/mol) in methanol–water (50:50 v/v).

Polymer ^a	Chiral binaphthyl	CD		CPL	
	derivative	g_{abs}	λ (nm)	g_{lum}	λ (nm)
PPP	(R)-BNP	$+2.1 \times 10^{-2}$	341	-2.4×10^{-2}	414
		-9.8×10^{-2}	376		
	(S)-BNP	-2.8×10^{-2}	342	$+3.1 \times 10^{-2}$	415
		$+9.9 \times 10^{-2}$	378		

^a Polymer concentration: 2.0×10^{-5} M (expressed in terms of the repeating unit of **PPP**).

Polymer Spheres. Next, the author measured the absorption spectra of the supernatants of the mixed solutions after removing the polymer assembly by filtration. The procedure for sample preparation is depicted in Figure 5. The supernatant showed an absorption band of **BNP** but none of **PPP**, although the normalized absorbance of **BNP** was weaker than that of the pure **BNP** solution (see Figure 6). The result indicates that only free **BNP** is present in the supernatant and that all **PPPs** and a portion of **BNPs** are consumed upon the formation of the polymer assembly. Then, the author estimated the molar ratio of **BNP** in the polymer assembly to determine its stoichiometry. The details of the estimation method are provided in the Experimental Section. The results are shown in Figure 7a and Table 3. It is apparent from Figure 7a that the molar ratio of **BNP** in the polymer assembly achieves saturation when the value of **[PPP]:[BNP]** is 1:0.5 – 1:0.6, even though the concentration of **BNP** in the mixture can still be increased. This indicates that the stoichiometry of the unit structure of the polymer assembly is composed of two **PPP** repeating units and one **BNP** molecule, as depicted in Figure 7b. It can be argued that **BNP** plays an essential role in mediating the interchain π -stacking between **PPPs** through electrostatic and π – π interactions, yielding a multilayer type π -stacked structure (see Figure 10a). The plausible models based on the present experimental results are schematically depicted in Figures 7b and 7c.

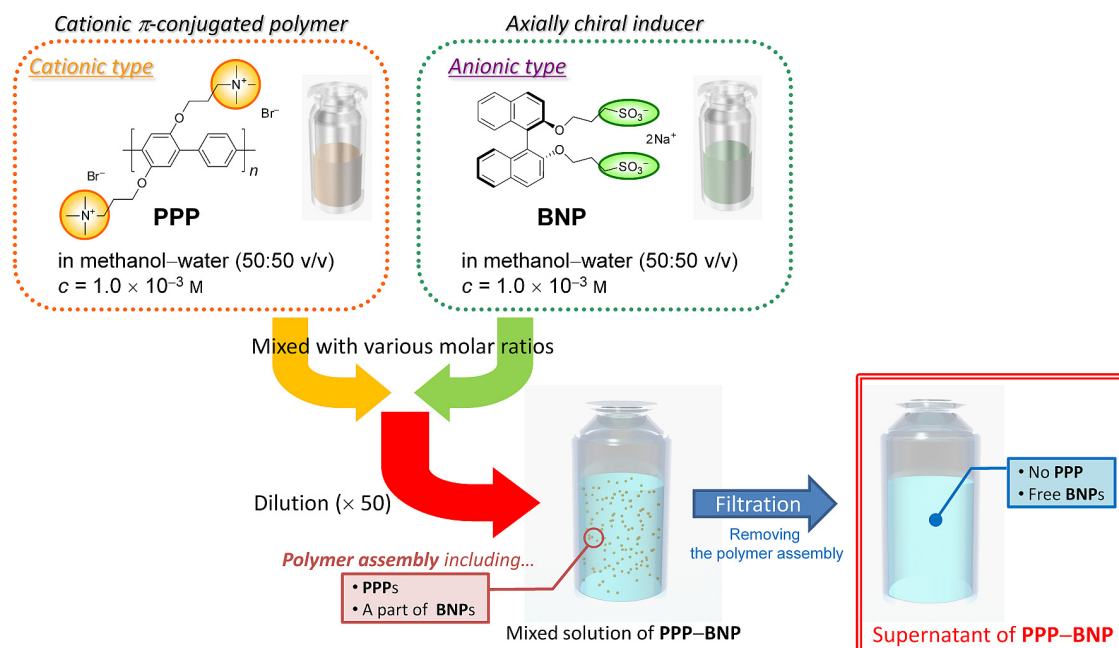


Figure 5. The procedure for preparing the supernatant of **PPP-BNP**.

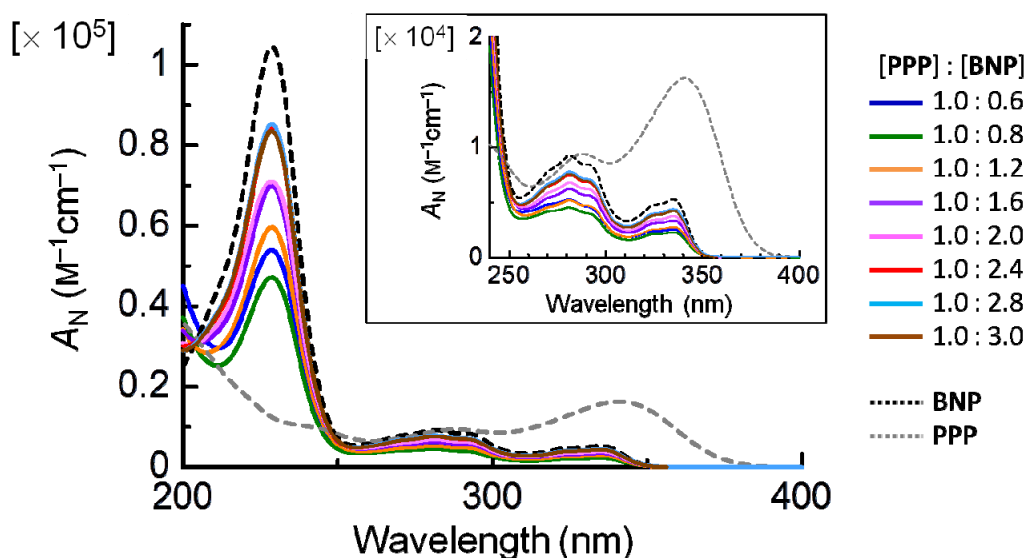


Figure 6. The UV-vis absorption spectra of the supernatant of **PPP-BNP** in methanol-water (50:50 v/v), where the polymer assembly has been removed by filtration. The normalized absorbance (A_N) is defined as $A_N = A/([\mathbf{BNP}] \times d)$, where A is the absorbance and d is the light path length. The inset shows the expanded spectra in the region from 240 to 400 nm. The concentration of **PPP** before filtration is 2.0×10^{-5} M. The concentration of **BNP** ranges from 1.2×10^{-5} to 6.0×10^{-5} M.

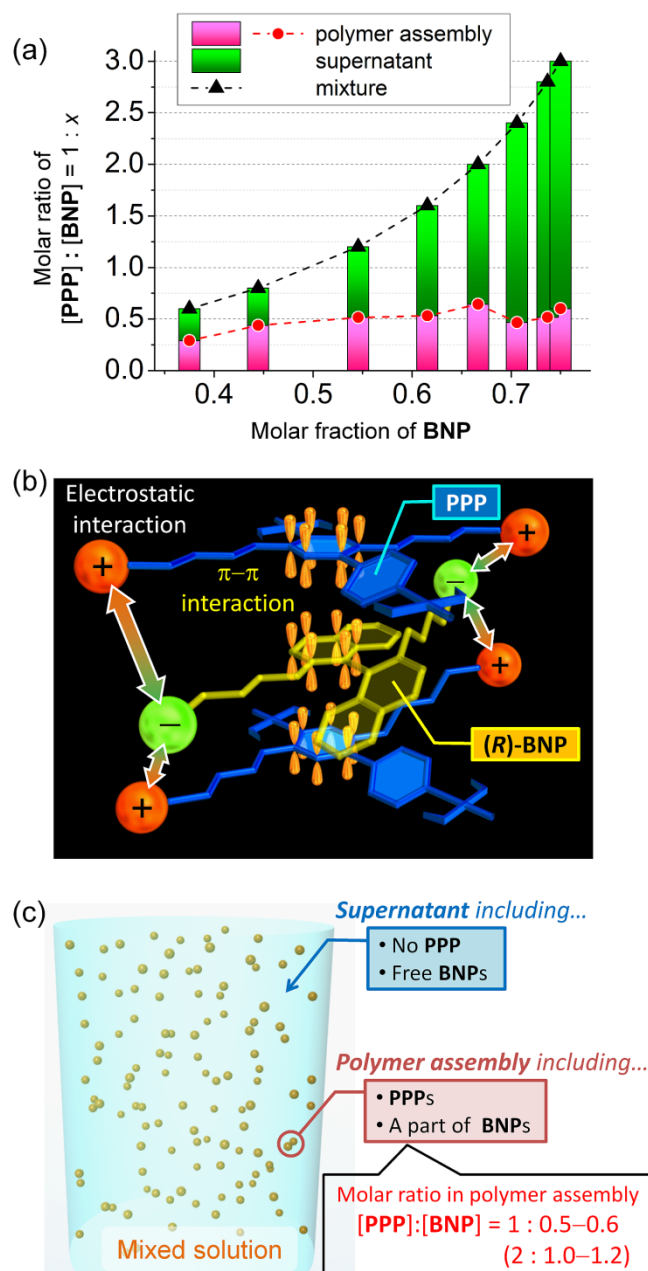


Figure 7. (a) The molar fraction of **BNP** in the mixture of **PPP** and **BNP**, which is estimated by the normalized absorbance of **BNP** (A_N) in the supernatant (see Experimental Section and Table 3). The pink bars and red dashed line show the molar ratio of **BNP** in the polymer assembly, whereas the green bars show the molar ratio in the supernatant. The black dashed line shows the molar ratio of **BNP** in the mixtures of **PPP-BNP**. (b) A plausible model of the electrostatic and π - π interactions between two **PPP** repeating units and one **(R)-BNP** molecule. (c) An image of the mixed solution of **PPP-BNP**.

Table 3. The molar ratio of **BNP** in the polymer assembly.

Molar ratio in the mixture ^a [PPP]:[BNP] = 1:x	[PPP] (M)	[BNP] (M)	Normalized absorbance at 229 nm (M ⁻¹ cm ⁻¹) ^b	Percentage of BNP in the supernatant (%) ^c	Percentage of BNP in the polymer assembly (%) ^d	Molar ratio in the polymer assembly ^e [PPP]:[BNP] = 1:y
0.6	2.0 × 10 ⁻⁵	1.2 × 10 ⁻⁵	5.40 × 10 ⁴	51.6	48.4	0.29
0.8		1.6 × 10 ⁻⁵	4.72 × 10 ⁴	45.1	54.9	0.44
1.2		2.4 × 10 ⁻⁵	5.96 × 10 ⁴	57.1	42.9	0.52
1.6		3.2 × 10 ⁻⁵	6.98 × 10 ⁴	66.8	33.2	0.53
2.0		4.0 × 10 ⁻⁵	7.09 × 10 ⁴	67.9	32.1	0.64
2.4		4.8 × 10 ⁻⁵	8.42 × 10 ⁴	80.6	19.4	0.47
2.8		5.6 × 10 ⁻⁵	8.52 × 10 ⁴	81.5	18.5	0.52
3.0		6.0 × 10 ⁻⁵	8.36 × 10 ⁴	80.0	20.0	0.60
BNP	0	2.0 × 10 ⁻⁵	1.05 × 10 ⁵	-	-	-

^a Molar ratio of the repeating unit of **PPP** and **BNP** in the mixture.

^b Normalized absorbance of **BNP** in the supernatant, where the polymer assembly has been removed by filtration. Normalized absorbance (A_N) is defined as $A_N = A/([BNP] \times d)$, where A is an absorbance and d is a light path length.

^c Percentage of **BNP** in the supernatant was determined by a formula of $A_N/A_{N(BNP)} \times 100$ (%), where $A_{N(BNP)}$ is the normalized absorbance of pure **BNP** solution and the value is $1.05 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$ at 229 nm.

^d Percentage of **BNP** in the polymer assembly was determined by a formula of $(1 - A_N/A_{N(BNP)}) \times 100$ (%).

^e Molar ratio of the repeating unit of **PPP** and **BNP** in the polymer assembly, which was determined by multiplying the molar ratio in the mixture by the percentage of **BNP** in the polymer assembly.

The optimal mixing ratio, i.e., the ratio at which the polymer assembly is most efficiently formed, was determined with a Job's plot using the absorbance at 384 nm of **PPP**–**BNP** in methanol–water (50:50 v/v). The total concentration of **PPP** and **BNP** was held constant at 5.0×10^{-5} M. The absorption band at 384 nm is attributed to the polymer assembly. As shown in Figure 8, the formation of the polymer assembly most effectively occurs at a 0.67 molar fraction of **BNP**, which corresponds to a molar ratio of $[\text{PPP}]:[\text{BNP}] = 1.0:2.0$. That is, the polymer assembly is most efficiently formed when **PPP** and **BNP** are mixed with a molar ratio of 1.0:2.0.

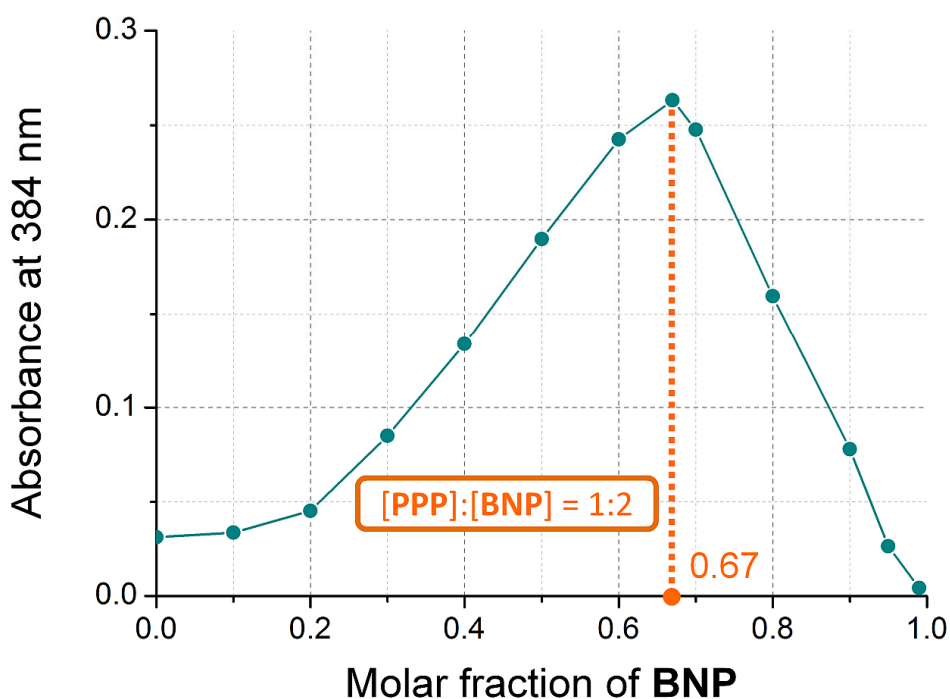


Figure 8. The Job's plot of the absorbance at 384 nm of **PPP**–**BNP** in methanol–water (50:50 v/v). The total concentration of **PPP** and **BNP** is kept constant at 5.0×10^{-5} M. The optimum mixing ratio ($[\text{PPP}]:[\text{BNP}]$) to most efficiently yield the polymer assembly is found to be 1.0:2.0.

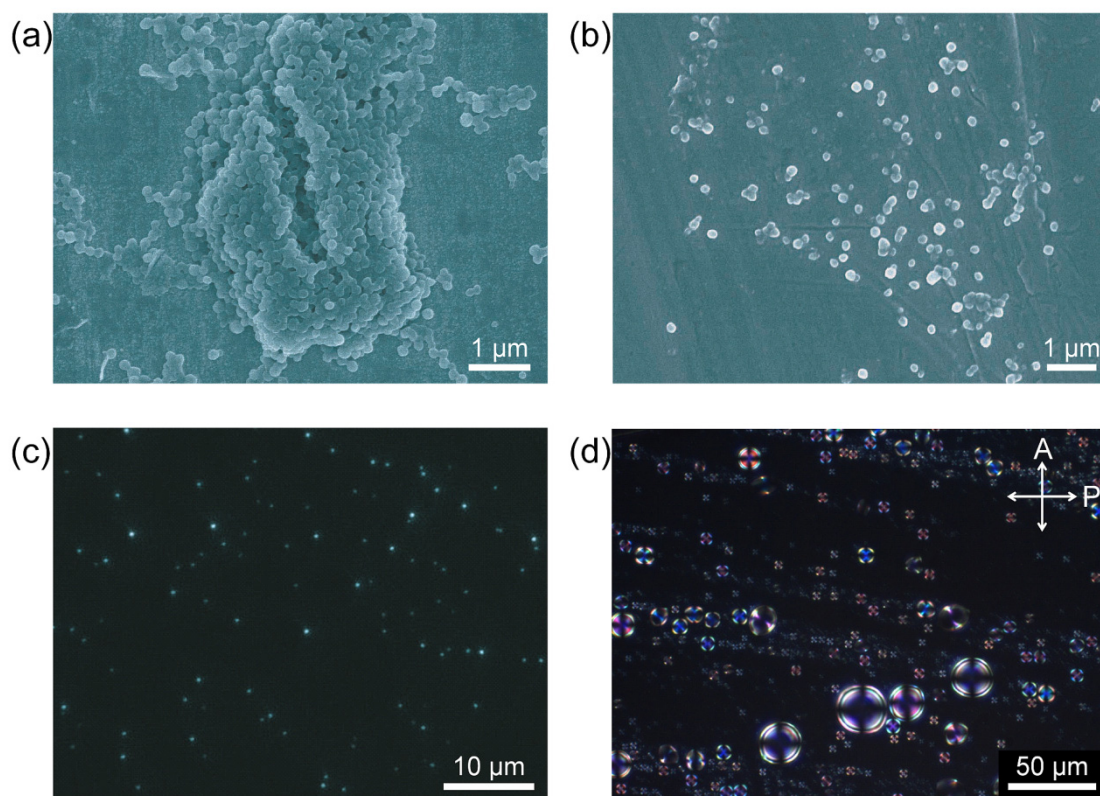


Figure 9. SEM images of the polymer assemblies (**PPP–BNP**) (1.0:2.0 mol/mol) prepared by (a) drying the mixed solution of **PPP** and **BNP** at RT and (b) freeze-drying the mixed solution. (c) A fluorescence microscope image of **PPP–BNP** (1.0:2.0 mol/mol) spin-coated on a glass plate. The wavelength of excitation is 365 nm. The fluorescent filter only transmits emitted light of wavelengths longer than 420 nm. (d) POM image of **PPP–BNP** (1.0:2.0 mol/mol) in methanol–water (50:50 v/v) at RT. The crossed arrows represent the directions of the polarizer and the analyzer of POM.

Figures 9a and 9b show the scanning electron microscope (SEM) images of the **PPP–BNP** (1.0:2.0 mol/mol) assembly. Details of the sample preparation are given in the Experimental Section. The SEM images indicate two types of spherical morphologies; the polymer spheres prepared by drying the mixed solution of **PPP** and **BNP** at RT cluster to form globules (Figure 9a), whereas those prepared by freeze-drying are well separated from each other (Figure 9b). The sphere sizes range from 140 to 255 nm with an average size of approximately 200 nm. This is in good agreement with the results of the dynamic light scattering (DLS) measurements, which

indicated an average sphere size of 220 ± 57 nm. Figure 9c displays a fluorescence microscope image of the polymer spheres prepared by spin-coating at 1000 rpm on a glass plate. A mercury-vapor lamp with the wavelength of 365 nm was used as the excitation light, and a fluorescent filter was employed to remove wavelengths below 420 nm. As seen in Figure 9c, each sphere exhibits blue fluorescence.

Spherulites Consisting of Polymer Assemblies. To elucidate the inner structure of the polymer sphere, the author examined polymer spheres dispersed in methanol–water (50:50 v/v) using a polarized optical microscope (POM) at RT. To obtain finer POM images of the polymer spheres, it is desirable to use a sample of large particles for the POM measurement. To enlarge the particle size, the polymer spheres were prepared by adding the **BNP** solution to the **PPP** solution very slowly and then leaving the mixture at RT for 7 days without stirring. It is of particular interest that Maltese Cross patterns with extinction rings are observed in all spheres, as shown in Figure 9d. Note that no polymer sphere exists in the dark field of POM. It has been reported that π -conjugated polymers upon drying show the Maltese Cross pattern,^{25–27} however, the patterns are observed only in parts of the polymer film, but not all over the film. This is because the polymers form the microstructure partially and the rest exists as a glassy state. On the other hand, in this study, each polymer sphere in a solution exhibits a Maltese Cross pattern. The result indicates that each sphere is constructed from a polymer spherulite.^{26,28,29} The polymer spherulite is a spherical aggregate consisting of crystalline lamellae and interspaced noncrystalline sites, where the former (crystalline lamellae) radiate from the center of the spherulite. The appearance of a Maltese Cross pattern implies that the axis of the interchain π -stacked structure coincides with the polarization directions of the analyzer or the polarizer of POM (Figures 10b, 10c, and 10d).²⁹ Furthermore, the extinction rings indicate the formation of twisted lamellar structures along the radial axis of the spherulite. In this study, the twisted lamellae consist of helically π -stacked conjugated polymers. The plausible models of the polymer assemblies and spherulite are depicted in Figures 10a and 10b. The spherulites observed in POM are spherical aggregates of the polymer assemblies bearing the interchain helical π -stacking structure, whose helical axes are parallel to the

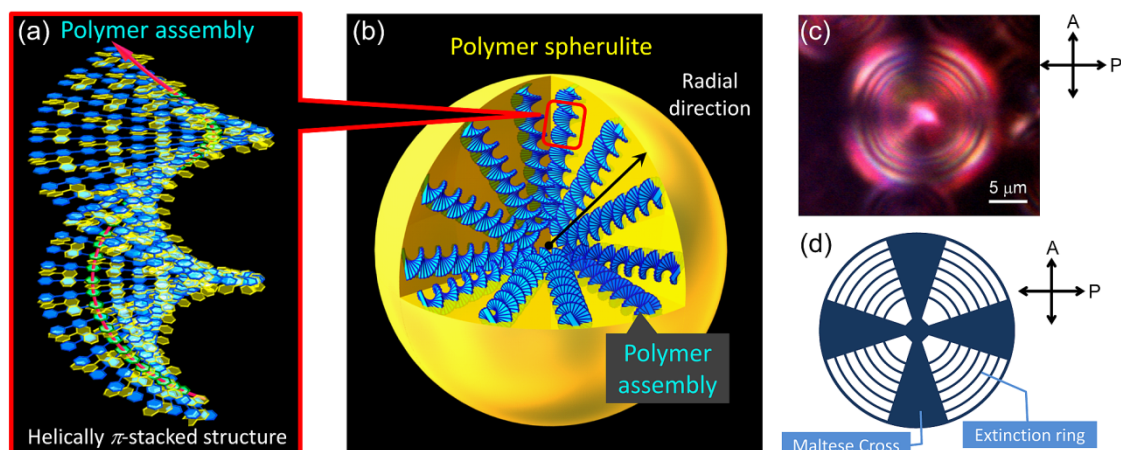


Figure 10. (a) The plausible model of assembly of polymers with the helically π -stacked structure. **PPP** and **BNP** are represented in blue and yellow, respectively. (b) The plausible model of a spherulite consisting of polymer assemblies. (c) A Maltese Cross image with the extinction rings observed in POM for a spherulite of **PPP-(R)-BNP** (1.0:2.0 mol/mol) in methanol–water (50:50 v/v) at RT. (d) The schematic pattern of the Maltese Cross image with extinction rings.

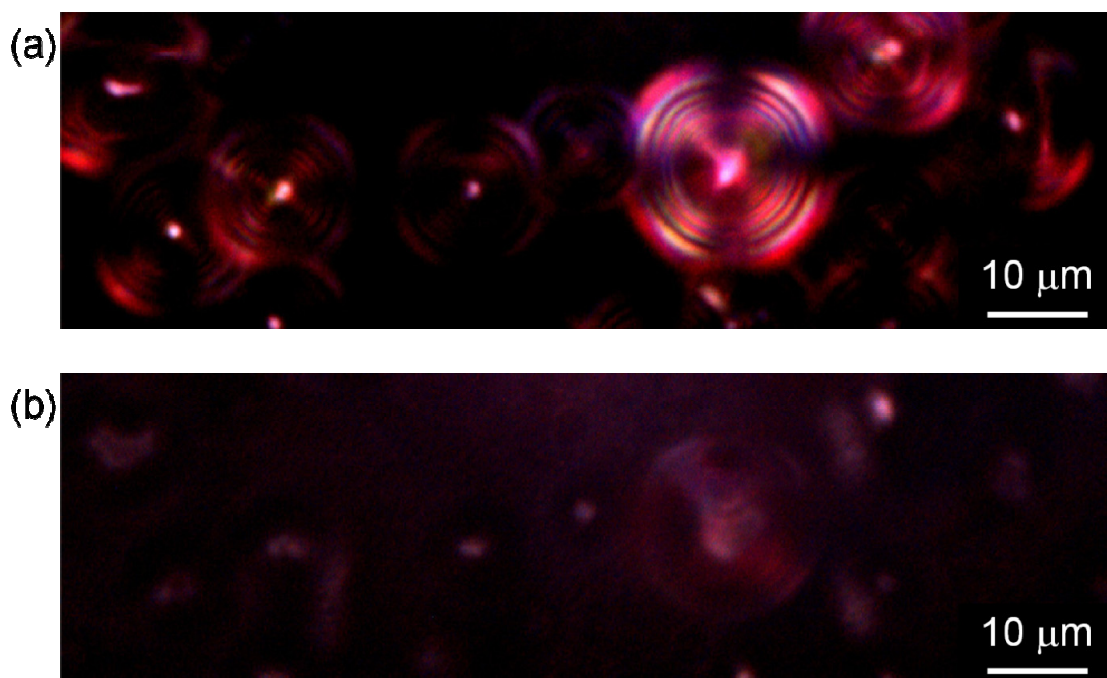


Figure 11. POM images of **PPP-BNP** (1.0:2.0 mol/mol) in methanol–water (50:50 v/v) (a) before and (b) after heating.

radial direction of the spherulite, as seen in Figure 10b. The present system is the first example of a chiroptical spherulite that is hierarchically constructed from π -conjugated polymers. It is worthy noting that the Maltese Cross pattern disappeared without change in the pitch of the extinction rings upon thermal heating (Figure 11). At the same time, the absorption and CD bands around 384 nm decreased in intensity with a slight blue-shift and disappeared (Figure 1c). These results suggest that the decomposition of the polymer spherulite might occur simultaneously with that of the polymer assembly, although the spherulite is a hierarchically higher-ordered structure than the polymer assembly.

Conclusion

In summary, the author found that the mixture of a cationic poly(*para*-phenylene) derivative (**PPP**) and an anionic chiral binaphthyl derivative (**BNP**) forms a hierarchically self-organized assembly with an interchain helically π -stacked structure stabilized by the presence of both electrostatic and π - π interactions. The electrostatic and π - π interactions are essential to the stability of the π -stacked structure, resulting in large dissymmetry factors of $|10^{-2}|$ – $|10^{-1}|$ in absorption and luminescence. It was demonstrated that the polymer assemblies further gathered to form spherulites, which can be regarded as semi-crystalline nanospheres, and the spherulites exhibit circularly polarized blue luminescence. The fabricated spherulites could be useful as novel chiral nanomaterials for the next-generation of plastic optoelectronics.

Experimental Section

1. Measurements. NMR spectra were obtained with JEOL AL-400 or Bruker AVANCE-600. Chemical shifts are represented in parts per million downfield from tetramethylsilane (TMS) or (trimethylsilyl)propionic-2,2,3,3- d_4 acid sodium salt (TSP- d_4) as internal standards. Elemental analyses were performed by Perkin-Elmer 2400 CHN Elemental Analyzer, Yanako CHN Corders (MT-3, MT-5 and MT-6), JSL JM-10, Mitsubishi chemical analytech AQF-100 and Dionex ICS-1500. High-resolution mass spectra (HRMS) were obtained by using JEOL JMS-HX110A (FAB), Thermo Fisher Scientific EXACTIVE (ESI), and Thermo Fisher Scientific MALDI DUO orbitrapXL (MALDI).

Size exclusion chromatography (SEC) result was obtained with a system consisting of an Asahipak GF-310 HQ column 300×7.5 mm (Shodex) and a JASCO RI-2031 Plus RI detector, where the instrument was calibrated by polyethylene glycol standard. The eluent was 0.1 M NaClO_4 aq./acetonitrile (5/5) at a flow rate of 0.5 mL/min.

Ultraviolet–visible (UV–vis) absorption spectra were measured with JASCO V-570 UV/VIS/NIR spectrophotometer. Photoluminescence (PL) spectra were measured with JASCO FP-750 spectrofluorometer. Circular dichroism (CD) spectra were measured with JASCO J-820 spectropolarimeter. Circularly polarized luminescence (CPL) spectra were measured with JASCO CPL-200S spectrometer. All optical measurements were performed using a quartz cell. Dynamic light scattering (DLS) measurements were performed using Otsuka Electronics FPAR-1000 fiber-optics particle analyzer. Scanning electron microscopy (SEM) was performed with JEOL JSM-7500F. The samples were coated with Pt-Pd alloy using JEOL JFC-1600 ion coater before measurements of SEM. Fluorescence microscopy was performed by using Nikon eclipse TE2000-U with a mercury-vapor lamp (Excitation wavelength: 365 nm) and a fluorescent filter (transmission ≥ 420 nm). Polarized optical microscopy (POM) was performed with Carl Zeiss Axio Imager.M1m. X-ray diffraction (XRD) measurement was performed with Rigaku ultra X18 diffractometer. XRD pattern was recorded with an X-ray generator with Nickel filtered $\text{CuK} \alpha$ radiation (40 kV/300 mA: $\lambda = 0.154$ nm) and a flat plate camera (RINT2500, Rigaku).

2. Materials. All the chemicals were commercially available and used as received. (*R*)- and (*S*)-1,1'-bi-2-naphthol were purchased from Kankyo Kagaku Center Co. Ltd. 1,4-Phenylenediboronic acid was purchased from Lancaster Co. Ltd. All other chemicals were purchased from Aldrich Chemical Co. Ltd., Tokyo Kasei Co. Ltd. and Wako Co. Ltd. Solvents were dried and distilled before use.

3. Synthesis. All syntheses were carried out under argon atmosphere.

1,4-Dibromo-2,5-bis(3-bromopropoxy)benzene (1). To a stirred solution of triphenylphosphine (TPP, 20.80 g, 79.3 mmol) in tetrahydrofuran (THF, 120 mL) was added dropwise a solution of diethyl azodicarboxylate (DEAD, 34.55 g, 40 wt% in toluene, 79.3 mmol) and 3-bromo-1-propanol (11.06 g, 79.6 mmol) in THF (50 mL) at 0 °C. Then, to the mixture was added dropwise a solution of 2,5-dibromohydroquinone (9.68 g, 36.1 mmol) in THF (60 mL), and the reaction mixture was stirred at RT for 24 h. After removing the insoluble solid by filtration, the filtrate was concentrated under reduced pressure. The residue was dissolved in Et₂O, and washed with water and brine, dried (Na₂SO₄), and concentrated. The crude product was purified by column chromatography (silica gel, chloroform) to give **1** as a white solid (7.96 g, 43.2 %): ¹H NMR (400 MHz, CDCl₃, TMS): δ = 2.34 (quint, *J* = 6.0 Hz, 4H; OCH₂CH₂), 3.66 (t, *J* = 6.0 Hz, 4H; CH₂Br), 4.11 (t, *J* = 6.0 Hz, 4H; OCH₂), 7.13 ppm (s, 2H; Ar-*H*); ¹³C NMR (100 MHz, CDCl₃, TMS): δ = 29.9, 32.2, 67.6, 111.4, 118.7, 150.0 ppm; HRMS (MALDI, *m/z*): [*M*⁺] calcd for C₁₂H₁₄Br₄O₂: 505.7722; Found: 505.7718; Anal calcd for C₁₂H₁₄Br₄O₂: C 28.27, H 2.77, Br 62.69; Found: C 28.84, H 2.86, Br 62.69.

1,4-Dibromo-2,5-bis[3-(*N,N,N*-trimethylammonium)propoxy]benzene dibromide (2). A solution of **1** (0.76 g, 1.5 mmol) and trimethylamine (2.96 g, 30 wt% in water, 15.0 mmol) in THF (15 mL) was stirred overnight at RT. The resulting precipitate was collected by filtration and washed with THF to give **2** as a white powder (0.85 g, 89.7 %): ¹H NMR (400 MHz, D₂O, TSP-*d*₄): δ = 2.35 (sext, *J* = 5.7 Hz, 4H; OCH₂CH₂), 3.23 (s, 18H; N⁺CH₃), 3.64 (quint, *J* = 8.3 Hz, 4H; N⁺CH₂), 4.20 (t, *J* = 5.7 Hz, 4H; OCH₂), 7.37 ppm (s, 2H; Ar-*H*); ¹³C NMR (100 MHz, D₂O, TSP-*d*₄): δ = 25.6, 55.9, 67.0, 69.9, 113.9, 122.0, 152.2 ppm; HRMS (FAB, *m/z*): [*M*-Br⁻] calcd for

$C_{18}H_{32}Br_4N_2O_2$: 545.0008; Found: 545.0027; Anal calcd for $C_{18}H_{32}Br_4N_2O_2$: C 34.42, H 5.14, N 4.46, Br 50.89; Found: C 33.61, H 5.26, N 4.50, Br 49.59.

1,4-Phenylenediboronic acid bis(1,3-propanediol) cyclic ester (3). A suspension of 1,4-phenylenediboronic acid (5.00 g, 30.2 mmol) and 1,3-propanediol (5.63 g, 74.0 mmol) in CH_2Cl_2 (190 mL) was refluxed for 24 h. The solvent was removed under reduced pressure, and the residue was washed with ethanol to give **3** as a white powder (6.94 g, 93.6 %): 1H NMR (400 MHz, $CDCl_3$, TMS): δ = 2.05 (quint, J = 5.4 Hz, 4H; OCH_2CH_2), 4.16 (t, J = 5.4 Hz, 8H; OCH_2), 7.73 ppm (s, 4H; Ar- H); ^{13}C NMR (400 MHz, $CDCl_3$, TMS): δ = 27.4, 61.9, 132.5 ppm; HRMS (ESI, m/z): $[M+H]^+$ calcd for $C_{12}H_{16}B_2O_4$: 247.1307; Found: 247.1302; Anal calcd for $C_{12}H_{16}B_2O_4$: C 58.62, H 6.56; Found: C 58.36, H 6.49.

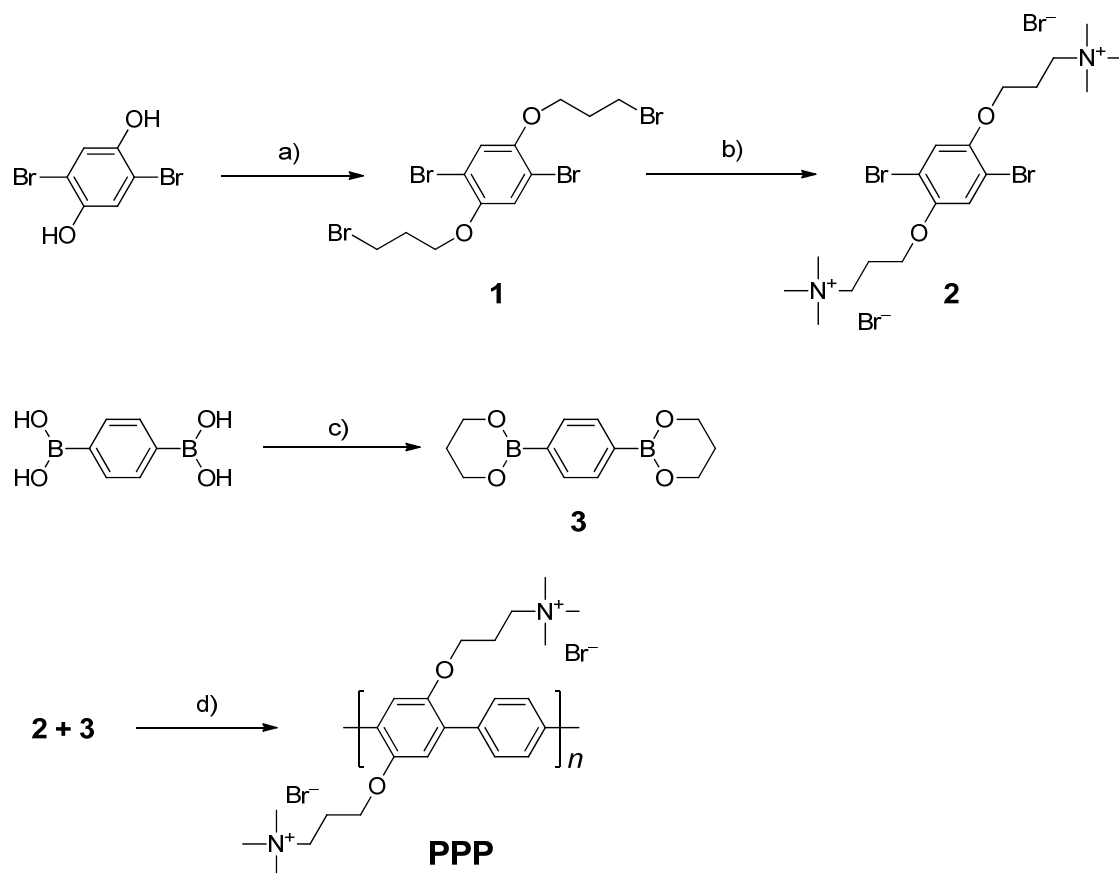
Poly({2,5-bis[3-(*N,N,N*-trimethylammonium)propoxy]-1,4-phenylene}-*alt*-1,4-phenylene) dibromide (PPP). A solution of **2** (0.63 g, 1.0 mmol), **3** (0.25 g, 1.0 mmol), palladium(II) acetate (14 mg, 0.061 mmol), and Na_2CO_3 (0.85 g, 8.0 mmol) in *N,N*-dimethylformamide (DMF, 30 mL) and water (40 mL) was stirred at 80 °C for 24 h. The reaction mixture was cooled to RT, poured into a diluted HBr aqueous solution (400 mL), and vigorously stirred overnight in the presence of ethylenediaminetetraacetic acid (EDTA, 1 g). After filtration, the filtrate was concentrated to about 100 mL by evaporation, dropped into a large amount of acetone (700 mL), and vigorously stirred overnight. The resulting precipitate was collected by filtration and dissolved in water. The above processes were repeated twice to purify the polymer. The resulting solution was freeze-dried to obtain **PPP** as an orange solid (0.39 g, 70.5 %): 1H NMR (400 MHz, $DMSO-d_6$, TMS): δ = 2.19 (s, 4H; OCH_2CH_2), 3.16 (s, 18H; NCH_3), 3.52 (s, 4H; CH_2N), 4.16 (s, 4H; OCH_2), 7.17-7.90 ppm (m, 6H; Ar- H); ^{13}C NMR (100 MHz, $DMSO-d_6$, TMS): δ = 22.8, 52.2, 63.1, 66.5, 114.6, 116.3, 125.9, 128.7, 129.9, 149.6 ppm; SEC (0.1 M $NaClO_4$ aq./acetonitrile (5/5) vs. polyethylene glycol): M_n = 3.5×10^3 g/mol, M_w = 4.9×10^3 g/mol, M_w/M_n = 1.4.

2,2'-Bis(3-sulfonatopropoxy)-1,1'-binaphthalene disodium salt (BNP). To a solution of (*R*)- or (*S*)-1,1'-bi-2-naphthol (5.73 g, 20 mmol) in EtOH (250 mL) was added dropwise a solution of NaOH (1.76 g, 44 mmol) in EtOH (100 mL) at RT, and the mixture was refluxed for 1 h. Then, 1,3-propanesultone (5.38 g, 44 mmol) was

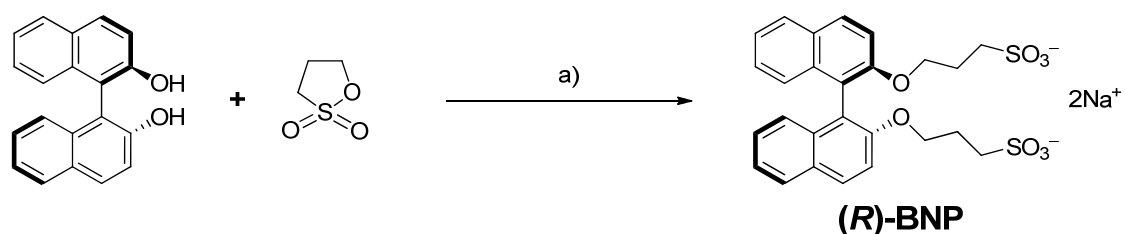
added to the mixture, and the reaction mixture was refluxed for additional 1h. The resulting precipitate was filtered, washed with EtOH, and recrystallized twice from water/ethanol to give **BNP** as a white solid ((**R**)-**BNP**: 3.23 g, 28.1 %; (**S**)-**BNP**: 2.89 g, 25.1 %).

(R)-BNP: ^1H NMR (400 MHz, D_2O , TSP- d_4): δ = 1.77 (sext, J = 5.6 Hz, 4H; OCH_2CH_2), 2.18 (t, J = 7.8 Hz, 4H; $\text{CH}_2\text{SO}_3\text{Na}$), 3.94 (dq, J = 83.6 Hz, J = 5.6 Hz, 4H; OCH_2), 6.72 (t, J = 8.2 Hz, 2H; Ar- H), 6.85 (d, J = 8.2 Hz, 2H; Ar- H), 7.10 (t, J = 8.2 Hz, 2H; Ar- H), 7.43 (d, J = 8.2 Hz, 2H; Ar- H), 7.77 (d, J = 8.2 Hz, 2H; Ar- H), 7.92 ppm (d, J = 8.2 Hz, 2H; Ar- H); ^{13}C NMR (100 MHz, D_2O , TSP- d_4): δ = 27.2, 50.4, 71.3, 119.1, 122.9, 127.1, 127.4, 129.6, 131.0, 132.3, 132.8, 136.2, 156.3 ppm; HRMS (ESI, m/z): $[\text{M}+\text{Na}^+]$ calcd for $\text{C}_{26}\text{H}_{24}\text{Na}_2\text{O}_8\text{S}_2$: 597.0600; Found: 597.0574; Anal calcd for $\text{C}_{26}\text{H}_{24}\text{Na}_2\text{O}_8\text{S}_2$: C 54.35, H 4.21, S 11.16; Found: C 53.62, H 4.40, S 10.96.

(S)-BNP: ^1H NMR (400 MHz, D_2O , TSP- d_4): δ = 1.76 (sext, J = 5.6 Hz, 4H; OCH_2CH_2), 2.18 (t, J = 7.6 Hz, 4H; $\text{CH}_2\text{SO}_3\text{Na}$), 3.93 (dq, J = 87.2 Hz, J = 5.6 Hz, 4H; OCH_2), 6.68 (t, J = 8.0 Hz, 2H; Ar- H), 6.83 (d, J = 8.0 Hz, 2H; Ar- H), 7.07 (t, J = 8.0 Hz, 2H; Ar- H), 7.41 (d, J = 8.0 Hz, 2H; Ar- H), 7.75 (d, J = 8.0 Hz, 2H; Ar- H), 7.91 ppm (d, J = 8.0 Hz, 2H; Ar- H); ^{13}C NMR (100 MHz, D_2O , TSP- d_4): δ = 27.2, 50.4, 71.3, 119.1, 122.9, 127.0, 127.4, 129.6, 131.0, 132.3, 132.8, 136.2, 156.2 ppm; HRMS (ESI, m/z): $[\text{M}+\text{Na}^+]$ calcd for $\text{C}_{26}\text{H}_{24}\text{Na}_2\text{O}_8\text{S}_2$: 597.0600; Found: 597.0573; Anal calcd for $\text{C}_{26}\text{H}_{24}\text{Na}_2\text{O}_8\text{S}_2$: C 54.35, H 4.21, S 11.16; Found: C 53.40, H 4.37, S 10.99.



Scheme 2. The synthetic route for preparation of the cationic poly(*para*-phenylene) derivative (**PPP**). a) 3-Bromo-1-propanol, diethyl azodicarboxylate (DEAD), triphenylphosphine (TPP), THF, RT, 24 hrs; b) Trimethylamine, THF, RT, 24 hrs; c) 1,3-Propanediol, dichloromethane, 40 °C, 24 hrs; d) Palladium(II) acetate, sodium carbonate, DMF, water, 80 °C, 24 hrs.



Scheme 3. The synthetic route for preparation of the anionic axially chiral binaphthyl derivative (**BNP**). a) Sodium hydroxide, ethanol, 80 °C, 2 hrs.

4. Sample preparation. All samples were prepared by mixing solutions of **PPP** ($c = 1.0 \times 10^{-3}$ M, expressed as the repeating unit) and **BNP** ($c = 1.0 \times 10^{-3}$ M) in methanol–water (50:50 v/v) at RT. All the solvents used are methanol–water (50:50 v/v).

4.1. UV–vis absorption, CD, PL, CPL, and DLS measurements. The polymer (**PPP**) and the chiral binaphthyl derivative (**BNP**) were separately dissolved in methanol–water (50:50 v/v) at the concentration of 1.0×10^{-3} M, and then the solutions were mixed with various molar ratios. Subsequently, the mixtures were diluted with the mixed solvent to give a concentration of the polymer = 2.0×10^{-5} M. All ε and $\Delta\varepsilon$ in UV–vis absorption and CD spectra were evaluated in terms of the concentration of the polymer.

4.2. SEM measurements. According to the above procedure, a mixed solution of **PPP** and **BNP** was prepared with the molar ratio of 1.0:2.0. The mixed solution was dried at RT under normal pressure, or by a freeze-drying.

4.3. Fluorescence microscope measurements. According to the above procedure, a mixed solution of **PPP** and **BNP** was prepared with the molar ratio of 1.0:2.0. The mixed solution was spin-coated at 1000 rpm on a glass plate to obtain the sample.

4.4. XRD measurements. **PPP** solution (1.0×10^{-3} M) and **BNP** solution (1.0×10^{-3} M) were mixed with the molar ratio of 1.0:2.0, and then the mixture was left at RT for 2 days to obtain the precipitate, which was collected to be used as a XRD sample.

4.5. POM measurements. **BNP** solution (1.0×10^{-3} M) was added slowly to **PPP** solution (1.0×10^{-3} M) and the mixture was left at RT for 7 days without stirring, where the molar ratio of $[\text{BNP}]/[\text{PPP}]$ was 1.0:2.0. Then, the mixture was dropped on a glass plate, covered by a thin glass plate, and observed with POM at RT.

5. Estimation of the molar ratio of BNP in the polymer assembly.

To estimate the molar ratio of **BNP** in the polymer assembly, the author measured the UV–vis absorption spectra of the supernatant of the **PPP–BNP** solution. The **PPP–BNP** solution, which was prepared using the same procedure as mentioned in the optical measurements, was filtered through a membrane filter (Millex-VV, pore size: 0.1 μm), which yielded the supernatant by removing the polymer assembly. The

procedure is depicted in Figure 5. The absence of **PPP** in the supernatant was confirmed by the UV–vis absorption spectra, where no **PPP** absorption band was observed, as shown in Figure 6. The UV–vis absorption measurement of the supernatant gave a normalized absorbance of **BNP** (A_N) by using the equation $A_N = A/([\mathbf{BNP}] \times d)$, where A is the absorbance and d is the light path length (see Figure 6 and Table 3). When all **BNPs** exist in the supernatant, A_N coincides with the normalized absorbance of a pure **BNP** solution [$A_{N(\mathbf{BNP})}$, black dashed line in Figure 6]. However, when a portion of **BNP** is included in the polymer assembly, A_N shows a weaker absorption intensity than $A_{N(\mathbf{BNP})}$. Because the absorption intensity is proportional to the number of molecules in a solution, the author estimated the percentages of **BNP** in the supernatant [$A_N/A_{N(\mathbf{BNP})} \times 100$ (%)] and in the polymer assembly [$(1 - A_N/A_{N(\mathbf{BNP})}) \times 100$ (%)] by using the above formulas. Finally, the molar ratio of **[PPP]:[BNP]** in the polymer assembly was determined by multiplying the molar ratio in the mixture by the percentage of **BNP** in the polymer assembly. The results are shown in Figure 7a and Table 3.

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- (23) Positive bisignate Cotton effect means that positive and negative Cotton effects of CD couplet are observed at longer and shorter wavelengths, respectively. On the other hand, negative bisignate Cotton effect means that negative and positive Cotton effects of CD couplet are observed at longer and shorter wavelengths, respectively.
- (24) Dissymmetry factors in absorption (g_{abs}) and in luminescence (g_{lum}) are defined as follows: $g_{\text{abs}} = \Delta\varepsilon/\varepsilon = (\varepsilon_{\text{L}} - \varepsilon_{\text{R}})/\varepsilon = 2(\varepsilon_{\text{L}} - \varepsilon_{\text{R}})/(\varepsilon_{\text{L}} + \varepsilon_{\text{R}})$, where ε_{L} and ε_{R} are the left- and right-handed molar extinction coefficients, respectively; $g_{\text{lum}} = \Delta I/I = (I_{\text{L}} - I_{\text{R}})/I = 2(I_{\text{L}} - I_{\text{R}})/(I_{\text{L}} + I_{\text{R}})$, where I_{L} and I_{R} are the left- and right-handed luminescent intensities, respectively.
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Chapter 4

Interchain Helically π -Stacked Assembly of Cationic Chiral Poly(*para*-phenylene) Derivatives Enforced by Anionic π -Conjugated Molecules through Both Electrostatic and π - π Interactions

Introduction

Helical conjugated polymers (HCPs) have attracted current interest because of their peculiar optoelectronic functionalities, such as induced solenoid magnetism,¹ circularly polarized luminescence (CPL),²⁻⁵ and nonlinear second harmonic optics,⁶ and therefore they are regarded as next-generation plastic materials. Several approaches for synthesizing HCPs have recently been reported. Among them, the introduction of a chiral moiety into the side chain of the polymer is the most simple and straightforward method. Various types of HCPs based on polyacetylene [PA],⁷⁸ poly(*para*-phenylene) [PPP],⁹ poly(*meta*-phenylene) [PMP],¹⁰ polypyrrole,¹¹ polythiophene [PT],¹¹ and polyfluorene [PF]^{5, 12} derivatives, all of which bear chiral substituents in their side chains, have been synthesized. A part of these HCPs are shown to form helically associated species through supramolecular assemblies and to exhibit chiroptical properties. Meanwhile, aromatic polymers with zigzag main chains such as PMP and poly(*meta*-phenylene ethynylene) derivatives are known to have intrachain helicene-type helical structure, like a spring in the shape of a coil.² Although it has been assumed that polymers with linear conjugated skeletons, such as PPP derivatives, have an intrachain helically twisted main chain with a certain degree of dihedral angle between the phenylene units, no direct evidence has hitherto been put forward.

It is known that the degree of helicity is evaluated with the dissymmetry factor (expressed by g), and the dissymmetry factor of a chiral molecule in an isolated state is very small, on the order of 10^{-3} – 10^{-4} . Hence, it is desirable for the molecules to have

supramolecular structure and/or to become a molecular assembly to attain large dissymmetry factors, simply because chirality amplification is expected in the molecular assembly. In cases of conjugated polymers, spontaneous alignment and helical arrangement using liquid crystallinity are promising ways to attain an amplified dissymmetry factor.^{13, 14} It is possible to attain high dissymmetry factors when the conjugated polymers are helically arranged in thermotropic or lyotropic chiral liquid crystal phases. However, aligned polymer films are often encountered with artifacts in circular dichroism (CD) and CPL spectra, causing inevitable difficulty and uncertainty in evaluating the intrinsic dissymmetry factor through chiral spectroscopic measurements.

Here, the author presents a novel approach for preparing helically π -stacked assemblies of ionic conjugated polymers with high dissymmetry factors. The assemblies are enforced in stability by cooperatively functioning electrostatic and π - π interactions between cationic π -conjugated polymers and anionic aromatic molecules. The author synthesized cationic and chiral poly(*para*-biphenylene) [**PPP1**] and poly(*para*-terphenylene) [**PPP2**] derivatives where cationic and asymmetric center types of chiral moieties are incorporated in the side chains. CD measurements indicate that these polymers have intrachain helically twisted structure where one helical sense is predominant. This report is the first to demonstrate intrachain helicity due to the one-handed twisting of the conjugated backbone in the PPP derivatives. Furthermore it is found that when the anionic achiral naphthalene derivative is added to the polymer solution, a polymer assembly is formed. After annealing treatment, **PPP2** in the polymer assembly was arranged and then formed interchain helically π -stacked structure, whereas **PPP1** formed the interchain structure just by mixing with the anionic molecules. By investigating their chiroptical properties, the intrachain and interchain helical structure coexisting in the polymer assembly are unambiguously identified. The polymer assemblies exhibit high dissymmetry factors of 10^{-2} – 10^{-1} that are increased by 10–100 times owing to the chirality amplification upon the formation of the polymer assembly. It is worth emphasizing that the annealing of a disperse system such as a solution of the **PPP2** polymer assembly is effective for enhancing the dissymmetry factor. This enhancement is because the annealing can

improve the higher-ordered structure of conjugated polymers, similar to the heating effect in the liquid crystal state.

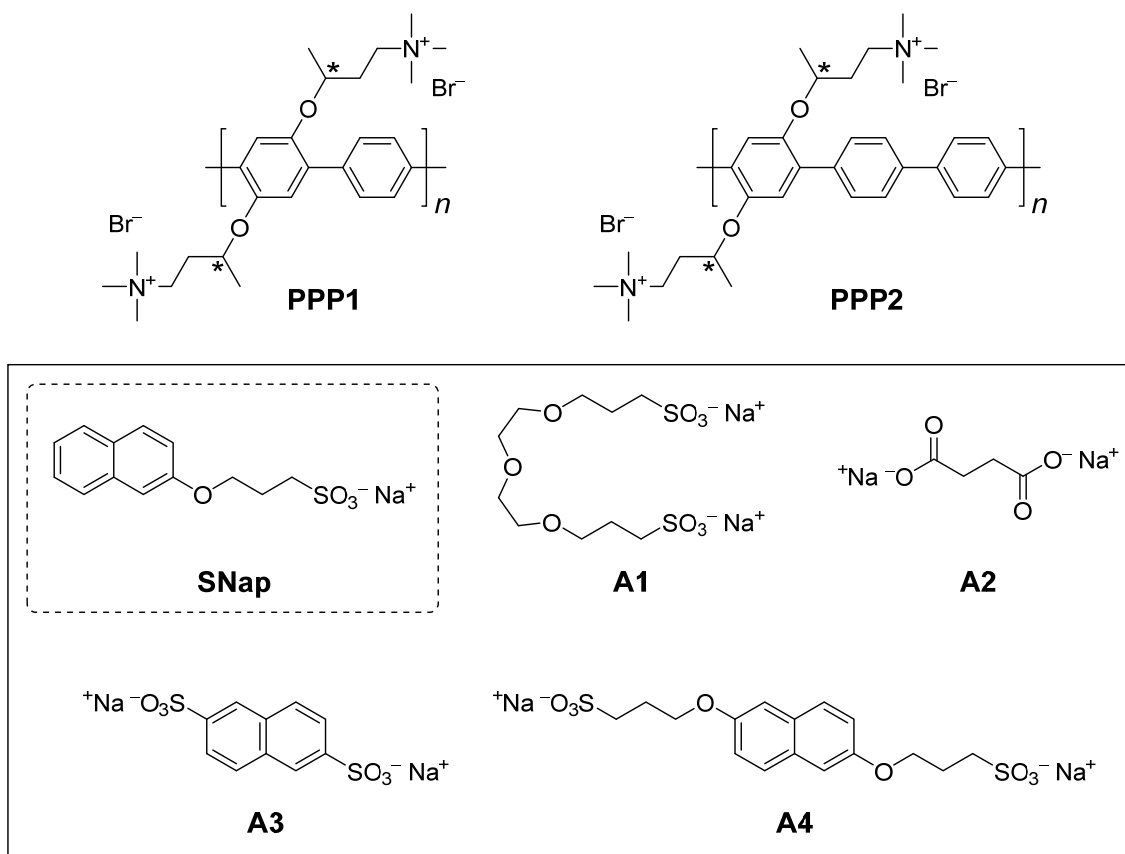
Results and Discussion

Synthesis of PPP1 and PPP2. Cationic chiral poly(*para*-phenylene) derivatives were synthesized by introducing both chiral carbons and tetraalkylammonium cations into the side chains, as shown in Scheme 1. The polymers containing biphenylene and terphenylene moieties as repeating units are abbreviated as **PPP1** and **PPP2**, respectively. The synthesis routes for **PPP1s** and **PPP2s** are shown in Scheme 2. The counter anion was purified by an ion-exchange process. Low molecular weight oligomers and salts were removed by a dialysis treatment with a regenerated cellulose dialysis membrane (Spectra/Por® 6, molecular weight cut-off: 8,000). Polar solvents such as water and methanol were good solvents for the polymers, whereas typical organic solvents such as acetone, chloroform, and tetrahydrofuran (THF) were poor ones.

To evaluate the average molecular weights of the polymers, size exclusion chromatography (SEC) was performed by using a cation-coated column, where the column packing material used as the stationary phase possesses cationic groups to prevent the adsorption of cationic polymers. The SEC results were shown as follows: $M_n = 24,200$, $M_w = 265,800$, and $M_w/M_n = 11.0$ for (*R,R*)-**PPP1**; $M_n = 8,600$, $M_w = 46,600$, and $M_w/M_n = 5.4$ for (*S,S*)-**PPP1**; $M_n = 760$, $M_w = 350,600$, and $M_w/M_n = 461.1$ for (*R,R*)-**PPP2**; and $M_n = 670$, $M_w = 52,500$, and $M_w/M_n = 78.6$ for (*S,S*)-**PPP2**. All the chromatograms of the SEC measurements showed broad peaks, resulting in the quite high polydispersity indices (M_w/M_n). Moreover the SEC results were less reproducible. This is because the polymers were partially adsorbed to the column stationary phase despite the use of cation-coated materials. Thus the author concluded the SEC measurements gave less reliable results.

On the other hand, static light scattering (SLS) in water was also performed to estimate the absolute molecular weights of the polymers through Zimm plot analysis. However, the required polymer concentration (10 mg/mL in water) was too high to dissolve the polymers completely. As a result, the M_w values estimated to be $7.5 \times$

10^6 – 9.9×10^5 , which indicates aggregation of the polymers. This is due to the hydrophobic conjugated backbones that easily aggregate each other via hydrophobic and π – π interactions. Thus, the author failed to quantitatively evaluate the average molecular weights of the polymers.



Scheme 1. Cationic chiral poly(*para*-phenylene) derivatives (**PPP1** and **PPP2**) and anionic additives (**SNap** and **A1–A4**).

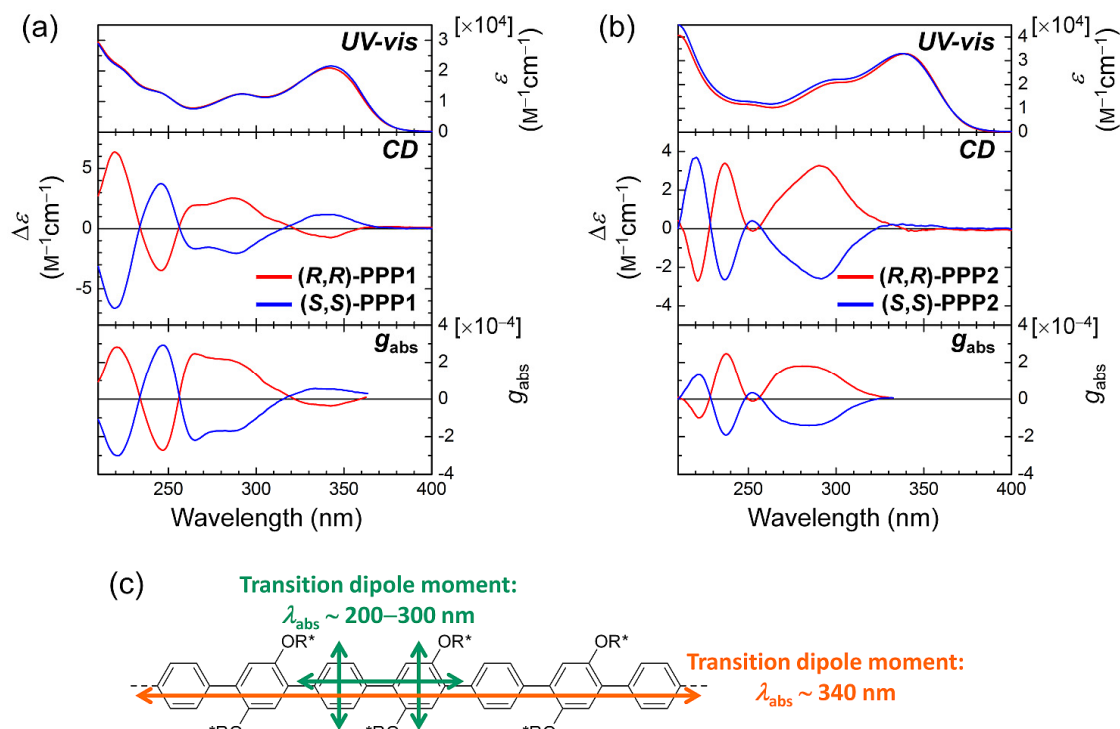


Figure 1. UV–vis absorption spectra, CD spectra, and g_{abs} factors of (a) **PPP1s** and (b) **PPP2s** in methanol ($c = 5.0 \times 10^{-5}$ M). (c) Schematic model of a poly(*para*-phenylene) derivative with transition dipole moments.

Chiroptical properties of PPP1 and PPP2. Figures 1a and b depict UV–vis absorption spectra, circular dichroism (CD) spectra, and dissymmetric factors in absorption (g_{abs}) of **PPP1s** and **PPP2s** in methanol. The concentrations were kept constant at 5.0×10^{-5} M (expressed in terms of the repeating unit). In the UV–vis absorption spectra, all of the polymers showed absorption bands in the wavelength region of 200–380 nm which originates from the π – π^* transition of the π -conjugated backbone. The absorption bands around 340 nm correspond to the transition dipole moment parallel to the main chains (orange arrow in Figure 1c), whereas the absorption bands ranging from 200 to 300 nm correspond to those on phenylene and biphenylene moieties (green arrows in Figure 1c).¹⁵⁻¹⁹ Even when dissolved in water or methanol–water mixtures as an alternative solvent, the polymer showed almost the same absorption spectrum as in methanol (see Figure 2). In addition, the shapes and intensities of the absorption bands remained unchanged even when the polymer

solutions were heated up to 60–95 °C (see Figures 3–6). These results indicate that the absorption band is attributable to the isolated polymer chain, but not to the aggregated one. Exceptionally, **PPP2** in water showed an absorption band peaked at a longer wavelength (350 nm), which was blue-shifted with increasing temperature (Figures 5e and 6e). This result implies that **PPP2** partially aggregates in water. It may be because the conjugated backbone is highly hydrophobic and easily π -stackable between main chains due to the richness of non-substituted phenylene rings.

The CD spectra of (*R,R*)- and (*S,S*)-enantiomers of **PPP1s** and **PPP2s** showed Cotton effects with mirror images in sign, implying that the optical activity of the polymers depends strictly on the chirality of the side chains. The peak wavelengths, molar circular dichroism ($\Delta\epsilon$), and dissymmetry factors in absorption (g_{abs}) are summarized in Tables 1–4. Both **PPP1** and **PPP2** showed three CD bands with $\Delta\epsilon$ of approximately $5 \text{ M}^{-1}\text{cm}^{-1}$ in the wavelength region of 200–300 nm, which correspond to the absorption of phenylene rings (green arrows in Figure 1c). Previous studies revealed that axially chiral biphenyl derivatives showed three CD bands in the region of 200–300 nm.^{15–19} Mori et al.,¹⁵ who reported one of the studies about chiral biphenyls, demonstrated theoretically and experimentally that the axial chirality was induced onto biphenyls by introducing asymmetric centers at ortho-position of the phenyl–phenyl bond. Furthermore, they also demonstrated that most of the CD signals cancelled out each other between the rotamers because their axial chirality easily switched between *P*- and *M*-conformations via the axial rotation (Figure 7a) due to a small steric hindrance of the chiral substituent, and therefore such chiral biphenyl derivatives exhibited weak CD bands with $\Delta\epsilon$ of $2\text{--}8 \text{ M}^{-1}\text{cm}^{-1}$. From the above results, the weak CD bands of **PPP1** and **PPP2** indicate the existence of the axial chirality on neighboring phenylene rings in the polymer main chain, i.e., intrachain helicity due to the chiral side chains containing asymmetric centers. Induction of the axial chirality is also implied by the fact that **PPP1** and **PPP2** exhibited CD couplets in the wavelength region of 200–260 nm whereas the monomer **6** exhibited a monosignate CD band (Figure 8). According to the g_{abs} values on the order of 10^{-4} (see also Tables 1–4), it should be emphasized that although the intrachain helicity

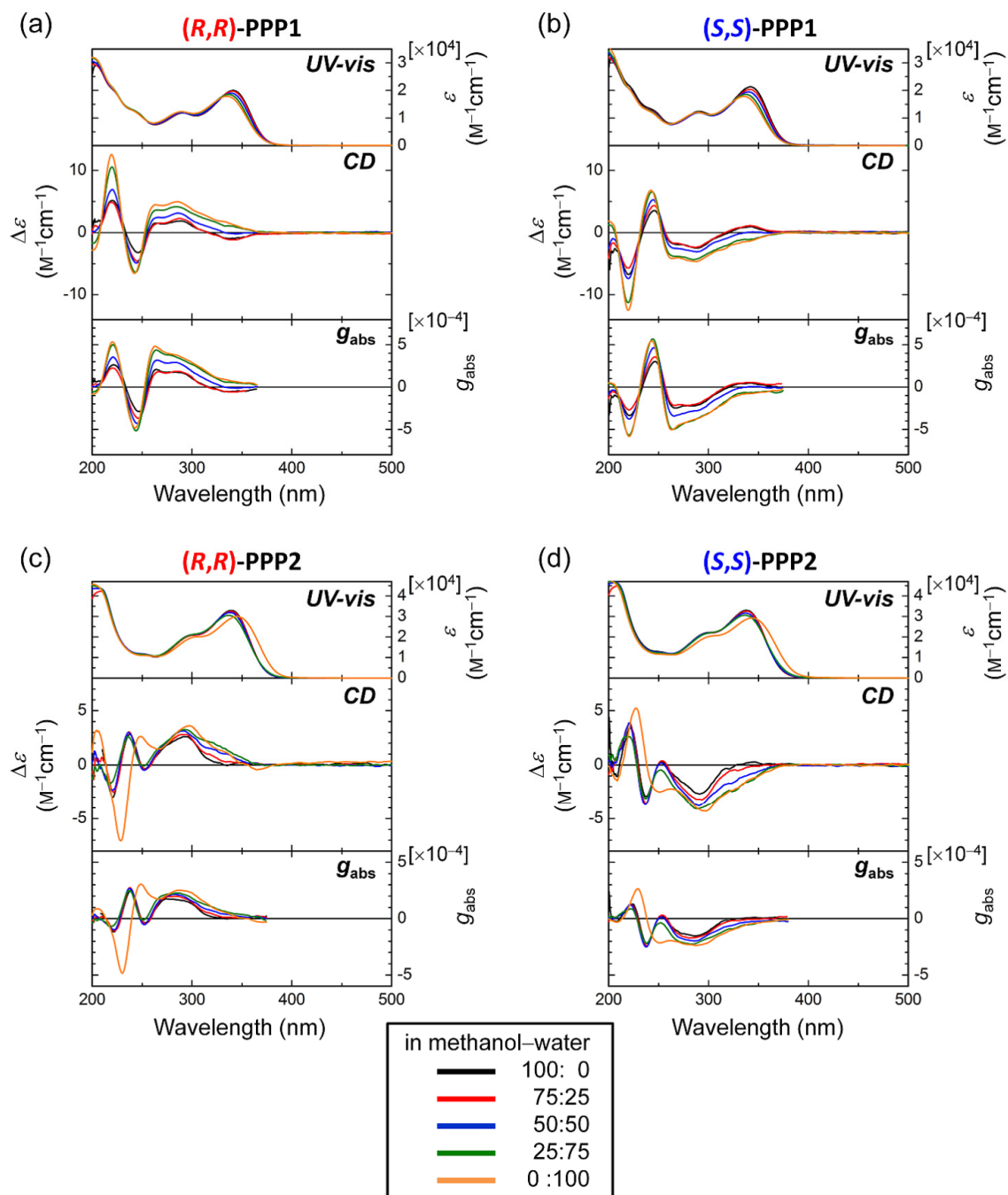


Figure 2. [Solvent dependence] UV-vis absorption spectra (upper), CD spectra (middle), and g_{abs} factors (lower) of (a) (R,R)-PPP1, (b) (S,S)-PPP1, (c) (R,R)-PPP2, and (d) (S,S)-PPP2 in methanol, water, and the mixtures ($c = 5.0 \times 10^{-5}$ M).

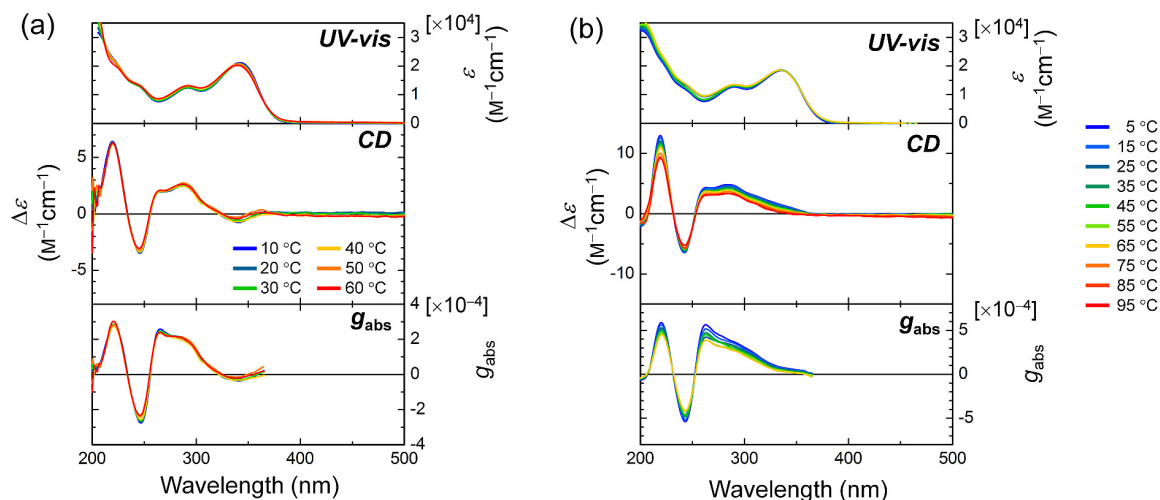


Figure 3. [Temperature dependence] UV–vis absorption spectra (upper), CD spectra (middle), and g_{abs} factors (lower) of (R,R)-PPP1 at various temperature (a) in methanol and (b) in water. The concentrations are 5.0×10^{-5} M.

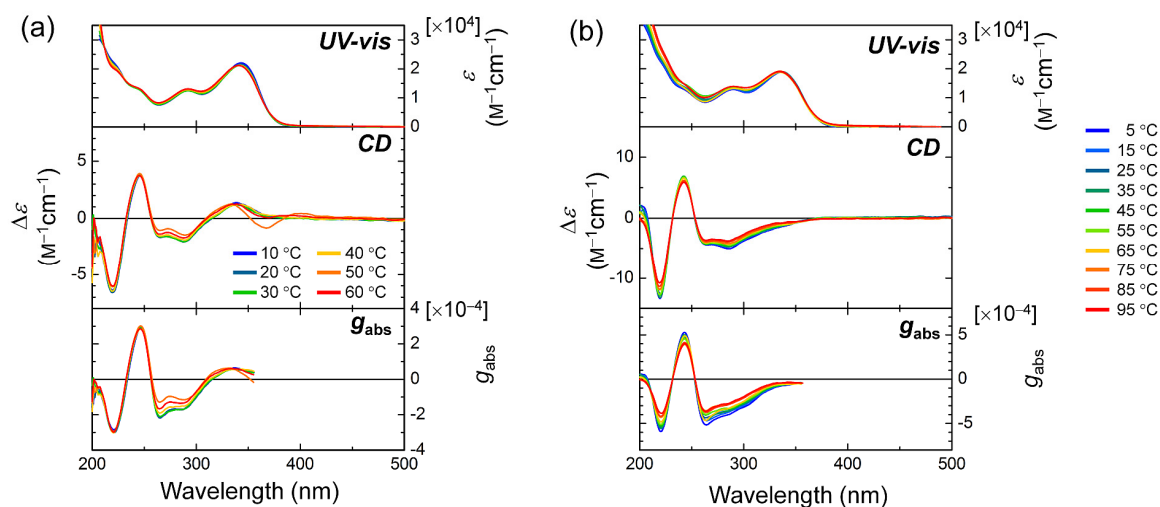


Figure 4. [Temperature dependence] UV–vis absorption spectra (upper), CD spectra (middle), and g_{abs} factors (lower) of (S,S)-PPP1 at various temperature (a) in methanol and (b) in water. The concentrations are 5.0×10^{-5} M.

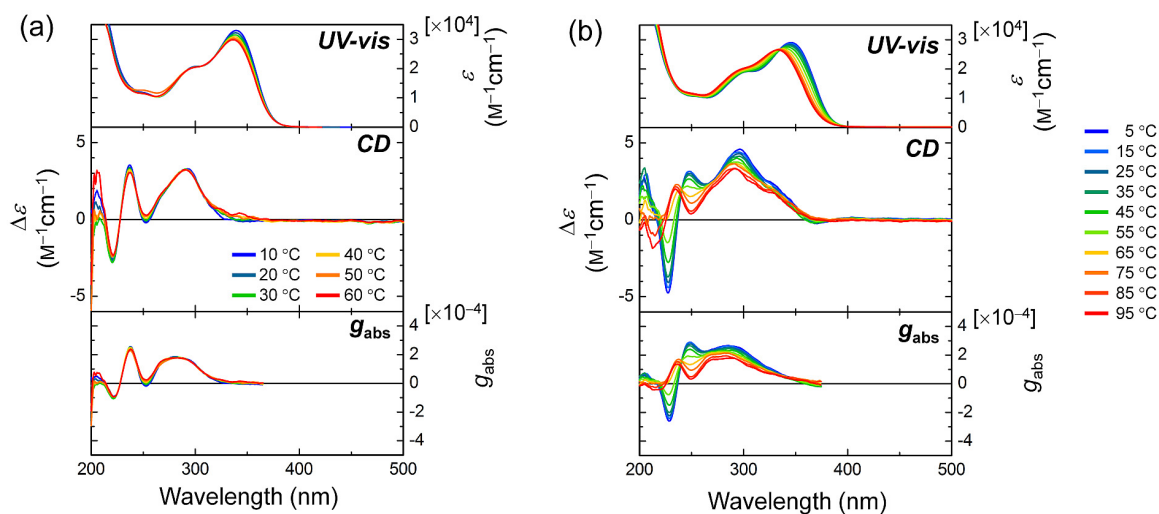


Figure 5. [Temperature dependence] UV-vis absorption spectra (upper), CD spectra (middle), and g_{abs} factors (lower) of (R,R)-PPP2 at various temperature (a) in methanol and (b) in water. The concentrations are 5.0×10^{-5} M.

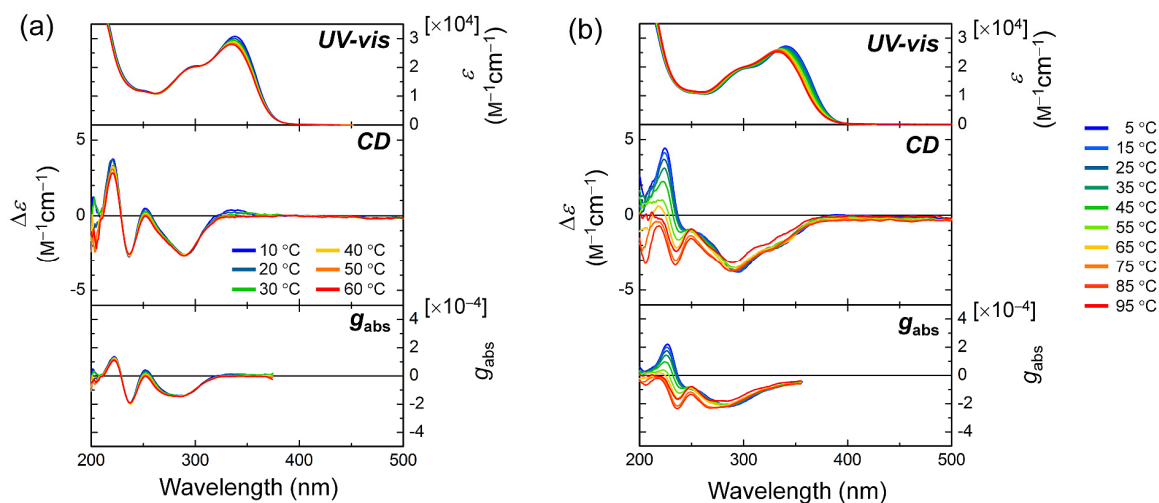


Figure 6. [Temperature dependence] UV-vis absorption spectra (upper), CD spectra (middle), and g_{abs} factors (lower) of (S,S)-PPP2 at various temperature (a) in methanol and (b) in water. The concentrations are 5.0×10^{-5} M.

Table 1. Optical properties of (*R,R*)-**PPP1** in water, methanol, and the mixtures.

Solvent	UV-vis absorption		Circular dichroism			Photo-luminescence		Quantum yield ^a
	$\lambda_{\max}$	ε	$\lambda_{\max}$	$\Delta\varepsilon$	g_{abs}^b	$\text{Em}_{\max}$	Ex	(%)
	(nm)	(M ⁻¹ cm ⁻¹)	(nm)	(M ⁻¹ cm ⁻¹)	($\times 10^{-4}$)	(nm)	(nm)	
methanol	341	2.00×10^4	289	+1.89	+1.74	405	344	32.4
			247	-3.22	-2.90			
			222	+5.19	+2.64			
methanol-water = 75:25	341	2.00×10^4	288	+2.27	+1.86	407	342	36.1
			246	-4.60	-3.69			
			221	+4.89	+2.25			
methanol-water = 50:50	339	1.90×10^4	286	+3.14	+2.89	411	342	32.8
			245	-4.90	-4.28			
			221	+6.92	+3.55			
methanol-water = 25:75	337	1.86×10^4	284	+4.15	+3.59	415	339	24.9
			244	-6.39	-5.17			
			221	+10.6	+5.02			
water	335	1.79×10^4	286	+4.98	+3.75	418	342	10.5
			243	-6.57	-4.84			
			220	+12.6	+5.34			

^a Quantum yield was estimated by using an integral sphere.^b Dissymmetry factor in absorbance^c The concentration of (*R,R*)-**PPP1** is 5.0×10^{-5} M.

Table 2. Optical properties of (*S,S*)-**PPP1** in water, methanol, and the mixtures.

Solvent	UV-vis absorption		Circular dichroism			Photo-luminescence		Quantum yield ^a
	$\lambda_{\max}$	ε	$\lambda_{\max}$	$\Delta\varepsilon$	g_{abs}^b	$\text{Em}_{\max}$	Ex	(%)
	(nm)	(M ⁻¹ cm ⁻¹)	(nm)	(M ⁻¹ cm ⁻¹)	($\times 10^{-4}$)	(nm)	(nm)	
methanol	342	2.13×10^4	288	-2.49	-2.18	405	344	34.2
			246	+3.56	+3.02			
			220	-6.74	-3.35			
methanol-water = 75:25	341	2.04×10^4	287	-2.36	-2.03	407	342	37.4
			246	+4.34	+3.58			
			220	-5.73	-2.70			
methanol-water = 50:50	341	1.95×10^4	288	-3.09	-2.81	410	342	35.7
			245	+5.29	+4.67			
			220	-7.42	-3.78			
methanol-water = 25:75	337	1.86×10^4	286	-4.36	-3.92	416	340	25.9
			244	+6.56	+5.69			
			220	-11.3	-5.70			
water	335	1.78×10^4	288	-4.67	-3.79	417	339	12.2
			243	+6.80	+5.47			
			220	-12.5	-5.84			

^a Quantum yield was estimated by using an integral sphere.

^b Dissymmetry factor in absorbance

^c The concentration of (*S,S*)-**PPP1** is 5.0×10^{-5} M.

Table 3. Optical properties of (*R,R*)-**PPP2** in water, methanol, and the mixtures.

Solvent	UV-vis absorption		Circular dichroism			Photo-luminescence		Quantum yield ^a
	$\lambda_{\max}$	ε	$\lambda_{\max}$	$\Delta\varepsilon$	g_{abs}^b	$\text{Em}_{\max}$	Ex	(%)
	(nm)	(M ⁻¹ cm ⁻¹)	(nm)	(M ⁻¹ cm ⁻¹)	($\times 10^{-4}$)	(nm)	(nm)	
methanol	339	3.29×10^4	292	+2.62	+1.60	408	340	64.3
			238	+2.84	+2.51			
			221	-3.00	-1.17			
methanol-water = 75:25	339	3.25×10^4	290	+2.81	+1.90	409	340	64.6
			237	+3.05	+2.73			
			222	-2.52	-1.09			
methanol-water = 50:50	338	3.19×10^4	290	+3.14	+2.05	413	340	61.4
			237	+2.98	+2.67			
			220	-2.33	-0.92			
methanol-water = 25:75	337	3.06×10^4	292	+3.26	+2.16	419	340	44.2
			236	+2.60	+2.46			
			216	-1.83	-0.64			
water	345	3.00×10^4	298	+3.60	+2.37	419	344	31.5
			249	+2.64	+3.06			
			229	-7.05	-4.73			

^a Quantum yield was estimated by using an integral sphere.^b Dissymmetry factor in absorbance^c The concentration of (*R,R*)-**PPP2** is 5.0×10^{-5} M.

Table 4. Optical properties of (*S,S*)-**PPP2** in water, methanol, and the mixtures.

Solvent	UV-vis absorption		Circular dichroism			Photo-luminescence		Quantum yield ^a
	$\lambda_{\max}$	ε	$\lambda_{\max}$	$\Delta\varepsilon$	g_{abs}^b	$\text{Em}_{\max}$	Ex	(%)
	(nm)	(M ⁻¹ cm ⁻¹)	(nm)	(M ⁻¹ cm ⁻¹)	($\times 10^{-4}$)	(nm)	(nm)	
methanol	338	3.30×10^4	291	-2.68	-1.49	408	340	53.0
			238	-2.93	-2.20			
			222	+3.45	+1.25			
methanol-water = 75:25	338	3.26×10^4	293	-3.21	-1.56	410	341	55.2
			238	-3.54	-2.41			
			221	+3.87	+1.23			
methanol-water = 50:50	337	3.17×10^4	291	-3.78	-1.90	414	339	51.0
			237	-3.68	-2.49			
			221	+3.88	+1.22			
methanol-water = 25:75	336	3.06×10^4	288	-4.08	-2.19	419	340	33.6
			237	-3.10	-2.14			
			220	+2.62	+0.81			
water	343	2.93×10^4	298	-4.30	-2.21	419	346	16.9
			251	-2.50	-2.16			
			227	+5.23	+2.49			

^a Quantum yield was estimated by using an integral sphere.

^b Dissymmetry factor in absorbance

^c The concentration of (*S,S*)-**PPP2** is 5.0×10^{-5} M.

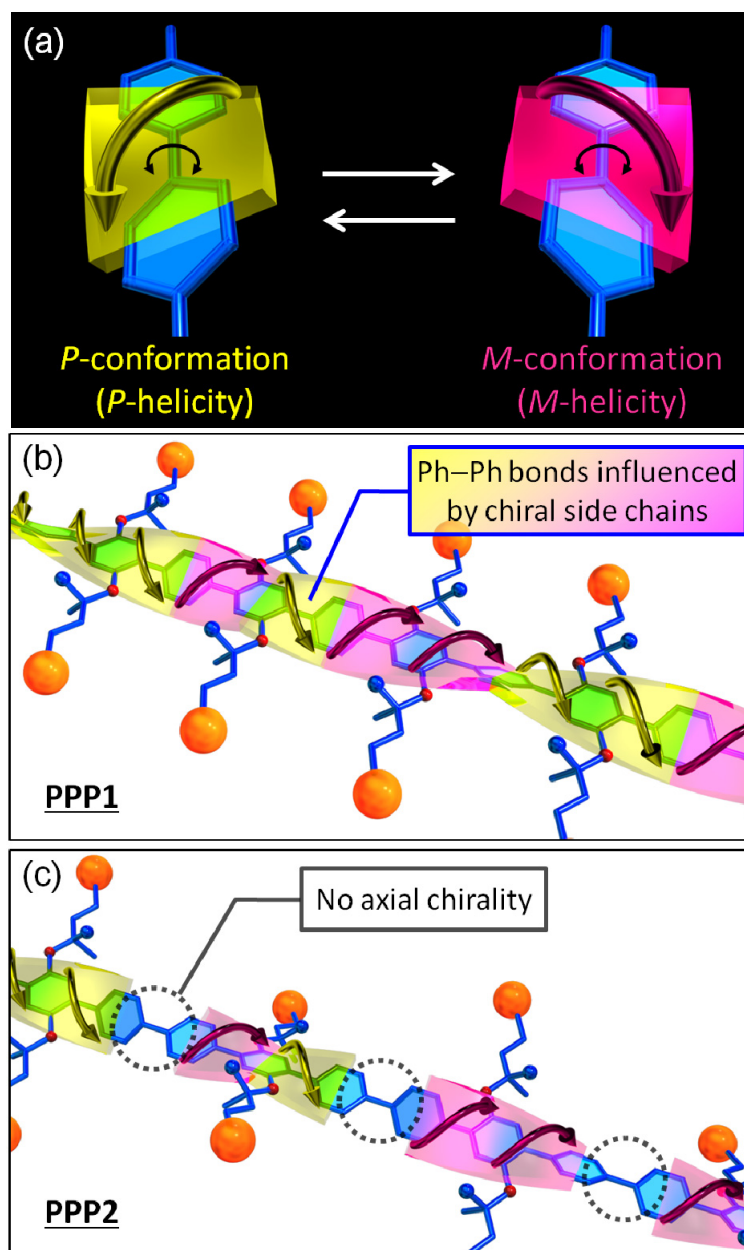


Figure 7. (a) Switching behavior of axial chirality on a biphenyl between *P*- and *M*-conformations through axial rotation. Schematic models of the intrachain helicity on (b) **PPP1** and (c) **PPP2** main chains. The chiral side chains containing the asymmetric center are located on the ortho-positions of all the phenylene–phenylene (Ph–Ph) bonds of **PPP1** main chain. Meanwhile, **PPP2** main chain has racemic bonds between non-substituted phenylenes (dot circles) where no axial chirality is induced due to the absence of chiral side chains.

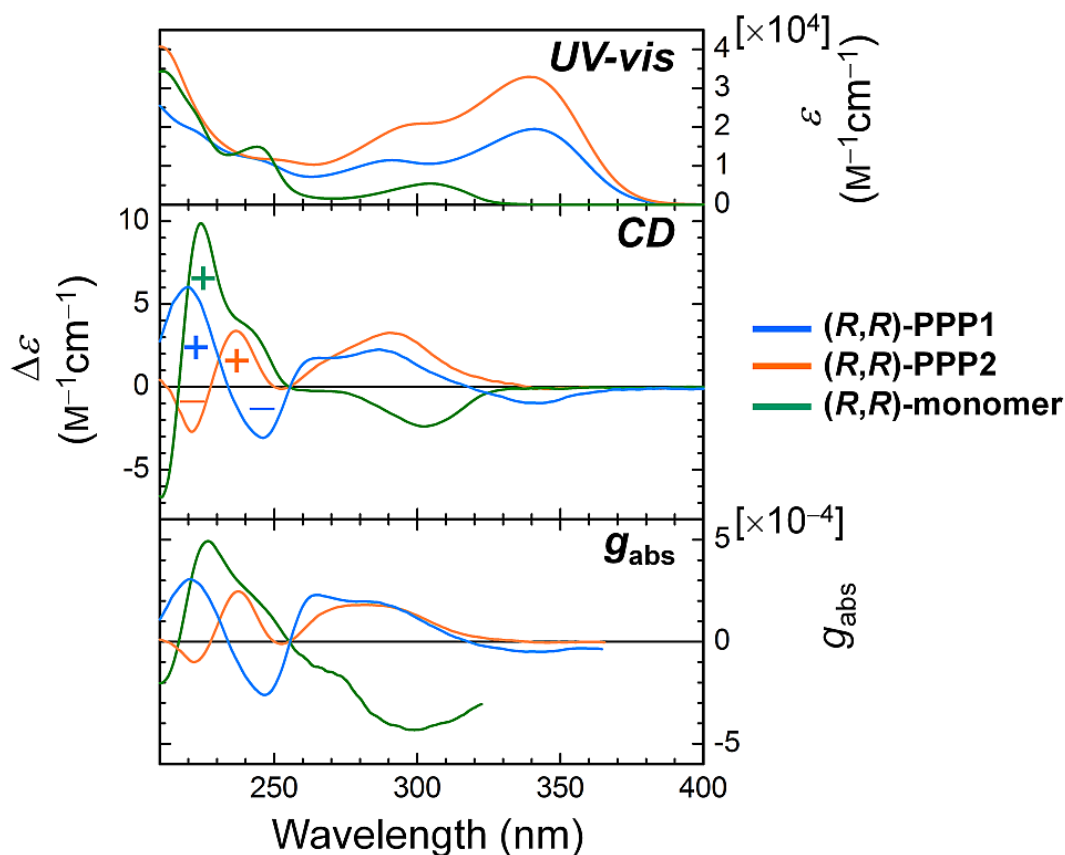


Figure 8. UV-vis absorption spectra (upper), CD spectra (middle), and g_{abs} factors (lower) of (R,R)-PPP1, (R,R)-PPP2, and (R,R)-monomer [(R,R)-6] in methanol [$c = 5.0 \times 10^{-5}$ M for (R,R)-PPP1, 5.1×10^{-5} M for (R,R)-PPP2, and 3.9×10^{-5} M for (R,R)-6].

exists in the PPP main chains, there is only a slight preference for one twisted conformation over the opposite. The small g_{abs} values agrees with the remark that the asymmetric-center-induced axial chirality on biphenyls easily switches between *P*- and *M*-conformations. Furthermore, signs of the CD couplets indicates the predominant helical sense of the intrachain helicity by using the exciton chirality theory.²⁰ For example, in the wavelength of 200–260 nm (R,R)-PPP1 showed a negative bisignate Cotton effect, i.e., a CD couplet consisting of negative and positive Cotton effects at longer and shorter wavelengths, respectively. This means that the neighboring

phenylenes in (*R,R*)-**PPP1** main chain prefer *M*-conformation, and therefore that the polymer has the intrachain helicity where left-handedness is predominant.

On the other hand, **PPP1** showed a weak CD band at around 340 nm corresponding to the main chain absorption, whereas **PPP2** did not. In **PPP1**, the chiral side chains are located on the ortho-positions of all phenylene–phenylene (Ph–Ph) bonds in the main chain, and hence the main chain absorption also showed a CD signal due to the slightly predominant twisted conformation on the π -conjugated backbone (Figure 7b). However **PPP2** has a racemic bond between non-substituted phenylenes where no axial chirality is induced due to the absence of nearby chiral side chains. As a result, the axial chirality on the biphenylene moieties was unable to extend over the main chain (Figure 7c). Except for **PPP2** in water, where the polymer tends to aggregate, the Cotton effects of **PPP1** and **PPP2** remained unchanged in both shape and intensity up to high temperatures such as 60–95 °C, and they were also independent of the mixing ratio of the solvent (Figures 2–6). These results indicate that the Cotton effect observed is not due to the chiral aggregation, but due to the intrachain helicity of the conjugated polymer backbone in an isolated chain. It can be argued that the present results first demonstrate the intrachain helicity in the π -conjugated backbone of PPP derivatives due to the chiral side chains containing asymmetric centers. The chain conformations of **PPP1** and **PPP2** depend on the chiral branched side chains.

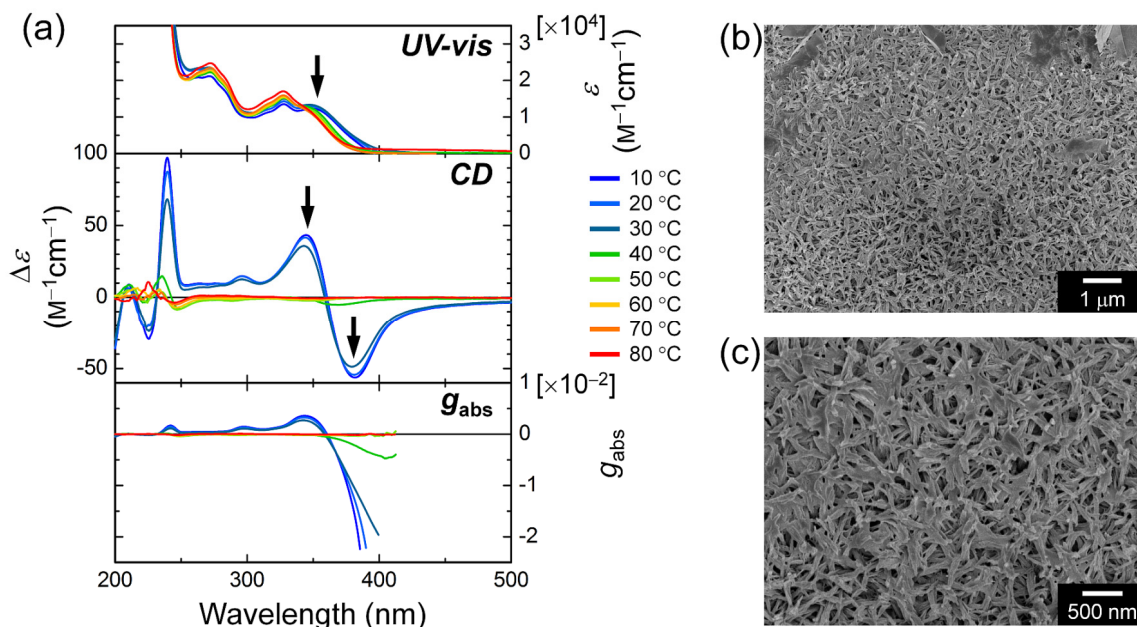


Figure 9. (a) UV-vis absorption spectra, CD spectra, and g_{abs} factors of (*R,R*)-PPP1-SNap (1:2 mol/mol) in water at various temperatures. The concentration of (*R,R*)-PPP1 is 2.0×10^{-5} M. (b, c) Scanning electron microscopy (SEM) images of (*R,R*)-PPP1-SNap (1:2 mol/mol) cast on a sample stage.

Chiral assembly of PPP1-SNap. The author investigated the effects on **PPP1** and **PPP2** by adding various anionic compounds (see Scheme 1). The synthetic routes for the anionic compounds are shown in Scheme 3. The author found that the polymers form a chiral assembly with an anionic sulfonate-substituted naphthalene derivative (abbreviated as **SNap**). Figure 9a shows UV-vis absorption spectra, CD spectra, and g_{abs} factor of a mixture of (*R,R*)-PPP1 and **SNap** [abbreviated as (*R,R*)-PPP1-SNap] (1:2 mol/mol) in water. In the UV-vis absorption spectrum, (*R,R*)-PPP1-SNap showed a new absorption band at a longer wavelength ($\lambda = 349$ nm) than the inherent band of **PPP1**, suggesting the formation of a polymer assembly with π -stacked structure. Concurrently, in the CD spectrum, a new *negative* bisignate Cotton effect was observed in the region of 300–400 nm corresponding to the polymer main chain. This effect may be due to the exciton coupling between the π -conjugated main chains of the polymers. Namely, **PPP1** forms a chiral assembly with interchain helically

π -stacked structure with the aid of **SNap**. According to the exciton chirality theory,²⁰ the helical sense in the chiral assembly is left-handed (*M*-helicity). The new absorption band at 349 nm and the corresponding CD band decreased in intensity with increasing temperature and finally disappeared (Figure 9a). This behavior indicates that these new bands are attributable to the polymer assembly formed with the aid of **SNap**. The bisignate Cotton effect in (*S,S*)-**PPP1-SNap** showed an opposite sign to the effect in (*R,R*)-**PPP1-SNap**, indicating that the helicity of the polymer assembly depends on the chirality of the polymer side chains. The g_{abs} value was $+3.59 \times 10^{-3}$ (at 344 nm) for (*R,R*)-**PPP1-SNap** (1:2 mol/mol), which is about 10 times larger than the value for the isolated chain of (*R,R*)-**PPP1** (see Table 1). This result implies that the chiral amplification occurred upon the formation of the polymer assembly. The polymer assembly was also confirmed using scanning electron microscopy (SEM). As seen in Figures 9b and c, SEM images of **PPP1-SNap** show entangled morphologies of polymer bundles with several hundreds nanometers in length.

It should be emphasized that (*R,R*)-**PPP1** showed two kinds of bisignate Cotton effects around 230 and 360 nm in CD spectra, corresponding to the *intrachain* and *interchain* helicity, respectively. The CD bands around 230 nm increased in intensity and became opposite in sign upon the formation of the polymer assembly. Namely, (*R,R*)-**PPP1** showed a negative bisignate Cotton effect in an isolated chain state, and a positive bisignate one in an aggregated state. This indicates that (*R,R*)-**PPP1** in an aggregated state prefers to form right-handed intrachain helicity. The increase in intensity of CD bands around 230 nm may be due to the suppression of axial rotation around the Ph–Ph bond upon the formation of the assembly, leading to an enhancement of the intrachain helicity. Interestingly, the recent work demonstrated that the *interchain* helically π -stacked structure in PPP derivative is favorably formed when the *intra*- and *interchain* helical senses are opposite to each other.²¹ This remark well rationalizes the present experimental result that (*R,R*)-**PPP1** with *right*-handed *intrachain* helicity formed the *interchain* helically π -stacked structure with *left*-handedness (Figure 10). It is implied that the helical sense of the *intrachain* helicity changes appropriately to the *interchain* helicity in the chiral assembly because the axial chirality on the aromatic main chain is easily switchable between *P*- and

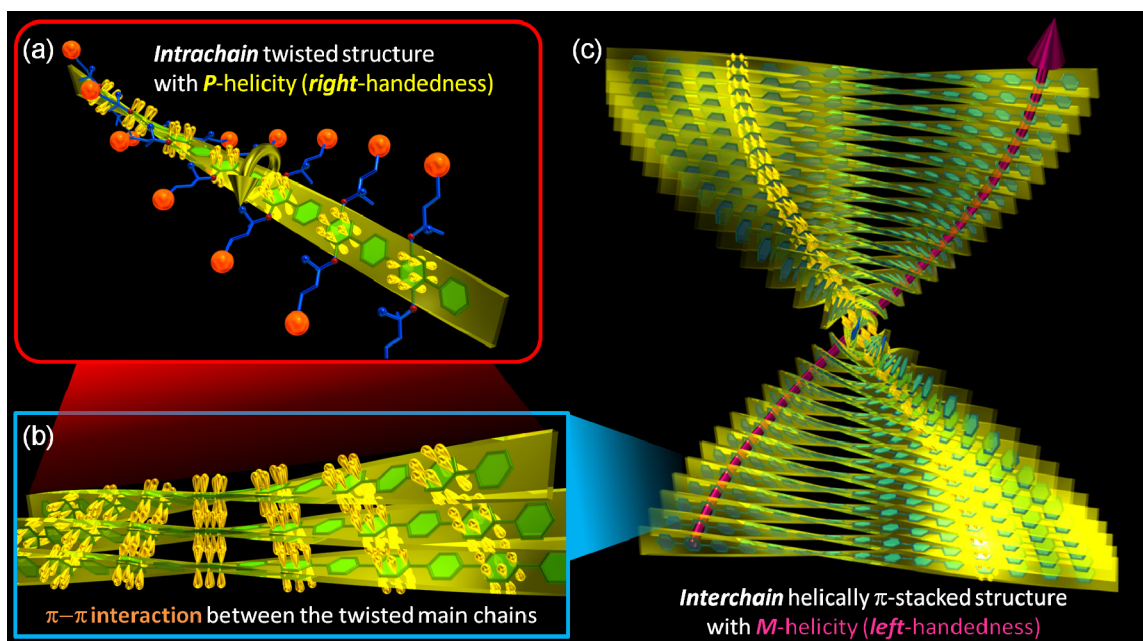


Figure 10. Schematic models of the hierarchical structure of (R,R)-PPP1 main chains in the chiral assembly. The yellow transparent belts represent the twisted π -conjugated backbones of the polymer. (a) Right-handed intrachain twisted structure of the (R,R)-PPP1 main chain. (b) π -Stacked structure among three twisted main chains of (R,R)-PPP1. (c) Left-handed interchain helically π -stacked structure consisting of twisted (R,R)-PPP1 main chains.

M-conformations through the axial rotation around the Ph–Ph bond, which results in the inversion of the *intrachain* helical sense. As a consequence, it is found that the *intra*- and *interchain* helicity coexist in the assembly of (R,R)-PPP1 with S_{Nap} and that the polymer assembly has the hierarchical structure as shown in Figure 10. Note that the CD band around 230 nm is attributed to (R,R)-PPP1, but not S_{Nap}. In UV–vis spectra, the absorption band of S_{Nap} at 270 nm increased in intensity with increasing S_{Nap} amount (see Figure 11), but no notable change was observed in CD spectra. This result indicates that the CD band around 230 nm is not due to the induced CD of S_{Nap}, but to the inherent CD of (R,R)-PPP1.

The author also found that both electrostatic and π - π interactions between the cationic PPP derivative and the anionic additive are indispensable for the formation of

a polymer assembly with helically π -stacked structure. Figure 12 shows UV-vis absorption and CD spectra of the mixtures of (*R,R*)-PPP1 with aliphatic additives (**A1** and **A2**) or aromatic ones (**A3** and **A4**) in aqueous solution. Although the aliphatic additives gave no remarkable change in the UV-vis absorption and CD spectra of the polymer (Figures 12a and b), the aromatic additives caused a red-shift of the absorption band corresponding to the conjugated main chain and produced a new CD band in the wavelength region (Figures 12c and d). The changes in the UV-vis absorption and CD spectra result from the formation of a polymer assembly with interchain helicity. Thus, it is demonstrated that not only the anionic moieties but also the aromatic rings are required for the anionic additive compound. These results are supported by the previous report.³

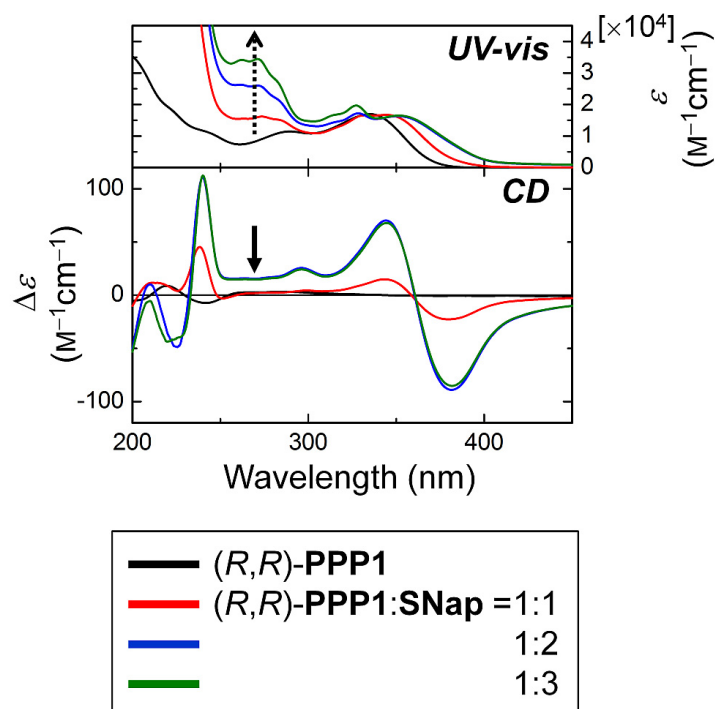


Figure 11. UV-vis absorption (upper) and CD spectra (lower) of the mixtures of (*R,R*)-PPP1 and SNap in water. The concentration of (*R,R*)-PPP1 in the mixtures is kept constant at 2.0×10^{-5} M. In UV-vis spectra, the absorption band of SNap at 270 nm increased in intensity with increasing SNap (expressed by dashed arrow), but no notable change was observed in CD spectra (solid arrow).

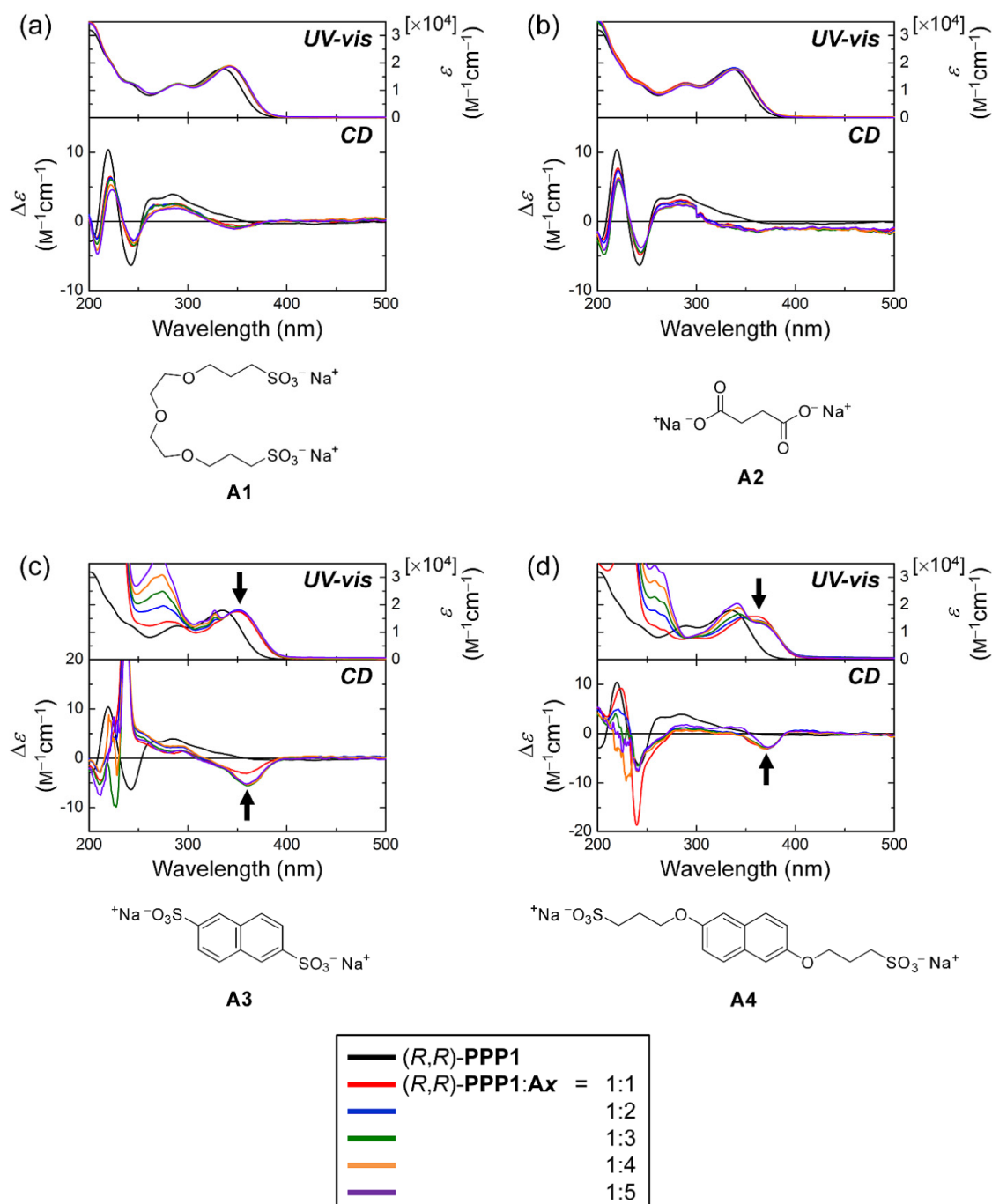


Figure 12. UV–vis absorption (upper) and CD spectra (lower) of the mixtures of (*R,R*)-**PPP1** and various anionic additives (**A1–A4**) in water. The concentration of (*R,R*)-**PPP1** in the mixtures is kept constant at 2.0×10^{-5} M.

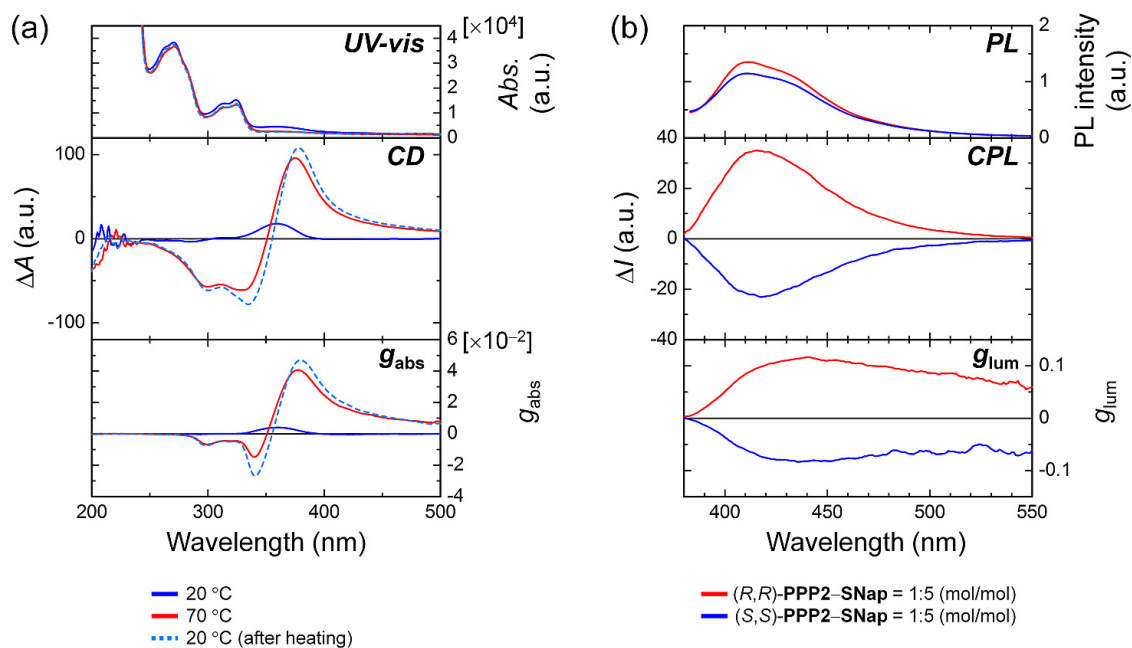


Figure 13. (a) UV-vis absorption spectra, CD spectra, and g_{abs} factors of (R,R)-PPP2-SNap (1:5 mol/mol) in water before and after annealing treatment. When adding **SNap** to the aqueous solution of **PPP2**, a part of the polymer was precipitated (see Figure 14). Hence absorbance (*Abs.*) and ΔA are used in the Y-axis labels instead of ϵ and $\Delta\epsilon$ to exclude the factor of concentration. (b) PL spectra, CPL spectra, and g_{lum} factors of annealed solutions of (R,R)-PPP2-SNap (1:5 mol/mol) and (S,S)-PPP2-SNap (1:5 mol/mol) in water. The initial concentration of (R,R)-PPP2 is 2.0×10^{-5} M.

Chiral assembly of PPP2-SNap. Figure 13a shows the UV-vis absorption spectra, CD spectra, and g_{abs} factors of a mixture of (R,R)-PPP2 and **SNap** [abbreviated as (R,R)-PPP2-SNap] (1:5 mol/mol) in water. As mentioned above, **PPP2** partially aggregates in water, and therefore the addition of **SNap** leads to enhancement of the aggregation but not the interchain helicity (Figure 13a, blue solid line). However, after annealing the mixture at 70 °C, the *positive* bisignate Cotton effect was observed in the wavelength region corresponding to the absorption of the polymer main chain (Figure 13a, red solid line). This result indicates that **PPP2** forms an assembly bearing interchain helically π -stacked structure upon the thermal heating.

Interestingly, the induced CD band remained unchanged even after cooling from 70 °C to 20 °C (Figure 13a, light blue dashed line). This is because **PPP2**, unlike **PPP1**, partially maintains the assembly at high temperature (70 °C) owing to its highly π -stacked structure, and the thermal arrangement of the polymer chains occurs during the annealing process. It has been reported that aromatic conjugated polymers strongly assemble when the solid film is annealed, and consequently the interchain helical structure is reinforced.^{14,22} However, to our knowledge, such an arrangement of conjugated polymers occurring in solution or in a dispersion system has not been reported so far. The (*R,R*)-**PPP2** assembly exhibited an induced CD band whose sign is opposite to that of the (*R,R*)-**PPP1** assembly. According to the exciton chirality theory,²⁰ the interchain helicity of the (*R,R*)-**PPP2** assembly has a right-handed helical sense; that is, *P*-helicity. It can be argued that the helical sense of the PPP-based assembly depends on not only the chirality of the side chains but also on the number of non-substituted phenylenes in the repeating unit. The g_{abs} values after annealing were -2.68×10^{-2} (at 341 nm) and $+4.70 \times 10^{-2}$ (at 380 nm) for (*R,R*)-**PPP2-SNap** (1:5 mol/mol), indicating that these g_{abs} values are approximately 100 times larger than those of the non-assembled (*R,R*)-**PPP2** (see Table 3). It is evident that the helicity of the PPP derivatives is enhanced to give an amplified g factor through the formation of the assembly with **SNap**. Therein, **SNap** plays a role in bringing the polymers close to each other by means of both electrostatic and π - π interactions. The degree of amplification for g_{abs} factor in (*R,R*)-**PPP2-SNap** is 10 times larger than in (*R,R*)-**PPP1-SNap**. This implies that the terphenylene repeating unit of **PPP2** is more favorable for π - π interaction between PPP main chains than the biphenylene repeating unit of **PPP1**, resulting in a stronger helically π -stacked structure in the assembly.

On the other hand, when tetrahydrofuran (THF) was added instead of **SNap** to an aqueous solution of the polymer, the assembly was also formed but only showed less reproducible CD band. This result implies that **SNap** is more useful for the generation of polymer assembly with highly helical π -stacked structure.

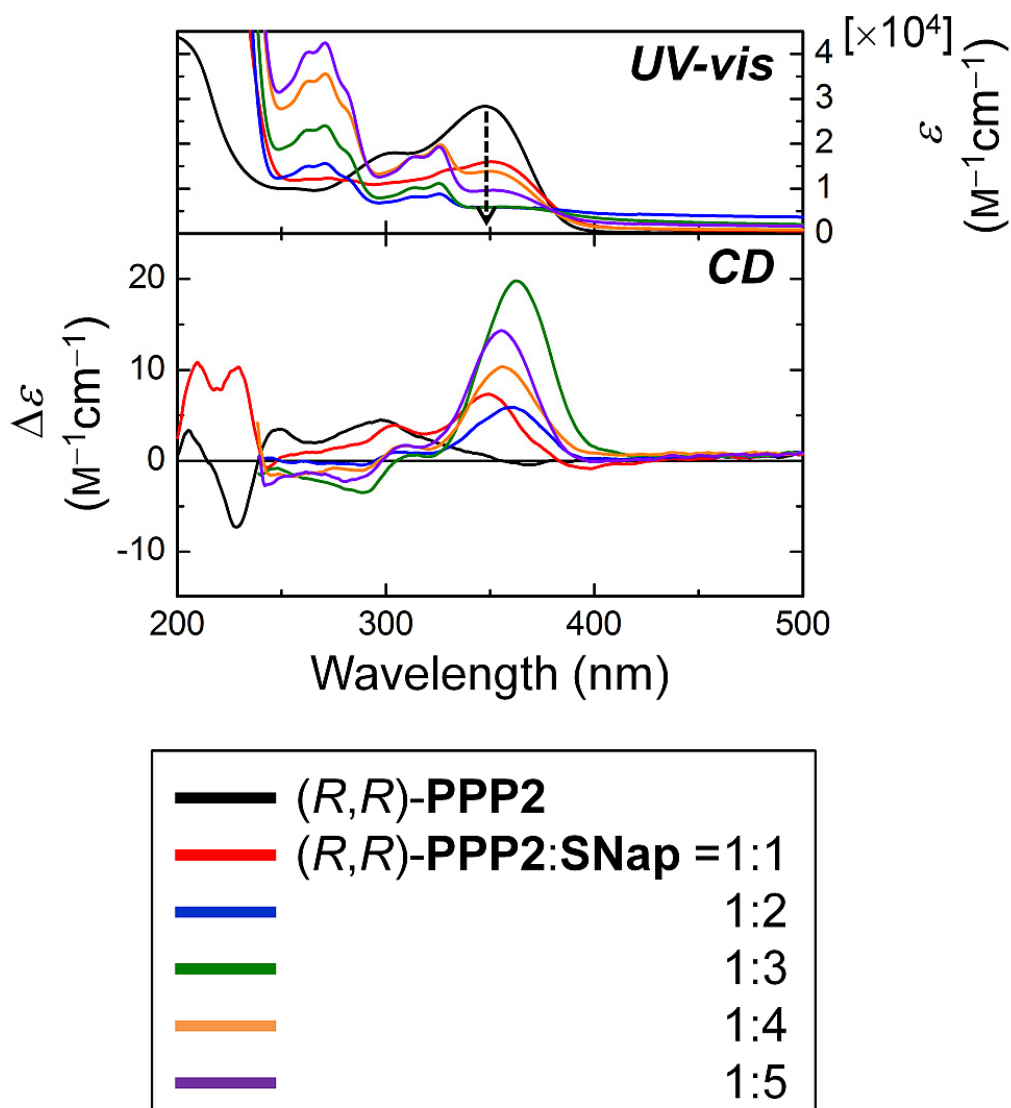


Figure 14. UV–vis absorption and CD spectra of the mixtures of *(R,R)*-**PPP2** and **SNap** in water. Absorbance of **PPP2** irregularly decreases in intensity with adding **SNap** (expressed by dashed arrow), which results from the precipitate of the polymer. The initial concentration of *(R,R)*-**PPP2** is kept constant at 2.0×10^{-5} M.

Circularly polarized luminescence of chiral assembly. **PPP2** exhibited CPL when mixed with **SNap** (1:5 mol/mol in **PPP2-SNap**) and followed by annealing (Figure 13b). (*R,R*)- and (*S,S*)-**PPP2-SNap** showed CPL bands with mirror images, indicating that the sign of the Cotton effect in CPL depends on the interchain helicity of the chiral assembly. (*R,R*)-**PPP2-SNap** exhibited a *positive* monosignate Cotton effect ($\Delta I = I_L - I_R > 0$) in the CPL spectrum, indicating the emission of *left*-handed circularly polarized light ($I_L > I_R$) with *P*-helicity. Note that I_L and I_R are luminescent intensity with left- and right-handed circular polarization, respectively. This result is consistent with the fact that the chiral assembly of (*R,R*)-**PPP2-SNap** has helically π -stacked structure with *P*-helicity, which is confirmed by the *positive* bisignate Cotton effect observed in the CD spectrum. Meanwhile, (*S,S*)-**PPP2-SNap** exhibited a *negative* monosignate Cotton effect in the CPL spectrum, indicating the emission of *right*-handed circularly polarized light with *M*-helicity. (*S,S*)-**PPP2-SNap** also showed a *negative* bisignate Cotton effect in the CD spectrum, and hence, the assembly of (*S,S*)-**PPP2-SNap** has helically π -stacked structure with *M*-helicity.³ The dissymmetry factors in luminescence (g_{lum}) are $+1.1 \times 10^{-1}$ (at 424 nm) for (*R,R*)-**PPP2-SNap** (1:5 mol/mol) and -7.9×10^{-2} (at 423 nm) for (*S,S*)-**PPP2-SNap** (1:5 mol/mol). It is worthwhile to note that the g_{lum} factor of 10^{-1} in conjugated polymers was hitherto achieved only when thermotropic or lyotropic LC conjugated polymers were helically self-organized in the LC phase.^{5, 12-14} The large g_{lum} value of 10^{-1} in **PPP2-SNap** could be attributed to the helical arrangement of the polymer main chains in solution during the annealing. Hence, the annealing treatment is effective for arranging the conjugated polymers into higher-ordered structure even in a dispersion system such as an aqueous solution, as well as in solid films. In contrast, **PPP1-SNap** showed no CPL. This is because **PPP1** may have been unfavorably arranged in the polymer assembly due to rapid aggregation. In addition, the assembly easily dissociates upon thermal heating without forming a higher-ordered structure, which is in contrast to the case of **PPP2**.

Conclusion

The author presented a novel approach for preparing interchain helically π -stacked assemblies of ionic conjugated polymers with high dissymmetry factors of 10^{-2} – 10^{-1} by utilizing both intermolecular electrostatic and π – π interactions. The author designed and synthesized cationic chiral PPP derivatives, **PPP1** and **PPP2**, with ammonium moieties linked with asymmetric centers in their side chains. In CD spectra, both **PPP1** and **PPP2** showed a bisignate Cotton effect corresponding to the exciton coupling between neighboring phenylene rings in the conjugated backbone, indicating the presence of intrachain helicity. This case is the first in which aromatic conjugated polymers with a linear main chain, such as PPP derivatives, are verified to exhibit intrachain helicity in solution. Upon the addition of an anionic aromatic additive, **SNap**, into the aqueous solution of **PPP1** or **PPP2**, chiral assemblies with interchain helically π -stacked structure were formed through electrostatic and π – π interactions between the cationic polymer and the anionic additive. Although the chiral assembly of **PPP1** was dissociated upon thermal heating, the helically π -stacked structure of the **PPP2** assembly was thermally reinforced. The annealed assembly of **PPP2**–**SNap** showed a large g_{lum} value of $|10^{-1}|$ even in a dispersion system such as aqueous solution, which is the same magnitude as the values achieved in LC conjugated polymers. The present approach based on the cooperative intermolecular electrostatic and π – π interactions is versatile and applicable for preparations of other types of polymer assemblies with chiroptical functions.

Experimental Section

1. Measurements. NMR spectra were obtained with JEOL JNM-AL400 or JNM-EX400. Chemical shifts are represented in parts per million downfield from tetramethylsilane (TMS) or (trimethylsilyl) propionic-2,2,3,3-*d*4 acid sodium salt (TSP-*d*4) as internal standards. Elemental analyses were performed by Yanako CHN Corders (MT-3, MT-5 and MT-6), JSL JM-10, Mitsubishi chemical analytech AQF-100, and Dionex ICS-1500. High-resolution mass spectra (HRMS) were obtained by using JEOL JMS-HX110A (FAB), JEOL JMS-MS700 (EI), Thermo Fisher Scientific EXACTIVE (ESI), and Thermo Fisher Scientific MALDI DUO orbitrapXL (MALDI).

Size exclusion chromatography (SEC) results were obtained with a system consisting of a TOSOH HLC-8320GPC instrument and TOSOH TSKgel G6000+3000PW_{XL}-CP columns. A mixture of 0.2 M NaNO₃ aq., 0.2 M CH₃COOH aq., and methanol (30 wt.%) was used as an eluent and the flow rate was 1.0 mL/min. Static light scattering (SLS) was performed with an Otsuka electronics DLS-8000 super-dynamic light scattering spectrophotometer.

Ultraviolet–visible (UV–vis) absorption spectra were measured with JASCO V-570 UV/VIS/NIR spectrophotometer. Photoluminescence (PL) spectra were measured with JASCO FP-750 and FP-6500 spectrofluorometers. Circular dichroism (CD) spectra were measured with JASCO J-820 spectropolarimeter. Circularly polarized luminescence (CPL) spectra were measured with JASCO CPL-200S spectrometer. All optical measurements were performed using a quartz cell. Optical purities of chiral compounds were evaluated with the specific rotation measured by JASCO P-2300 polarimeter.

2. Materials. All the chemicals were purchased from Aldrich Chemical Co. Ltd., Tokyo Kasei Co. Ltd., and Wako Co. Ltd. Solvents were dried and distilled before use. Disodium succinate (**A2**) was used without further purification. 2,6-Naphthalene- disulfonic acid disodium salt (**A3**) was recrystallized from water–EtOH before use.

3. Synthesis. All syntheses were carried out under argon atmosphere. All synthetic routes are shown in Schemes 2 and 3.

1,4-Diiodo-2,5-dimethoxybenzene (1). To a stirred solution of 1,4-dimethoxybenzene (30.5 g, 221 mmol) in acetic acid (600 mL), water (22.5 mL), and sulfuric acid (98 %, 7.5 mL) was added iodine (59.1 g, 233 mmol) and potassium iodate (23.6 g, 110 mmol), and then the mixture was refluxed for 6 h. After cooled to 0 °C, water (300 mL) was added to the reaction mixture. The insoluble solid was collected by filtration and the residue was refined by recrystallization (chloroform/ethanol) to obtain **1** as a white solid (62.9 g, 73.1 %): ¹H NMR (400 MHz, CDCl₃, TMS): δ = 3.83 (s, 6H, OCH₃), 7.20 ppm (s, 2H, Ar-*H*); ¹³C NMR (100 MHz, CDCl₃, TMS): δ = 57.2, 85.5, 121.6, 153.4 ppm; HRMS (EI, *m/z*): [M⁺] calcd for C₈H₈I₂O₂: 389.8614; Found: 389.8617; Anal calcd for C₈H₈I₂O₂: C 24.64, H 2.07, I 65.09; Found: C 24.63, H, 2.11, I 65.23.

2,5-Diiodohydroquinone (2). To a stirred solution of **1** (17.7 g, 45.4 mmol) in CH₂Cl₂ (50 mL) was added dropwise a solution of boron tribromide (25.0 g, 99.8 mmol) in CH₂Cl₂ (40 mL), and then the mixture was refluxed at 40 °C for 24 h. After cooled to RT, the reaction mixture was poured into ice-water (800 mL) and the precipitate was collected by filtration to obtain **2** as a white powder (16.0 g, 97.4 %): ¹H NMR (400 MHz, DMSO-*d*₆, TMS): δ = 7.15 (s, 2H, Ar-*H*), 9.80 ppm (s, 2H, OH); ¹³C NMR (100 MHz, DMSO-*d*₆, TMS): δ = 84.2, 123.5, 150.3 ppm; HRMS (EI, *m/z*): [M⁺] calcd for C₆H₄I₂O₂: 361.8301; Found: 361.8298; Anal calcd for C₆H₄I₂O₂: C 19.91, H 1.11, I 70.13; Found: C 19.79, H 1.23, I 70.05.

(*R*)-3-Hydroxybutyl tosylate [(*R*)-3]. The mixed solution of *para*-toluenesulfonyl chloride (11.7 g, 61.4 mmol) and (*R*)-(-)-1,3-butanediol (5.27 g, 58.4 mmol) in pyridine (40 mL) was stirred at 0 °C for 3 h. After adding water to the reaction mixture, the product was extracted with Et₂O (40 mL × 4), washed with saturated aqueous solution of copper (II) sulfate (100 mL × 6), water, and brine, dried by Na₂SO₄, and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, hexane/ethyl acetate = 1/1) to obtain (*R*)-**3** as a colorless liquid (8.22 g, 57.6 %): ¹H NMR (400 MHz, CDCl₃, TMS): δ = 1.19 (d, 3H, *J* = 5.4 Hz, CHCH₃), 1.69–1.84 (m, 3H, CHCH₂, OH), 2.45 (s, 3H, Ar-CH₃), 3.94 (m,

1H, CHCH₃), 4.17 (dq, 2H, J = 47.2 Hz, 5.4 Hz, TsOCH₂), 7.35 (d, 2H, J = 8.4 Hz, Ar-H), 7.80 ppm (d, 2H, J = 8.4 Hz, Ar-H); ¹³C NMR (100 MHz, CDCl₃, TMS): δ = 21.7, 23.6, 37.9, 64.1, 67.8, 127.9, 129.9, 133.0, 144.9 ppm; HRMS (EI, m/z): [M⁺] calcd for C₁₁H₁₆O₄S: 244.0769; Found: 244.0766; Anal calcd for C₁₁H₁₆O₄S: C 54.08, H 6.60, S 13.12; Found: C 54.17, H 6.62, S 13.21.

(S)-3-Hydroxybutyl tosylate [(S)-3] The same procedure with **(R)-3** by using (S)-(+)-1,3-butanediol (5.37 g, 59.6 mmol), *p*-toluenesulfonyl chloride (11.73 g, 61.5 mmol), and pyridine (40 mL) (5.96 g, 41.0 %): ¹H NMR (400 MHz, CDCl₃, TMS): δ = 1.19 (d, 3H, J = 5.4 Hz, CHCH₃), 1.67–1.83 (m, 3H, CHCH₂, OH), 2.45 (s, 3H, Ar-CH₃), 3.94 (m, 1H, CHCH₃), 4.17 (dq, 2H, J = 47.2 Hz, 5.4 Hz, TsOCH₂), 7.35 (d, 2H, J = 8.4 Hz, Ar-H), 7.80 ppm (d, 2H, J = 8.4 Hz, Ar-H); ¹³C NMR (100 MHz, CDCl₃, TMS): δ = 21.7, 23.6, 37.9, 64.1, 67.9, 127.9, 129.9, 132.9, 144.9 ppm; HRMS (FAB, m/z): [M+H⁺] calcd for C₁₁H₁₆O₄S: 245.0849; Found: 245.0853; Anal calcd for C₁₁H₁₆O₄S: C 54.08, H 6.60, S 13.12; Found: C 53.79, H 6.62, S 13.16.

(R)-(-)-1-Bromo-3-butanol [(R)-4]. After dehydrating lithium bromide monohydrate (9.88 g, 94.2 mmol) in vacuo at 85 °C for 3 h, **(R)-3** (7.32 g, 30.0 mmol) and tetrahydrofuran (THF, 45 mL) were added and then the mixture was refluxed at 70 °C for 40 h. After removing THF, the residue was dissolved in water, extracted with CH₂Cl₂ (30 mL $\times$ 5), dried by Na₂SO₄, and concentrated under reduced pressure. The crude product was distilled at 50 °C under reduced pressure to obtain **(R)-4** as a colorless liquid (2.78 g, 60.6 %): ¹H NMR (400 MHz, CDCl₃, TMS): δ = 1.25 (d, 3H, J = 6.2 Hz, CHCH₃), 1.88 (s, 1H, OH), 1.98 (q, 2H, J = 6.2 Hz, BrCH₂CH₂), 3.53 (m, 2H, BrCH₂) 4.04 ppm (sext, 1H, J = 6.2 Hz, CHOH); ¹³C NMR (100 MHz, CDCl₃, TMS): δ = 23.5, 30.3, 41.5, 66.1 ppm; HRMS (EI, m/z): [M-H⁺] calcd for C₄H₉BrO: 150.9764; Found: 150.9764; Anal calcd for C₄H₉BrO: C 31.40, H 5.93, Br 52.22; Found: C 30.98, H 5.73, Br 52.18; [α]_D²² -40.9° (*c* 1.11, CHCl₃).

(S)-(+)-1-Bromo-3-butanol [(S)-4]. The same procedure with **(R)-4** by using lithium bromide monohydrate (6.78 g, 64.7 mmol), **(S)-3** (5.05 g, 20.7 mmol), and THF (40 mL) to give **(S)-4** as a colorless liquid (1.72 g, 54.5 %): ¹H NMR (400 MHz, CDCl₃, TMS): δ = 1.25 (d, 3H, J = 6.2 Hz, CHCH₃), 1.89 (s, 1H, OH), 1.98 (q, 2H, J = 6.2 Hz, BrCH₂CH₂), 3.53 (m, 2H, BrCH₂) 4.03 ppm (sext, 1H, J = 6.2 Hz, CHOH); ¹³C NMR

(100 MHz, CDCl₃, TMS): δ = 23.5, 30.3, 41.5, 66.0 ppm; HRMS (EI, m/z): [M-H⁺] calcd for C₄H₉BrO: 150.9764; Found: 150.9765; Anal calcd for C₄H₉BrO: C 31.40, H 5.93, Br 52.22; Found: C 31.12, H 5.94, Br 52.26; [α]_D²¹ +41.0° (*c* 1.03, CHCl₃).

(*R,R*)-1,4-Diiodo-2,5-bis(1-methyl-3-bromopropoxy)benzene [(*R,R*)-5]. To a stirred solution of triphenylphosphine (TPP, 1.82 g, 6.94 mmol) in THF (5 mL) was added dropwise a solution of diethyl azodicarboxylate (DEAD, 40 wt% in toluene, 3.15 mL, 6.93 mmol) and (*S*)-4 (1.06 g, 6.93 mmol) in THF (15 mL) at 0 °C. Then, to the mixture was slowly added dropwise a solution of **2** (1.14 g, 3.15 mmol) in THF (15 mL), and then the reaction mixture was stirred at RT for 24 h. After removing a precipitate by filtration, the filtrate was concentrated under reduced pressure. The residue was dissolved in chloroform, washed with water and brine, dried by Na₂SO₄, and concentrated. The crude product was purified by column chromatography (silica gel, chloroform) to give (*R,R*)-5 as a white solid (0.99 g, 49.5 %): ¹H NMR (400 MHz, CDCl₃, TMS): δ = 1.34 (d, 6H, *J* = 6.0 Hz, OCHCH₃), 2.23 (dm, 4H, *J* = 87.6 Hz, CH₂CH₂Br), 3.60 (m, 4H, CH₂Br), 4.51 (m, 2H, OCHCH₃), 7.25 ppm (s, 2H, Ar-*H*); ¹³C NMR (100 MHz, CDCl₃, TMS): δ = 19.5, 29.8, 39.6, 74.9, 88.1, 124.8, 151.9 ppm; HRMS (FAB, m/z): [M⁺] calcd for C₁₄H₁₈Br₂I₂O₂: 629.7763; Found: 629.7778; Anal calcd for C₁₄H₁₈Br₂I₂O₂: C 26.61, H 2.87, Br 25.29, I 40.17; Found: C 26.78, H 2.90, Br 24.62, I 40.21; [α]_D²³ -49.4° (*c* 0.61, CHCl₃).

(*S,S*)-1,4-Diiodo-2,5-bis(1-methyl-3-bromopropoxy)benzene [(*S,S*)-5]. The same procedure with (*R,R*)-5 by using **2** (1.81 g, 5.00 mmol), (*R*)-4 (1.68 g, 11.0 mmol), TPP (2.89 g, 11.0 mmol), DEAD (40 wt% in toluene, 5.00 mL, 11.0 mmol), and THF (65 mL) to give (*S,S*)-5 as a white solid (0.87 g, 27.4 %): ¹H NMR (400 MHz, CDCl₃, TMS): δ = 1.34 (d, 6H, *J* = 6.4 Hz, OCHCH₃), 2.26 (dm, 4H, *J* = 86.0 Hz, CH₂CH₂Br), 3.58 (m, 4H, CH₂Br), 4.50 (m, 2H, OCHCH₃), 7.25 ppm (s, 2H, Ar-*H*); ¹³C NMR (100 MHz, CDCl₃, TMS): δ = 19.5, 29.8, 39.6, 74.8, 88.1, 124.8, 151.9 ppm; HRMS (MALDI, m/z): [M⁺] calcd for C₁₄H₁₈Br₂I₂O₂: 629.7763; Found: 629.7767; Anal calcd for C₁₄H₁₈Br₂I₂O₂: C 26.61, H 2.87, Br 25.29, I 40.17; Found: C 26.99, H 2.86, Br 21.78, I 41.58; [α]_D²⁷ +48.4° (*c* 1.00, CHCl₃).

(*R,R*)-1,4-Diiodo-2,5-bis[1-methyl-3-(*N,N,N*-trimethylammonium)propoxy]benzene dibromide [(*R,R*)-6]. A solution of (*R,R*)-5 (0.42 g, 0.67 mmol) and

trimethylamine (30 wt% in water, 1.41 g, 7.16 mmol) in THF (15 mL) was stirred at RT for 72 h. After adding Et₂O (70 mL) to the reaction mixture, the product was extracted with water (40 mL $\times$ 5), washed Et₂O (50 mL $\times$ 1), and concentrated under reduced pressure. The residue was dried in vacuo at 100 °C for 6 h to give **(R,R)-6** as a white powder (0.49 g, 98.9 %): ¹H NMR (400 MHz, D₂O, TSP-*d*4): δ = 1.40 (d, 6H, J = 6.7 Hz, OCHCH₃), 2.27 (q, 4H, J = 6.7 Hz, CH₂CH₂N⁺(CH₃)₃), 3.20 (s, 18H, N⁺(CH₃)₃), 3.60 (m, 4H, CH₂CH₂N⁺(CH₃)₃), 4.60 (sext, 2H, J = 6.7 Hz, OCH), 7.52 ppm (s, 2H, Ar-*H*); ¹³C NMR (100 MHz, D₂O, TSP-*d*4): δ = 21.4, 31.9, 55.8, 66.2, 77.6, 90.7, 128.3, 154.1 ppm; HRMS (ESI, m/z): [M-Br⁻] calcd for C₂₀H₃₆Br₂I₂N₂O₂: 669.0044; Found: 669.0044; Anal calcd for C₂₀H₃₆Br₂I₂N₂O₂: C 32.02, H 4.84, Br 21.30, I 33.84, N 3.73; Found: C 31.74, H 4.75, Br 18.64, I 32.85, N 3.72; [α]²³_D -32.3° (*c* 0.61, MeOH).

(S,S)-1,4-Diiodo-2,5-bis[1-methyl-3-(N,N,N-trimethylammonium)propoxy]benzene dibromide [(S,S)-6]. The same procedure with **(R,R)-6** by using **(S,S)-5** (0.79 g, 1.25 mmol), trimethylamine (30 wt% in water, 2.54 g, 12.89 mmol), and THF (20 mL) to give **(S,S)-6** as a white powder (0.91 g, 96.4 %): ¹H NMR (400 MHz, D₂O, TSP-*d*4): δ = 1.40 (d, 6H, J = 7.1 Hz, OCHCH₃), 2.27 (q, 4H, J = 7.1 Hz, CH₂CH₂N⁺(CH₃)₃), 3.19 (s, 18H, N⁺(CH₃)₃), 3.62 (m, 4H, CH₂CH₂N⁺(CH₃)₃), 4.60 (sext, 2H, J = 7.1 Hz, OCH), 7.52 ppm (s, 2H, Ar-*H*); ¹³C NMR (100 MHz, D₂O, TSP-*d*4): δ = 21.4, 31.9, 55.8, 66.5, 77.7, 90.8, 128.5, 154.3 ppm; HRMS (ESI, m/z): [M-Br⁻] calcd for C₂₀H₃₆Br₂I₂N₂O₂: 669.0044; Found: 669.0044; Anal calcd for C₂₀H₃₆Br₂I₂N₂O₂: C 32.02, H 4.84, Br 21.30, I 33.84, N 3.73; Found: C 31.89, H 4.78, Br 20.60, I 33.60, N 3.73; [α]²⁷_D +32.1° (*c* 1.01, MeOH).

1,4-Phenylenediboronic acid bis(1,3-propanediol) cyclic ester (7). A suspension of 1,4-phenylenediboronic acid (5.00 g, 30.2 mmol) and 1,3-propanediol (5.63 g, 74.0 mmol) in CH₂Cl₂ (190 mL) was refluxed for 24 h. The solvent was removed under reduced pressure, and the residue was washed with ethanol to give **3** as a white powder (6.94 g, 93.6 %): ¹H NMR (400 MHz, CDCl₃, TMS): δ = 2.05 (quint, 4H, J = 5.4 Hz, OCH₂CH₂), 4.16 (t, 8H, J = 5.4 Hz, OCH₂), 7.73 ppm (s, 4H, Ar-*H*); ¹³C NMR (400 MHz, CDCl₃, TMS): δ = 27.4, 61.9, 132.5 ppm; HRMS (ESI, m/z): [M+H⁺] calcd for C₁₂H₁₆B₂O₄: 247.1307; Found: 247.1302; Anal calcd for C₁₂H₁₆B₂O₄: C 58.62, H 6.56;

Found: C 58.36, H 6.49.

(*R,R*)-Poly({2,5-bis[1-methyl-3-(*N,N,N*-trimethylammonium)propoxy]-1,4-phenylene}-*alt*-1,4-phenylene) dibromide [(*R,R*)-PPP1]. A solution of (*R,R*)-6 (0.385 g, 0.512 mmol), **7** (0.126 g, 0.512 mmol), palladium(II) acetate (5.77 mg, 0.026 mmol), and Na₂CO₃ (0.459 g, 4.33 mmol) in *N,N*-dimethylformamide (DMF, 10 mL) and deionized water (10 mL) was stirred at 95 °C for 72 h. After removing a black insoluble powder by filtration, the filtrate was poured into a diluted HBr aqueous solution (300 mL) and vigorously stirred overnight in the presence of ethylenediamine-tetraacetic acid (EDTA, 1 g). Then the mixture was filtered and the residue was washed with hot methanol. The filtrate was concentrated to about 100 mL under reduced pressure, dropped into a large amount of acetone (500 mL), and vigorously stirred overnight. The resulting precipitate was collected by filtration and dissolved in deionized water. The above processes were repeated twice to purify the polymer. Subsequently, the aqueous solution of the polymer passed through an ion exchange resin (Amberlite® IRA-402, regenerated by NaOH aq.) to exchange the anionic species ($X^- \rightarrow OH^-$), and then neutralized by HBr. Finally, low molecular weight fractions, oligomers, and impurities were removed by a dialysis treatment (Spectra/Por® Dialysis Membrane 6, MWCO: 8,000) in deionized water for a month. The resulting solution was freeze-dried to obtain (*R,R*)-PPP1 as a pale green solid (0.175 g, 59.6 %): ¹H NMR (400 MHz, DMSO-*d*₆, TMS): δ = 1.27 (br, 6H, OCH(CH₃)CH₂), 2.10 (br, 4H, OCHCH₂), 3.13 (br, 18H, N⁺CH₃), 3.53 (br, 4H, CH₂N⁺(CH₃)₃), 4.57 (br, 2H, OCH), 7.21 (s, 2H, Ar-*H*), 7.78 ppm (br, 4H; Ar-*H*); ¹³C NMR (100 MHz, DMSO-*d*₆, TMS): δ = 19.3, 29.5, 52.6, 62.8, 73.1, 118.5, 126.3, 129.3, 130.1, 131.6, 136.6, 148.8 ppm.

(*S,S*)-Poly({2,5-bis[1-methyl-3-(*N,N,N*-trimethylammonium)propoxy]-1,4-phenylene}-*alt*-1,4-phenylene) dibromide [(*S,S*)-PPP1]. The same procedure with (*R,R*)-PPP1 by using (*S,S*)-6 (0.444 g, 0.591 mmol), **7** (0.145 g, 0.591 mmol), palladium(II) acetate (7.13 mg, 0.032 mmol), Na₂CO₃ (0.508 g, 4.79 mmol), DMF (12 mL), and deionized water (12 mL) to give (*S,S*)-PPP1 as a pale green solid (0.267 g, 78.7 %): ¹H NMR (400 MHz, DMSO-*d*₆, TMS): δ = 1.27 (br, 6H, OCH(CH₃)CH₂), 2.09 (br, 4H, OCHCH₂), 3.14 (br, 18H, N⁺CH₃), 3.55 (br, 4H, CH₂N⁺(CH₃)₃), 4.57 (br,

2H, OCH), 7.21 (s, 2H, Ar-H), 7.77 ppm (br, 4H, Ar-H); ^{13}C NMR (100 MHz, DMSO-*d*₆, TMS): δ = 19.3, 29.4, 52.5, 62.7, 73.1, 118.4, 126.1, 129.1, 129.9, 131.4, 136.4, 148.6 ppm.

(*R,R*)-Poly({2,5-bis[1-methyl-3-(*N,N,N*-trimethylammonium)propoxy]-1,4-phenylene}-*alt*-{4,4'-biphenylene}) dibromide [(*R,R*)-PPP2]. The same procedure with (*R,R*)-PPP1 by using (*R,R*)-6 (0.375 g, 0.500 mmol), 4,4'-biphenyldiboronic acid bis(neopentyl glycol) cyclic ester (0.189 g, 0.500 mmol), palladium(II) acetate (6.02 mg, 0.027 mmol), Na₂CO₃ (0.439 g, 4.14 mmol), DMF (10 mL), and deionized water (10 mL) to give (*R,R*)-PPP2 as a pale green solid (0.302 g, 93.0 %): ^1H NMR (400 MHz, DMSO-*d*₆, TMS): δ = 1.26 (d, 6H, J = 6.0 Hz, OCH(CH₃)CH₂), 2.06 (br, 4H, OCHCH₂), 3.10 (br, 18H, N⁺CH₃), 3.46 (t, 4H, J = 8.0 Hz, CH₂N⁺(CH₃)₃), 4.54 (sext, 2H, J = 6.0 Hz, OCH), 7.20 (s, 2H, Ar-H), 7.76 (br, 4H, Ar-H), 7.86 ppm (br, 4H, Ar-H); ^{13}C NMR (100 MHz, DMSO-*d*₆, TMS): δ = 19.3, 29.4, 52.6, 62.8, 73.1, 118.6, 126.3, 126.5, 129.0, 130.1, 131.6, 137.0, 138.6, 148.8 ppm.

(*S,S*)-Poly({2,5-bis[1-methyl-3-(*N,N,N*-trimethylammonium)propoxy]-1,4-phenylene}-*alt*-{4,4'-biphenylene}) dibromide [(*S,S*)-PPP2]. The same procedure with (*R,R*)-PPP1 by using (*S,S*)-6 (0.375 g, 0.500 mmol), 4,4'-biphenyldiboronic acid bis(neopentyl glycol) cyclic ester (0.189 g, 0.500 mmol), palladium(II) acetate (5.78 mg, 0.026 mmol), Na₂CO₃ (0.430 g, 4.06 mmol), DMF (10 mL), and deionized water (10 mL) to give (*S,S*)-PPP2 as a pale green solid (0.231 g, 71.2 %): ^1H NMR (400 MHz, DMSO-*d*₆, TMS): δ = 1.26 (d, 6H, J = 6.0 Hz, OCH(CH₃)CH₂), 2.06 (br, 4H, OCHCH₂), 3.10 (br, 18H, N⁺CH₃), 3.46 (t, 4H, J = 8.0 Hz, CH₂N⁺(CH₃)₃), 4.53 (sext, 2H, J = 6.0 Hz, OCH), 7.20 (s, 2H, Ar-H), 7.76 (br, 4H, Ar-H), 7.85 ppm (br, 4H, Ar-H); ^{13}C NMR (100 MHz, DMSO-*d*₆, TMS): δ = 19.3, 29.4, 52.5, 62.7, 73.0, 118.4, 126.1, 126.4, 128.8, 129.9, 131.4, 136.9, 138.4, 148.6 ppm.

Sodium 3-(2-naphthyloxy)propylsulfonate (SNap). To a solution of 2-naphthol (2.89 g, 20.1 mmol) in EtOH (50 mL) was added dropwise a solution of NaOH (0.95 g, 23.6 mmol) in EtOH (50 mL) at RT. Then, 1,3-propanesultone (2.61 g, 21.4 mmol) and EtOH (50 mL) were added to the mixture, and the reaction mixture was stirred at RT for 24 h. The resulting precipitate was filtered, washed with EtOH, and recrystallized from water–EtOH to give SNap as a white solid (4.37 g, 75.5 %): ^1H

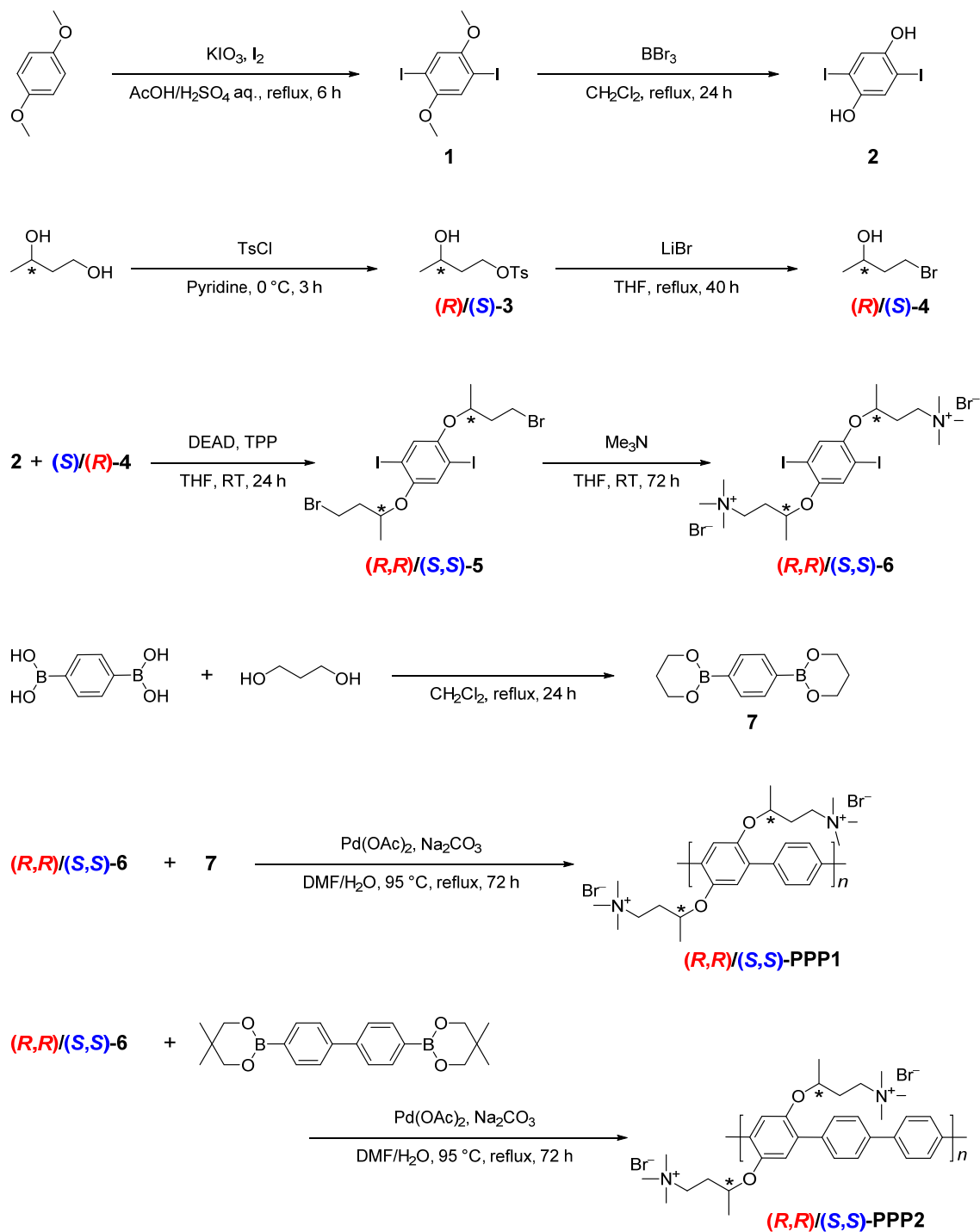
NMR (400 MHz, D₂O, TSP-*d*₄) : δ = 2.09 (quint, 2H, J = 7.1 Hz, OCH₂CH₂), 2.95 (t, 2H, J = 7.1 Hz, CH₂SO₃Na), 3.79 (t, 2H, J = 7.1 Hz, OCH₂), 6.92 (s, 1H, Ar-*H*), 6.95 (dd, 1H, J = 8.8 and 2.4 Hz, Ar-*H*), 7.30 (t, 1H, J = 8.0 Hz, Ar-*H*), 7.39 (t, 1H, J = 8.0 Hz, Ar-*H*), 7.58–7.61 (m, 2H, Ar-*H*), 7.67 ppm (d, 1H, J = 8.0 Hz, Ar-*H*); ¹³C NMR (400 MHz, D₂O, TSP-*d*₄) : δ = 27.0, 50.7, 69.0, 109.8, 121.0, 126.5, 129.1, 129.4, 130.2, 131.4, 132.0, 136.8, 158.5 ppm; HRMS (ESI) calcd for C₁₃H₁₃NaO₄S [M – Na⁺]: 265.0540; Found: 265.0539; Anal calcd for C₁₃H₁₃NaO₄S: C 54.16, H 4.55; Found: C 53.97, H 4.55.

Diethylene glycol bis(3-sulfonatepropyl) ether disodium salt (A1). To a solution of diethylene glycol (1.071 g, 10.1 mmol) in THF (70 mL) was added NaH (0.583 g, 24.3 mmol) at 0 °C, and then the mixture was stirred at RT for 1.5 h. After that, a solution of 1,3-propanesultone (2.95 g, 24.2 mmol) in THF (30 mL) was added dropwise. The reaction mixture was stirred at RT for 24 h. After quenching residual NaH with water, THF solvent was removed under reduced pressure. The resulting aqueous solution was washed by chloroform 4 times, and then water was removed. The residue was recrystallized from water–EtOH to give **A1** as a white solid (3.84 g, 96.5 %): ¹H NMR (400 MHz, D₂O, TSP-*d*₄): δ = 2.03 (quint, 4H, J = 6.8 Hz, CH₂CH₂SO₃Na), 2.99 (t, 4H, J = 6.8 Hz, CH₂SO₃Na), 3.63–3.70 ppm (m, 12H, CH₂OCH₂CH₂O); ¹³C NMR (100 MHz, D₂O, TSP-*d*₄): δ = 27.1, 50.7, 71.9, 72.0, 72.4 ppm; HRMS (ESI) calcd for C₁₀H₂₀Na₂O₉S₂ [M – Na⁺]: 371.0441; Found: 371.0439; Anal calcd for C₁₀H₂₀Na₂O₉S₂: C 30.46, H 5.11, S 16.26; Found: C 29.93, H 5.27, S 15.18.

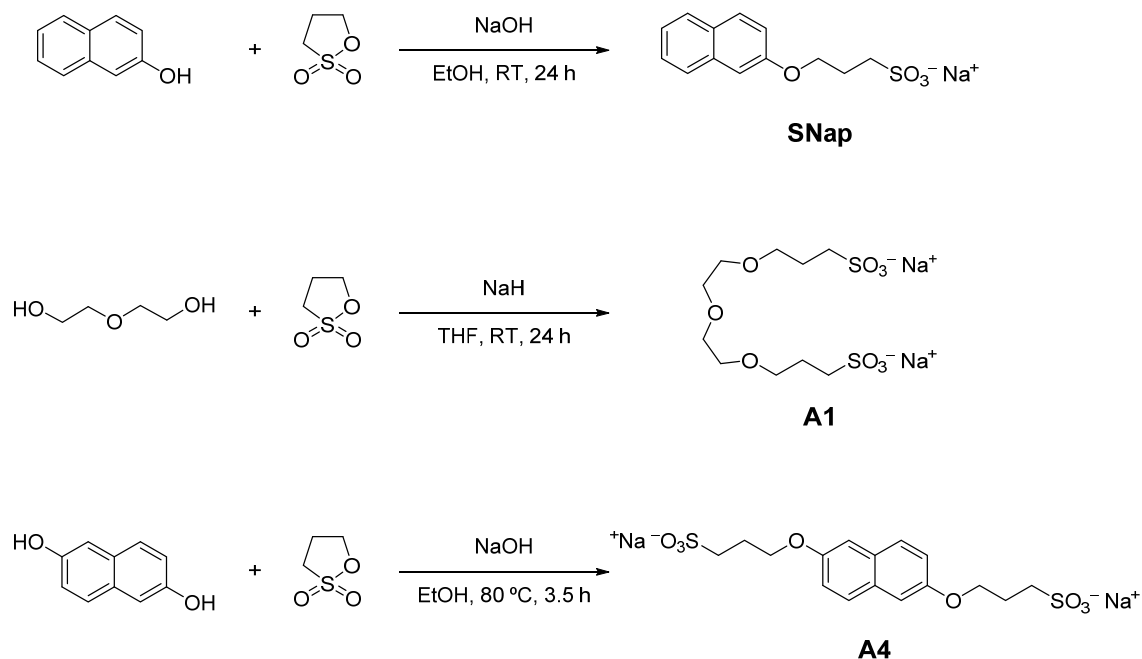
2,6-Bis(3-sulfonatepropoxy)naphthalene disodium salt (A4). A solution of NaOH (0.900 g, 22.5 mmol) in EtOH (50 mL) was added dropwise to a solution of 2,6-dihydroxynaphthalene (1.602 g, 10.0 mmol) in EtOH (120 mL) at RT, and then the mixture was refluxed at 80 °C for 1 h. After adding 1,3-propanesultone (2.69 g, 22.1 mmol), the reaction mixture was refluxed at 80 °C for 3.5 h. The resulting precipitate was filtrated and recrystallized from water–EtOH 3 times to give **A4** as light reddish white powder (2.325 g, 51.9 %): ¹H NMR (400 MHz, D₂O, TSP-*d*₄): δ = 2.24 (quint, 4H, J = 5.7 Hz, OCH₂CH₂), 3.11 (t, 4H, J = 5.7 Hz, CH₂SO₃Na), 4.15 (t, 4H, J = 5.7 Hz, OCH₂), 7.15 (d, 2H, J = 8.4 Hz, Ar-*H*), 7.21 (s, 2H, Ar-*H*), 7.69 ppm (d, 2H, J = 8.4 Hz, Ar-*H*); ¹³C NMR (100 MHz, D₂O, TSP-*d*₄): δ = 27.1, 50.8, 69.6, 110.7, 121.7,

Interchain Helically π -Stacked Assembly of Cationic Chiral Poly(para-phenylene) Derivatives Enforced by Anionic π -Conjugated Molecules through Both Electrostatic and π - π Interactions

131.3, 132.5, 157.5 ppm; HRMS (ESI) calcd for $C_{16}H_{18}Na_2O_8S_2$ $[M + Na^+]$: 471.0131; Found: 471.0127; Anal calcd for $C_{16}H_{18}Na_2O_8S_2$: C 42.86, H 4.05, S 14.30; Found: C 42.65, H 3.88, S 14.31.



Scheme 2. Synthetic routes of cationic chiral poly(*para*-phenylene) derivatives (**PPP1** and **PPP2**).



Scheme 3. Synthetic route of anionic additives (**SNap**, **A1**, and **A4**).

4. Sample Preparation

4.1. Optical measurements for the cationic polymers. The cationic polymers (**PPP1** or **PPP2**) were dissolved in water, methanol, and mixtures of water and methanol at the concentration of 2.0×10^{-5} M, respectively.

4.2. Optical measurements for mixtures of the cationic polymers and the anionic additives. The cationic polymers (**PPP1** or **PPP2**) and the anionic additives (**SNap**, **A1**, **A2**, **A3**, or **A4**) were separately dissolved in water at the concentration of 1.0×10^{-3} M, and then the solutions were mixed with various molar ratios at RT. Subsequently, the mixtures were diluted with water to give a concentration of the polymer = 2.0×10^{-5} M. All ε and $\Delta\varepsilon$ in UV-vis absorption and CD spectra were evaluated in terms of the concentrations of the polymers. The heating treatment to **PPP2-SNap** was performed by using a Peltier-type thermostat attached in JASCO J-820 spectropolarimeter.

4.3 SEM measurements. According to the above procedure, a mixed solution of **PPP1** and **SNap** was prepared with the molar ratio of 1:2. The mixed solution was dried at RT on a sample stage to give a solid sample for the SEM measurement.

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Chapter 5

Dynamic Control of Full-Colored Emission and Quenching of Photoresponsive Conjugated Polymers by Photostimuli

Introduction

Aromatic π -conjugated polymers (ACPs) are promising candidates for advanced functional materials and are expected to be applied in such organic devices as organic light-emitting diodes, organic field-effect transistors, organic photovoltaic cells, and chemical biosensors due to their semiconductive and optoelectronic properties.¹⁻⁸ The ACPs exhibit various colored fluorescence in the visible region due to changes in the main chain structures because their properties are fundamentally determined by the primary structure of the conjugated backbones. Furthermore, the fluorescent property can be modified and functionalized by controlling the secondary or higher-ordered structures of the main chains in an aggregated state. It is well known that linearly aligned and helically π -stacked ACPs show linear and circular dichroism in luminescence, respectively.⁹⁻¹³ In another case, aggregation-induced emission (AIE) and aggregation-enhanced emission (AEE) characteristics were reported in selected ACPs.¹⁴⁻¹⁶ Therefore, it is of great interest to investigate ACPs in the aggregated state that are quite different from those the isolated chain state.

The polymer nanosphere solution can be treated as an intermediate state between a solution state and a solid film state because the polymer nanoparticles uniformly disperse in a solvent, similar to their behavior in solution, whereas the polymer chains aggregate with each other, similarly to their behavior in a solid film. In other words, the polymer nanosphere solution can be regarded as a dispersed nano-ordered crystalline polymer system. This bilateral character of the nanosphere solution causes the polymer to exhibit high processability and fluidity as well as aggregation effects. In addition, the polymer nanosphere solution enables quantitative analysis of the aggregated state of polymers from the spectroscopic point

of view. Hence, the polymer nanosphere solution is useful for understanding the aggregation effect on ACPs as compared with the solution and solid film states.

Dynamic control of the fluorescence of ACPs using an external light stimulus is of particular interest because such photoresponsive polymers are essential for next-generation optoelectronic materials. Dithienylethene (DE) derivatives¹⁷⁻²⁰ are one class of the most attractive photoresponsive materials because of their outstanding fatigue resistance, thermal stability, and ability to undergo conformational changes between open and closed forms via photoisomerization, and therefore they are regarded as promising materials for the fabrication of photodynamically controllable luminescent devices^{21, 22} as well as photodynamically color-tunable systems.²³⁻²⁷ The DE derivatives are also known to display luminescent color changes via photoisomerization.^{20, 28-37} Similarly, conjugated polymers that contain DE moieties in the polymer backbones exhibit photochromism.^{20, 38-41} The chromism in both absorption and luminescence of the conjugated polymers is attributed to structural changes in the conjugated backbones resulting from the DE photoisomerization. Hence, it is necessary to properly design the molecular structure to realize the desired switching behavior and fluorescent colors.

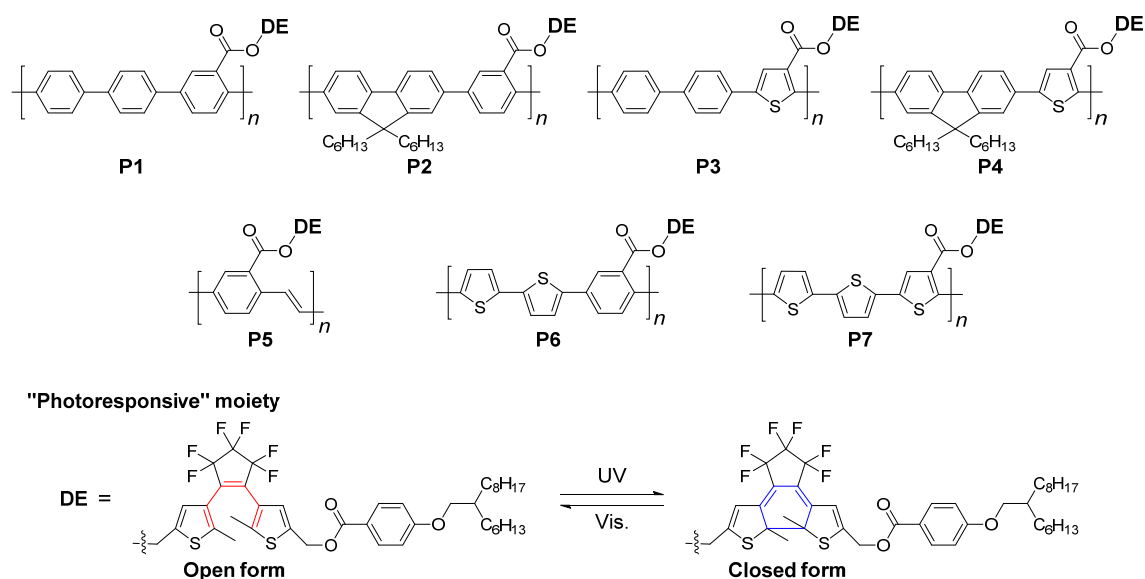
It is well known that in ACP nanoparticles doped with luminescent dopants, the ACP fluorescence is almost completely quenched and the fluorescence of the dopant is mainly observed.⁴² This is due to the intra-particle energy transfer from the ACP backbone to the dopant. Thus, it was previously reported that the ACP nanoparticles doped with photochromic dyes showed reversible fluorescence photoswitching between emission and quenching by photoisomerization of the dyes upon irradiation of external light stimuli.⁴²⁻⁴⁵ On the other hand, it was also reported that the ACPs incorporated with photochromic moieties showed reversible photo-modulation of the fluorescence by using light stimuli.⁴⁶⁻⁴⁸ In these polymer systems, the fluorescent moiety is independent of the photochromic moiety, resulting in high flexibility on the molecular design.

By introducing the DE moiety into the side chains of ACPs, the polymer fluorescence in solution and solid film was switchable between emission and quenching via reversible DE photoisomerization. In previous work, we reported the

photodynamic ON/OFF switching of linearly polarized luminescence (LPL) in macroscopically aligned ACPs and also that of circularly polarized luminescence (CPL) in helically π -stacked ACPs using ultraviolet (UV) and visible light stimuli.^{49,50} In these cases, the fluorescent conjugated backbones of the polymers were unchanged before and after DE photoisomerization, and therefore, the interchain structures were maintained. In addition, this material offers the advantage of free design of the fluorescent color because the fluorescent polymer backbone and the photoisomerized DE side chain are independent of each other from the viewpoint of the π -electronic structure. Very recently, we reported that three types of ACPs with the DE side chains showed red-, green-, and blue-colored fluorescence in the nanosphere solution, and they exhibited photoswitching behavior between emission and quenching by external light stimuli.⁵¹ However, the red-colored fluorescent ACP showed bluish purple-colored fluorescence in chloroform solution although it exhibited red-colored fluorescence in nanosphere solution and solid film. This is because the main chain of the red-colored fluorescent ACP consists of a polyfluorene backbone containing a very small amount of 4,7-di(2-thienyl)-2,1,3-benzothiadiazole (DBT) moiety, and the red-colored fluorescence of the DBT moiety is only observable in the aggregated state. This means that the photodynamic ON/OFF switching behavior of full-colored fluorescence has not been completely achieved in the isolated chain state such as in the chloroform solution.

In this work, we designed and synthesized several types of photoresponsive ACPs by incorporating a DE side chain into various conjugated main chains, i.e., poly(*p*-terphenylene) [**P1**], poly(fluorene-phenylene) [**P2**], poly(biphenylene-thienylene) [**P3**], poly(fluorene-thienylene) [**P4**], poly(*p*-phenylene-vinylene) [**P5**],⁴⁹ poly(bithienylene-phenylene) [**P6**],⁴⁹ and poly(terthiophene) [**P7**] (Scheme 1). The polymers exhibited various blue–red colored fluorescence corresponding to the conjugated length of the main chains. In solution and solid film, it was successfully demonstrated that the fluorescence of ACPs in the whole visible region was reversibly switchable between emission and quenching through photoisomerization of the DE side chains regardless of the fluorescence wavelengths (Figure 1). The quenching efficiency in cast films was higher than that in solutions as a result of the

aggregation effect. The reprecipitation method with ultrasonication enabled the polymers to form spherical aggregates with diameters of 20–70 nm in water. The resulting nanosphere solutions exhibited moderate fluorescent properties between those of solutions and solid films, and the fluorescence was also photoswitchable, except for the red-colored fluorescence of **P7**. Herein, we conducted a comprehensive investigation of the photoswitchable full-colored fluorescence of ACPs bearing DE side chains in both the isolated chain and the aggregated states.



Scheme 1. Structures of photoresponsive conjugated polymers.

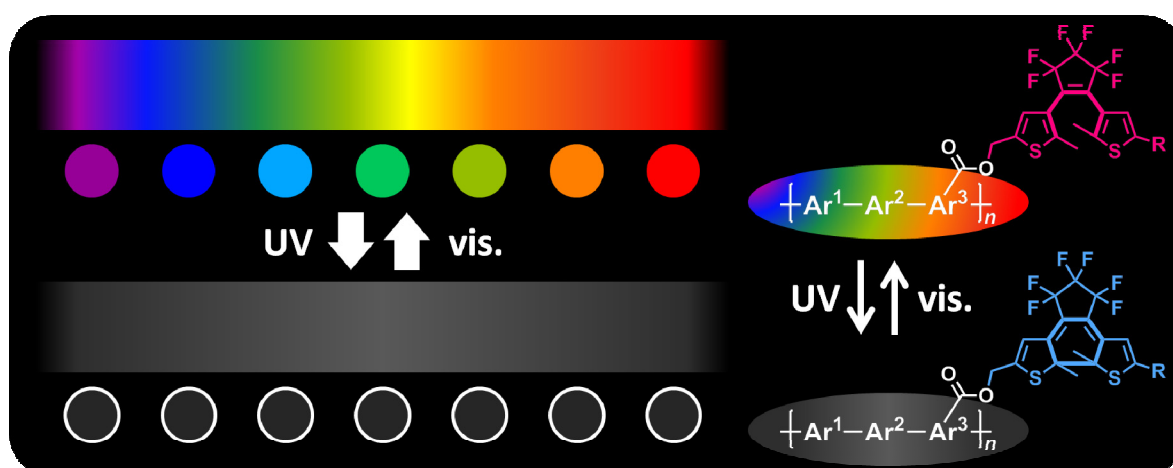


Figure 1. Scheme of photoswitching behavior of multi-colored fluorescence between emission and quenching by using DE photoisomerization.

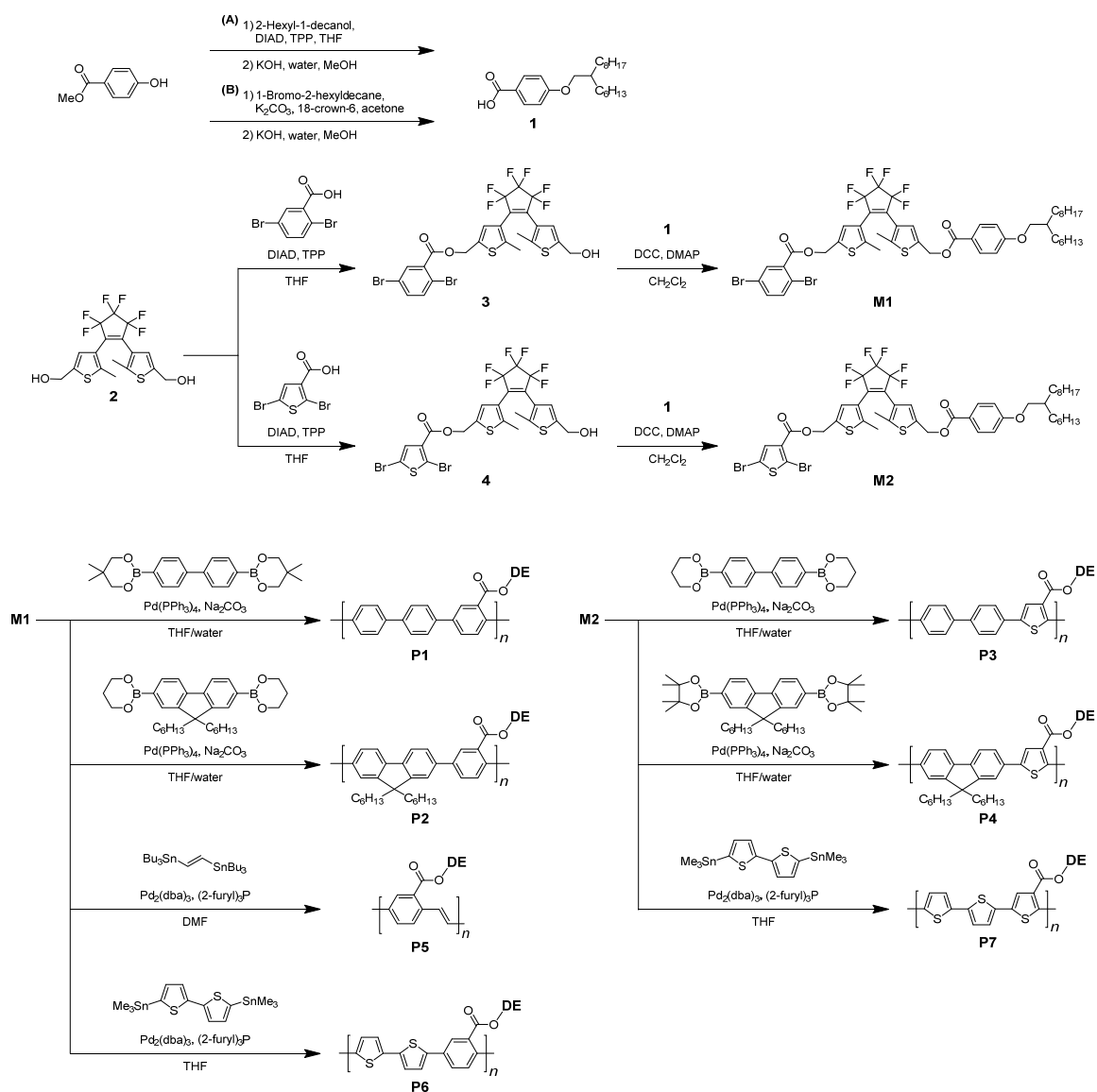
2. Results and Discussion

Synthesis and Characteristics of Photoresponsive Conjugated Polymers. The synthetic routes of the photoresponsive monomers and polymers are shown in Scheme 2. 2,5-Dibromobenzoic acid and 2,5-dibromo-3-thenoic acid were esterified with the DE derivative **2** via Mitsunobu reaction to give **3** and **4**, respectively. Esterification of the intermediate products with **1** in the presence of both *N,N'*-dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP) yielded the photoresponsive monomers, **M1** and **M2**, respectively. The photoresponsive conjugated polymers **P1–P4** were synthesized via a Suzuki coupling reaction between the monomers and diborate monomers, i.e., 4,4'-biphenyldiboronic acid cyclic ester and 9,9-dihexylfluorene-2,7-diboronic acid cyclic ester, in the presence of tetrakis(triphenylphosphine)palladium(0) [Pd(PPh₃)₄] as a catalyst. The **P5–P7** polymers were synthesized through a Stille coupling reaction between the monomers and distannyl monomers, i.e., 1,2-bis(tributylstannyl)ethylene and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene, in the presence of tris(dibenzylideneacetone)-dipalladium(0) [Pd₂(dba)₃] and tri-2-furylphosphine [(2-furyl)₃P] as catalysts.

The molecular structures of the monomers and the polymers were confirmed using nuclear magnetic resonance (NMR) measurements, mass spectrometry, and elemental analysis. All synthesized polymers were fusible and soluble in such organic solvents as tetrahydrofuran (THF), toluene, and chloroform (CHCl₃). Table 1 shows the average molecular weights of the polymers as evaluated by gel permeation chromatography (GPC). The number- and weight-average molecular weights (M_n and M_w) of the polymers range from 1.1×10^4 to 2.0×10^4 and 1.2×10^4 to 1.5×10^5 , respectively, resulting in a polydispersity index (PDI, M_w/M_n) of 1.1–7.5. The degree of polymerization (DP) was estimated as 10–19 using the M_n values. The DE moiety in the side chains successfully photoisomerized from the open form to closed form upon irradiation by UV light ($\lambda = 254$ nm). The level of DE conversion to closed form in a photostationary state (PSS) was estimated as 42–47% by using ¹H NMR results (see Experimental Section for more detail). In this work, a PSS is an equilibrium state between the open form and the closed form of the DE moiety under UV irradiation. After subsequent irradiation with visible light ($\lambda > 400$ nm), all

Chapter 5

proton signals corresponding to the DE open form were regenerated. These results indicated that reversible photoisomerization of DE moiety occurred even in the polymer side chains.



Scheme 2. Synthetic routes of photoresponsive conjugated polymers, **P1–P7**.

Table 1. Molecular weights of **P1–P7** and level of DE conversion to closed form in a PSS.

Polymer	M_n	M_w	M_w/M_n	DP ^a	Level of DE conversion to closed form in a PSS (%) ^b
P1	10,700	12,200	1.1	10	45
P2	15,500	31,000	2.2	12	45
P3	20,000	148,000	7.5	19	42
P4	20,000	150,000	7.4	16	42
P5 ^c	13,000	36,000	2.7	14	47
P6 ^c	14,200	18,800	1.3	14	42
P7	17,000	51,000	3.0	16	45

^a Degree of polymerization.

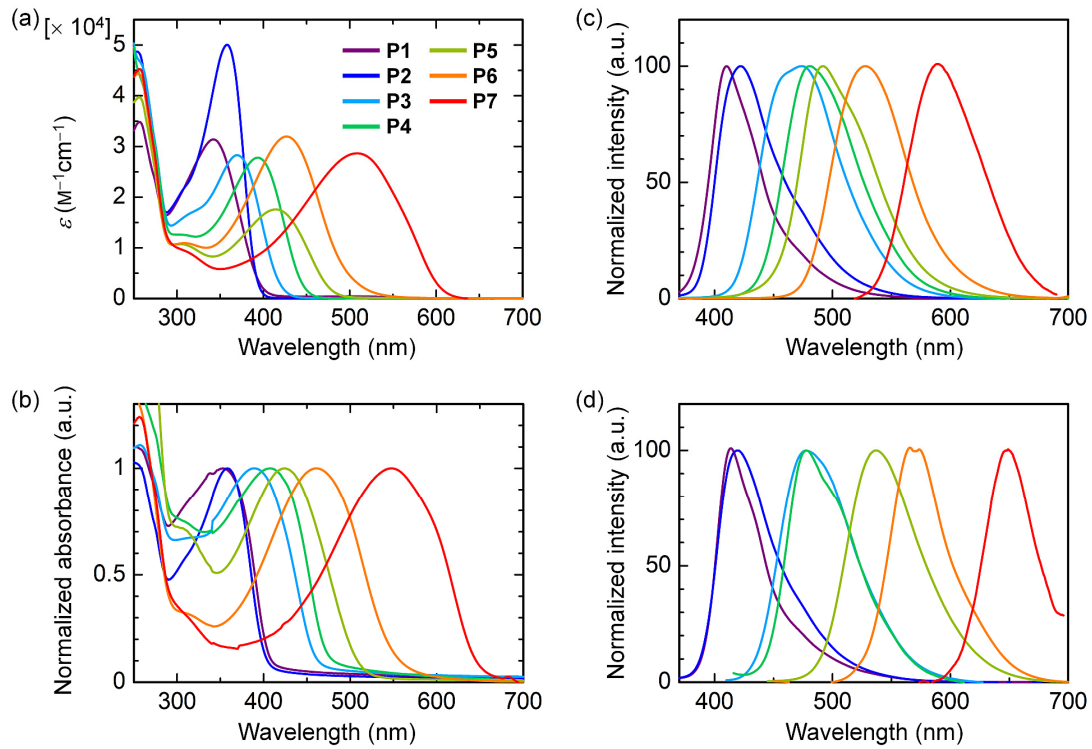
^b The values were estimated by using ¹H NMR results of the polymers in CDCl₃.

^c Reference (49).

Absorption and Fluorescence of P1–P7 Solutions and Cast Films. First, we investigated the optical properties of the **P1–P7** solutions and cast films. The absorption peaks of **P1–P7** in CHCl₃ solution ($c = 4.0 \times 10^{-5}$ M) and cast film are summarized in Table 2. The polymer cast films were prepared from CHCl₃–toluene solutions of the corresponding polymers. As shown in Figure 2a, the polymer solutions in an open state showed various absorption bands in the visible region of 300–600 nm, which corresponds to π – π^* transition of the polymer conjugated backbone. The polymer cast films showed absorption bands in a longer wavelength region than those of the CHCl₃ solutions (Figure 2b) because the effective conjugated length of the polymer main chains were increased in the solid state. More specifically, the absorption bands of **P1–P7** were red-shifted by 11 nm, 0 nm, 19 nm, 14 nm, 11 nm, 35 nm, and 40 nm, respectively (see Table 2). It is worth noting that the thienylene-containing polymers of **P3**, **P4**, **P6**, and **P7** exhibited larger red shifts in absorption than those of the thienylene-free polymers **P1**, **P2**, and **P5**. This effect results from the high π -stacking feature of the thienylene ring, which enhances the

Table 2. Absorption peaks of CHCl_3 solutions, nanosphere solutions, and cast films of **P1–P7** in an open state.

Polymer	CHCl_3 solution ^a	Nanospheres solution		Cast film	
	λ_{max} (nm)	λ_{max} (nm)	$\Delta\lambda_{\text{max}}$ ^b (nm)	λ_{max} (nm)	$\Delta\lambda_{\text{max}}$ ^b (nm)
P1	342	353	11	353	11
P2	358	359	1	358	0
P3	370	385	15	389	19
P4	394	402	8	408	14
P5	414	417	3	425	11
P6	426	450	24	461	35
P7	508	531	23	548	40

^a Polymer concentration: 4.0×10^{-5} M.^b Absorption peak shift from the λ_{max} of the polymer CHCl_3 solution.**Figure 2.** (a,b) UV–vis absorption and (c,d) normalized PL spectra of **P1–P7** in an open state. (a,c) CHCl_3 solutions ($c = 4.0 \times 10^{-5}$ M) and (b,d) cast films. Excitation wavelength: 350 nm for all CHCl_3 solutions and **P1** and **P2** cast films; 380 nm for **P3–P7** cast films.

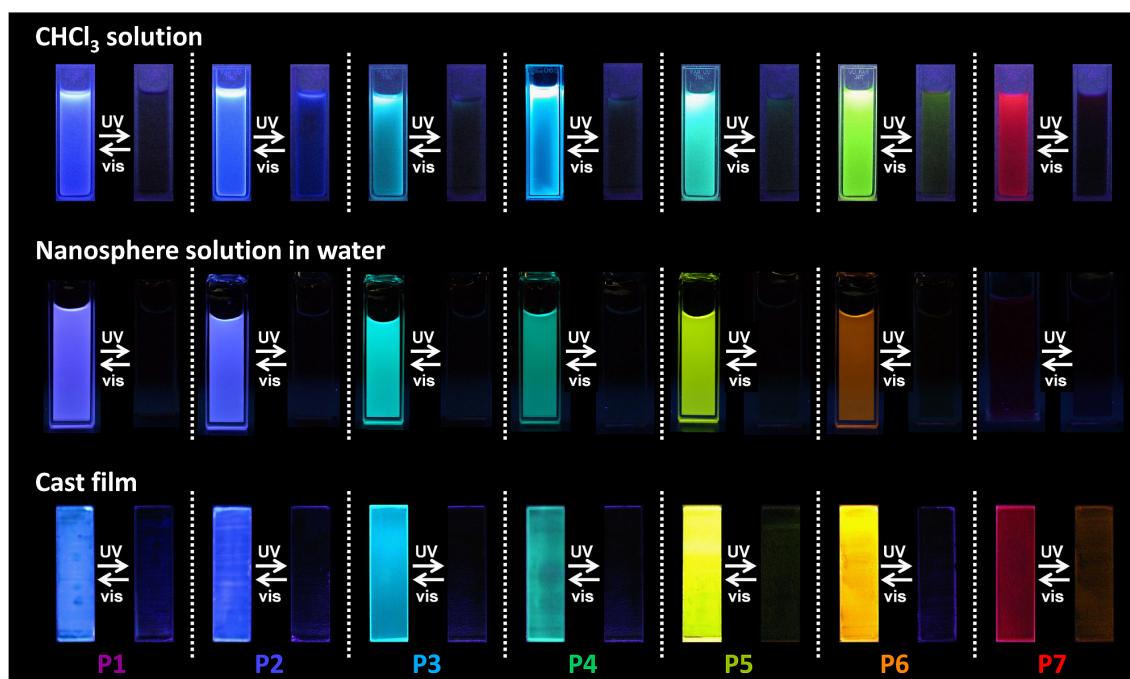


Figure 3. Photoswitching behavior between emission and quenching of full-colored fluorescence of **P1–P7** CHCl_3 solutions (upper), nanosphere solutions (middle), and cast films (lower) by UV and visible light stimuli. Excitation wavelength: $\lambda = 370$ nm.

coplanarity of the polymer conjugated backbone in a solid state. This observation is also supported by the fact that the degree of red shift increases with the number of thienylene rings in a polymer repeating unit, i.e., the absorption peak shift is 0–11 nm for thienylene-free polymers **P1**, **P2**, and **P5**; 14–19 nm for monothienylene-containing polymers **P3** and **P4**; 35 nm for the bithienylene-containing polymer **P6**; and 40 nm for terthienylene-containing polymer **P7**.

Figures 2c and d display the photoluminescence (PL) spectra of the polymers in the open state with excitation wavelengths at either 350 nm or 380 nm. The CHCl_3 solutions and cast films of the polymers exhibited various colored fluorescence that corresponded to $\pi^*-\pi$ transition of the polymer conjugated backbone. As shown in Figures 2c, 2d, and 3, the fluorescent color of the polymer solutions and cast films changed from blue to red with an increasing number of thienylene rings in the repeating unit, except for the PPV derivative **P5**. Specifically, thienylene-free **P1** and **P2** showed blue fluorescence, monothienylene-containing **P3** and **P4** displayed

Table 3. Fluorescence properties of **P1–P7** in CHCl₃ solution, nanosphere solution, and cast film.

Polymer	CHCl ₃ solution ^a			Nanosphere solution		Cast film	
	Em _{max} ^b (nm)	Φ _{open} ^c (%)	I _{open} /I _{PSS} ^d	Em _{max} ^b (nm)	I _{open} /I _{PSS} ^d	Em _{max} ^b (nm)	I _{open} /I _{PSS} ^d
P1	410 ^e	62	120	414 ^e	140	412 ^e	490
P2	422 ^e	85	190	420 ^e	320	419 ^e	790
P3	474 ^e	26	80	481 ^f	270	478 ^f	360
P4	480 ^e	24	50	480 ^f	235	478 ^f	290
P5	492 ^e	24	120	539 ^f	375	536 ^f	530
P6	528 ^e	23	90	571 ^f	180	575 ^f	320
P7	593 ^e	5	60	648 ^f	30	647 ^f	80

^a Polymer concentration: 4.0 × 10^{−5} M.^b Fluorescence peak of the polymer in an open state.^c Fluorescence quantum yield in an open state evaluated by using quinine sulfate in 1.0 M sulfuric acid as a standard.^d Fluorescence intensity ratio between the open state and PSS.^e Excitation wavelength: 350 nm.^f Excitation wavelength: 380 nm.

bluish-green fluorescence, bithienylene-containing **P6** displayed green and yellow fluorescence, and terthienylene-containing **P7** displayed red fluorescence. The fluorescence peak wavelengths of the polymers are listed in Table 3. This result also indicates that the thienylene ring enhances the coplanarity of the polymer main chain, and hence, the effective conjugated length. The fluorescence quantum yields of the polymer solutions in the open state (Φ_{open}) were evaluated using quinine sulfate in 1.0 M sulfuric acid as a standard, as summarized in Table 3. Thienylene-free **P1** and **P2**, which consist of phenylene and fluorene rings, showed high Φ_{open} values of 62% and 85%, respectively. However, thienylene copolymers **P3**, **P4**, and **P6** and PPV derivative **P5** showed lower Φ_{open} values of 23–26%. Furthermore, PT derivative **P7** showed a significant low Φ_{open} value of 5%, which might be due to a so-called “concentration quenching in fluorescence” phenomenon resulting from the high π-stacking feature of the thienylene rings.^{52–54}

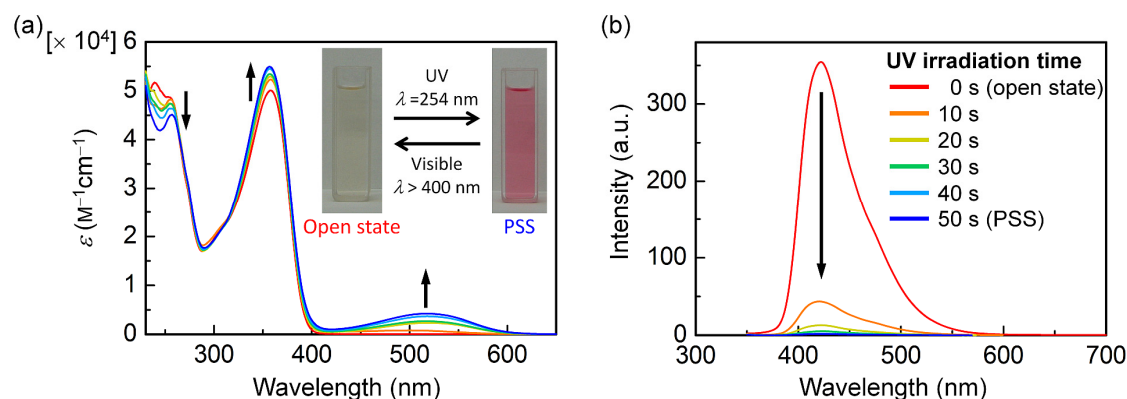


Figure 4. Spectral changes in (a) UV-vis absorption and (b) PL spectra of **P2** CHCl_3 solution ($c = 4.0 \times 10^{-5}$ M) under UV irradiation ($\lambda = 254$ nm). Inserts show the photo images of **P2** CHCl_3 solution in the open state and PSS. Excitation wavelength: 350 nm.

Photoswitching Behavior in Absorption and Fluorescence of P1–P7 Solutions and Cast Films. Next, we investigated the absorption and fluorescence changes upon irradiation by external light sources for **P1–P7** solutions and cast films. Figure 4 shows the spectral changes of the CHCl_3 solution of **P2** in an open state and a PSS. As shown in Figure 4a, the absorption band at approximately 255 nm gradually decreased in intensity as the DE moiety changed from the open form to the closed form upon irradiation by UV light ($\lambda = 254$ nm). At the same time, other absorption bands at approximately 360 nm and 520 nm increased in intensity, which correspond to the DE closed form. The absorption changes stopped after 50 s of UV irradiation because **P2** reached the PSS. Subsequent irradiation by visible light ($\lambda > 400$ nm) for 5 min caused photoisomerization of the DE moiety from the closed form to the open form, resulting in regeneration of the absorption spectrum of **P2** in the open state. The inserted images show the color change of the **P2** solution in the open state and PSS. All of the other polymer solutions also exhibited the same photoswitching behavior in absorption, as shown in Figure 5. It is worthy to emphasize that the DE moiety in the polymers can photoisomerize by external light stimuli although all the absorption bands overlap those of the polymer conjugated main chains (see Figures 9a and b). This suggests that the DE moiety receives photonic energy enough to be photoisomerized even if the conjugated backbone coexists.

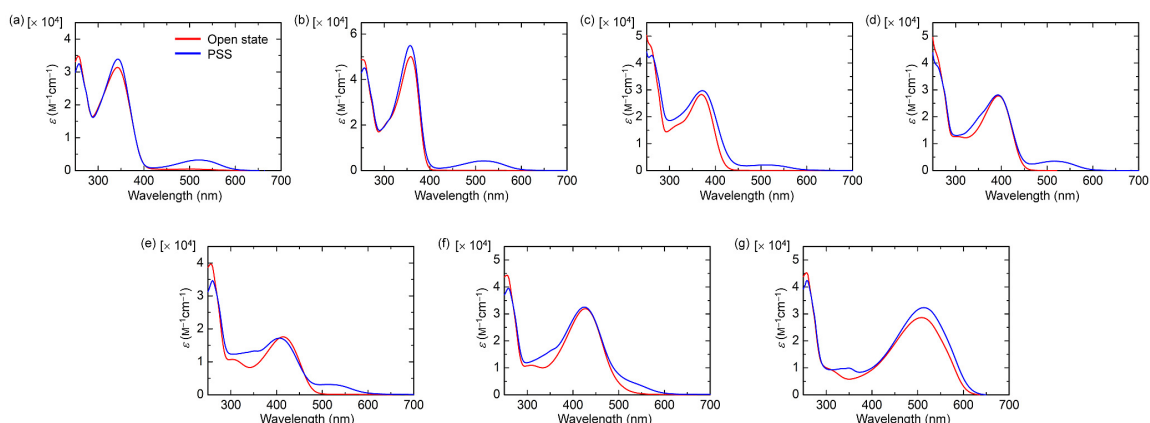


Figure 5. UV-vis absorption spectra of CHCl_3 solutions ($c = 4.0 \times 10^{-5}$ M) of (a) **P1**, (b) **P2**, (c) **P3**, (d) **P4**, (e) **P5**, (f) **P6**, and (g) **P7** in an open state (red line) and a PSS (blue line).

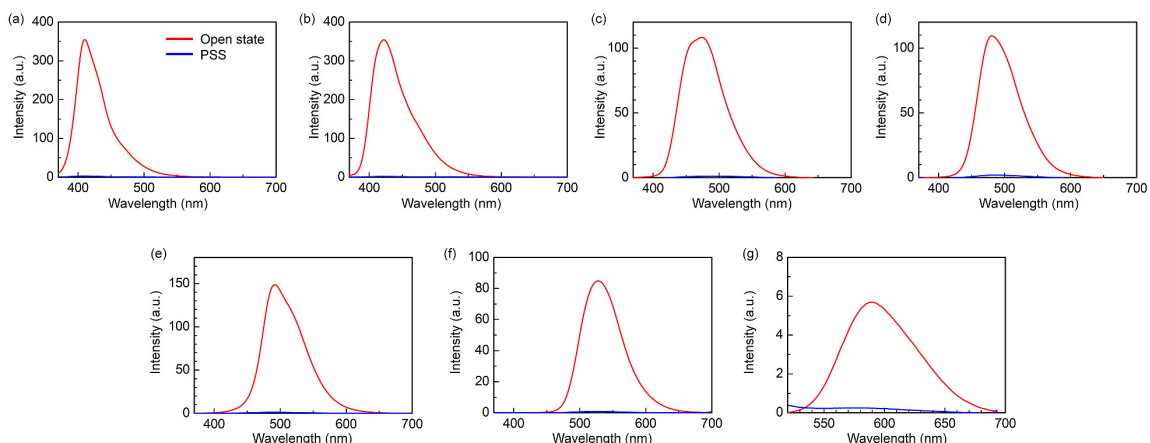


Figure 6. PL spectra of CHCl_3 solutions ($c = 4.0 \times 10^{-5}$ M) of (a) **P1**, (b) **P2**, (c) **P3**, (d) **P4**, (e) **P5**, (f) **P6**, and (g) **P7** in an open state (red line) and a PSS (blue line).

Figure 4b shows the fluorescent change of the CHCl_3 solution of **P2** via DE photoisomerization. The blue fluorescence band of **P2** in the open state drastically decreased in intensity upon irradiation by UV light ($\lambda = 254$ nm) and was completely quenched when **P2** reached the PSS. The various colored fluorescence of the other polymer solutions was also quenched by UV irradiation (see Figures 3 and 6). The fluorescence intensity ratios between the open state and PSS ($I_{\text{open}}/I_{\text{PSS}}$) of the polymer solutions were estimated as 50–190 and are summarized in Table 3. Fluorescence quenching might occur due to efficient energy transfer from the excited

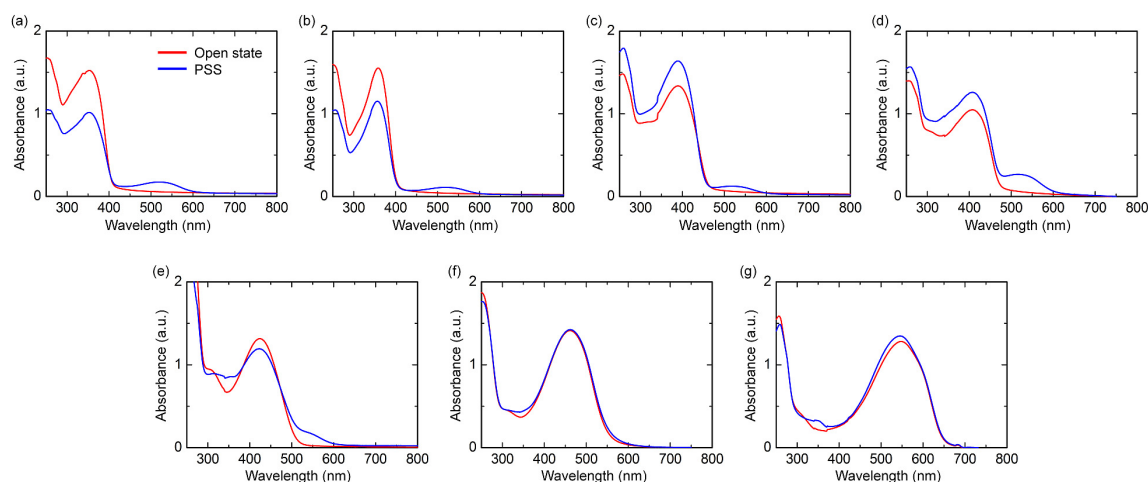


Figure 7. UV-vis absorption spectra of cast films of (a) **P1**, (b) **P2**, (c) **P3**, (d) **P4**, (e) **P5**, (f) **P6**, and (g) **P7** in an open state (red line) and a PSS (blue line).

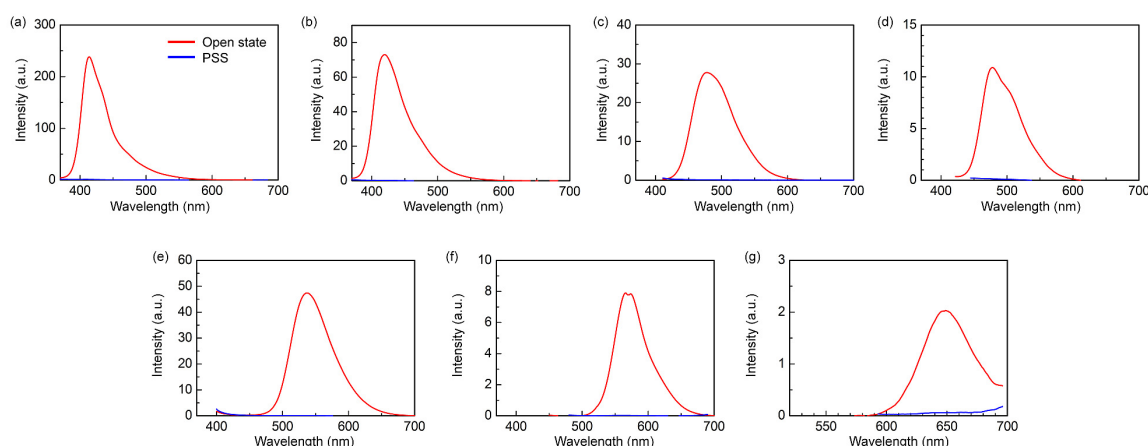


Figure 8. PL spectra of cast films of (a) **P1**, (b) **P2**, (c) **P3**, (d) **P4**, (e) **P5**, (f) **P6**, and (g) **P7** in an open state (red line) and a PSS (blue line).

polymer conjugated backbone to the DE side chain in the closed form, and the DE side chain subsequently releases the energy through nonradiative transition from the excited to ground states.⁴⁹⁻⁵¹ The quenched fluorescence was regenerated by irradiation with visible light ($\lambda > 400$ nm), which photoisomerized the DE closed form to the open form. As a result, CHCl_3 solutions of the polymers exhibited reversible photoswitching behavior in fluorescence between emission and quenching using external UV and visible light stimuli.

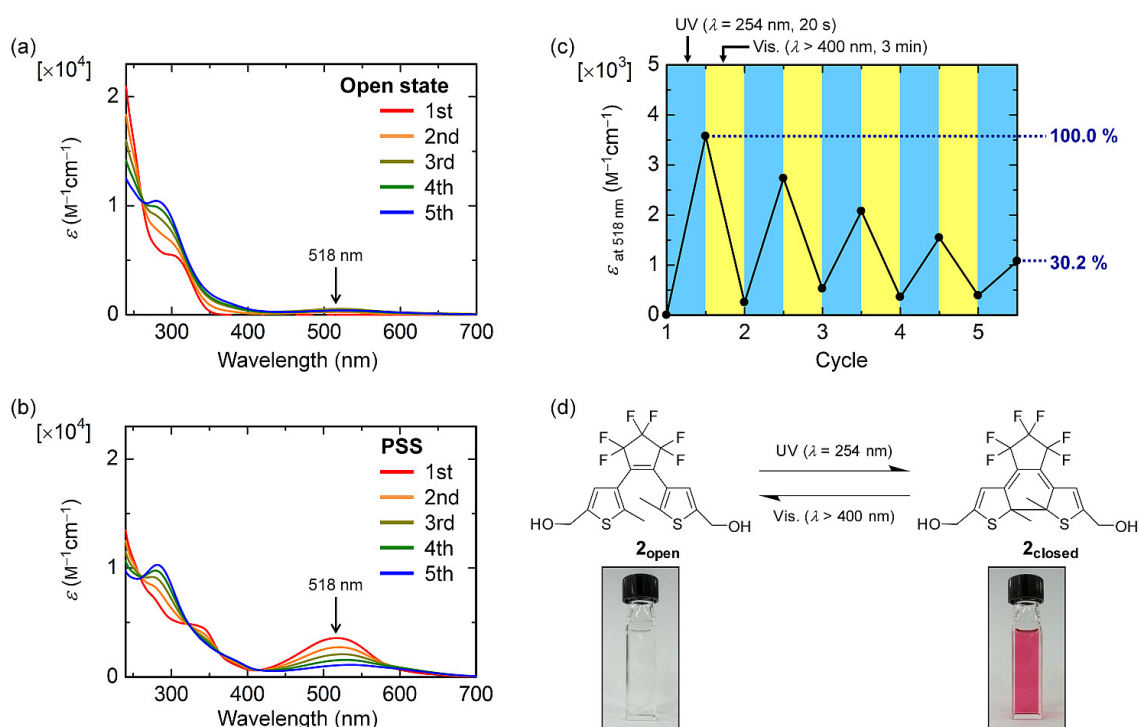


Figure 9. Spectral changes in UV–vis absorption of a CHCl_3 solution ($c = 4.0 \times 10^{-5} \text{ M}$) of DE moiety **2** in (a) an open state and (b) a PSS during the photoisomerization cycle. (c) Change in the extinction coefficient (ϵ) at 518 nm of **2** through the photoisomerization. A photoisomerization cycle consists of irradiation of UV light ($\lambda = 254 \text{ nm}$) for 20 s and then visible light ($\lambda > 400 \text{ nm}$) for 3 min. (d) Structural change of **2** through the photoisomerization. Insets show the photo images of **2** in a open state and a PSS.

Similar to the CHCl_3 solutions, **P1–P7** cast films also exhibited reversible spectral changes in absorption and fluorescence (Figures 7 and 8). Interestingly, the polymer cast films showed the distinct photoswitching behavior in fluorescence with high $I_{\text{open}}/I_{\text{PSS}}$ values of 80–790 (see Table 3). The $I_{\text{open}}/I_{\text{PSS}}$ values of the cast films are larger than those of the CHCl_3 solutions, indicating that the energy of the excited polymer backbone efficiently transfers to the DE side chain in a solid state, i.e., in a cast film where the polymer chains are located close to each other. Figure 3 shows photographs of the CHCl_3 solutions and cast films of **P1–P7** in the open state and the PSS, which visually demonstrates the reversible photoswitching behavior of various colored fluorescence.

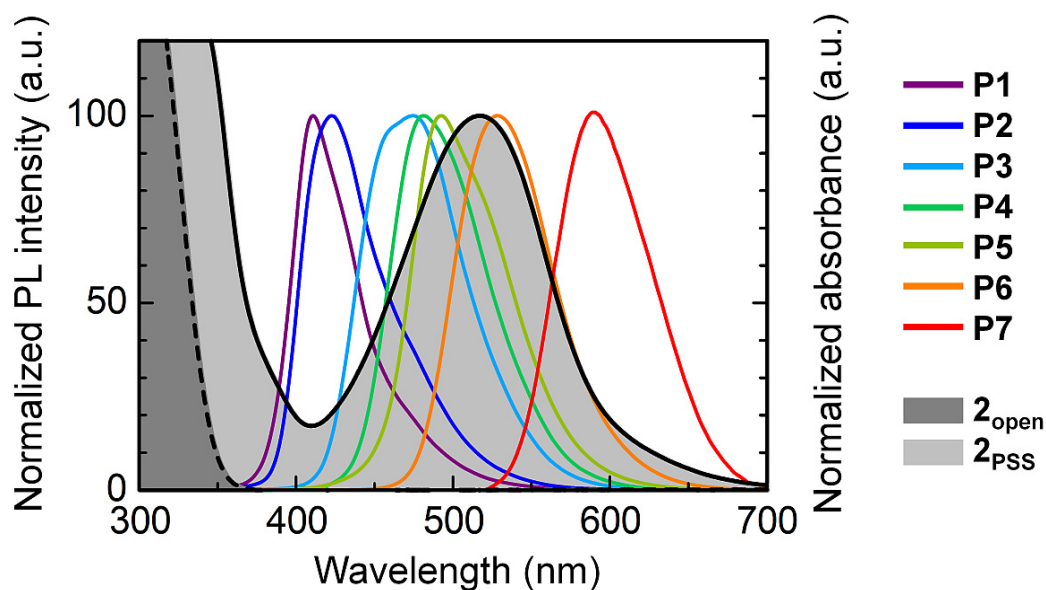


Figure 10. PL spectra of CHCl_3 solutions ($c = 4.0 \times 10^{-5} \text{ M}$) of **P1–P7** in an open state and UV–vis absorption spectra of CHCl_3 solutions ($c = 4.0 \times 10^{-5} \text{ M}$) of DE moiety **2** in an open state (dark gray area) and a PSS (light gray area).

It should be noted that the DE moiety in an open state has no absorption band in the region of 350–800 nm (see Figure 10), and hence no photoisomerization occurs on the DE moiety upon the irradiation of excitation light of $\lambda = 350$ and 380 nm. On the other hand, the DE moiety in a PSS has an absorption band covering the wavelength of 300–400 nm. Thus, the DE moiety may partially photoisomerize from the closed to open form under irradiation of the excitation light, resulting in changes in the absorption spectra. To avoid the photoisomerization, the photoluminescence spectra of the polymers in a PSS were measured in a short time (less than 14 sec).

Fatigue Resistance in Fluorescence Photoswitching of Polymers. We investigated the fatigue resistance of all the polymer films. As shown in Figure 11, the photoswitching behavior was maintained after repeating the photoisomerization cycle 5 times although the PL intensity decreased to 2.6–25.4 %. Moreover, Figure 12 shows spectral changes in UV–vis absorption of the polymer films in an open state. As indicated by the black arrows, the absorption band at 250 nm, corresponding to the DE moiety, also decreased in intensity with repeating the photoisomerization cycle. On the other hand, the absorption bands corresponding to the conjugated main chains were unchanged, except the case of **P5**. These results indicate that the DE moiety partially changed into an un-photochromic byproduct, suppressing the full regeneration of the polymer fluorescence. Because the UV light ($\lambda = 254$ nm) used for DE photoisomerization has relatively high energy and can damage the photochromic conjugated structure of DE, the un-photochromic byproduct might be formed. This is also supported by the spectral change in UV–vis absorption of the DE moiety, **2**, during the photoisomerization cycle (Figures 9a and b). In both the open state and PSS, the absorption band at 250 nm decreased in intensity with repeating the photoisomerization cycle, whereas the absorption band at 300 nm increased in intensity. This result indicates that the DE moiety gradually changed into an un-photochromic byproduct. The extinction coefficient at 518 nm, which corresponds to the DE closed form, also decreased to 30.2 % after 5 cycles of the photoisomerization (see Figure 9c), implying a loss of the photochromic property. The decrease in fatigue resistance of all the polymers, therefore, is due to the degradation of the DE moiety. Interestingly, the absorption band of **P5** main chain decreased in intensity and blue-shifted with every photoisomerization cycle, as shown Figure 12e (green arrow). Such a change in absorption denotes a decrease in the conjugated length of **P5** main chain, indicating that the polymer conjugated backbone is photo-oxidized by irradiating UV light. However, **P5** showed relatively better fatigue resistance from the viewpoint of PL intensity, as shown in Figure 11. Thus, in this case, the photoswitching behavior of the fluorescence is affected by the degradation of DE moiety rather than the photo-oxidization of the conjugated main chain.

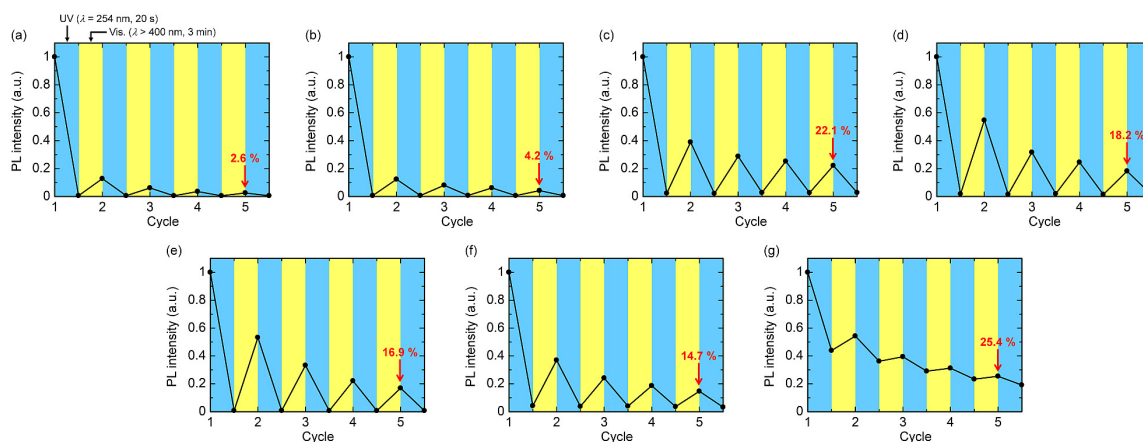


Figure 11. Changes in PL intensity of cast films of (a) **P1**, (b) **P2**, (c) **P3**, (d) **P4**, (e) **P5**, (f) **P6**, and (g) **P7** during the photoisomerization cycle. A photoisomerization cycle consists of irradiation of UV light ($\lambda = 254$ nm) for 20 s and then visible light ($\lambda > 400$ nm) for 3 min.

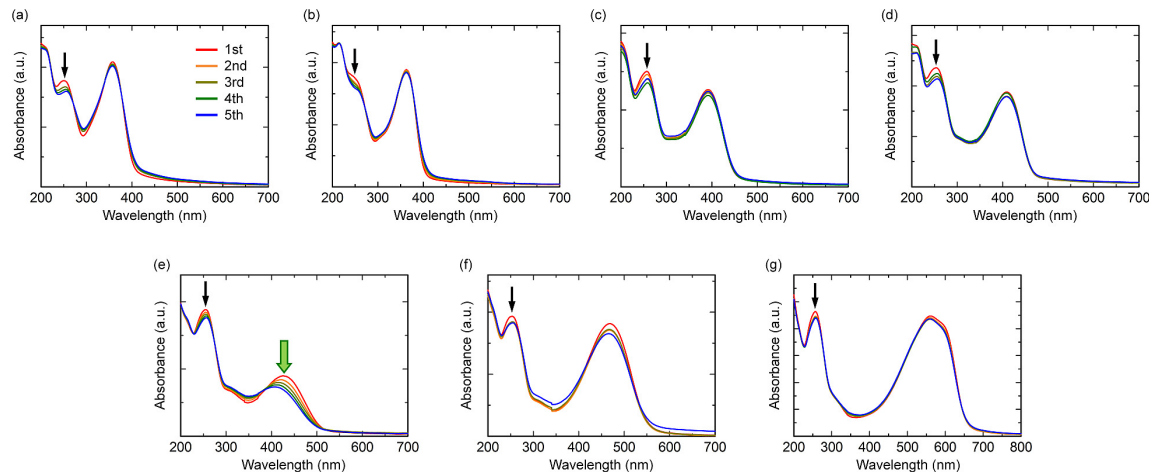


Figure 12. Spectral changes in UV-vis absorption of cast films of (a) **P1**, (b) **P2**, (c) **P3**, (d) **P4**, (e) **P5**, (f) **P6**, and (g) **P7** in an open state during the photoisomerization cycle. A photoisomerization cycle consists of irradiation of UV light ($\lambda = 254$ nm) for 20 s and then visible light ($\lambda > 400$ nm) for 3 min.

Preparation Method for Polymer Nanosphere Solutions. Polymer nanospheres dispersed in water were prepared using the reprecipitation method with ultrasonication.⁵⁵ A schematic of the procedure is shown in Figure 13a, and the process details are described as follows. Solutions of the polymers (0.31–0.48 mg, see Table 4) in THF (1.5 mL) were added dropwise into water (10 mL) at 0°C under ultrasonication using an ultrasonic homogenizer (130 W, 20 kHz). The THF solvent was removed under reduced pressure at 55°C to give the polymer nanosphere solutions in water. Figure 13b shows photo images of **P1–P7** nanosphere solutions in water. The polymer nanospheres remained dispersed in water even if they were held at room temperature for several months, indicating the high stability of the nanospheres.



Figure 13. (a) Schematic procedure of reprecipitation method. (b) Photo images of **P1–P7** nanosphere solutions in water.

Table 4. Conditions for nanosphere preparation and the particle size of the nanospheres.

Polymer	Conditions for nanosphere preparation ^a		Particle size (nm)	
	Polymer amount (mg)	(μ mol)	Average	Distribution
P1	0.479	0.47	50	30–80
P2	0.464	0.38	40	30–60
P3	0.452	0.44	45	30–50
P4	0.312	0.25	60	40–75
P5	0.398	0.44	70	50–90
P6	0.428	0.41	20	15–50
P7	0.412	0.39	35	25–50

^a The polymers were dissolved in THF (1.5 mL) and then added dropwise into water (10 mL) under ultrasonication.

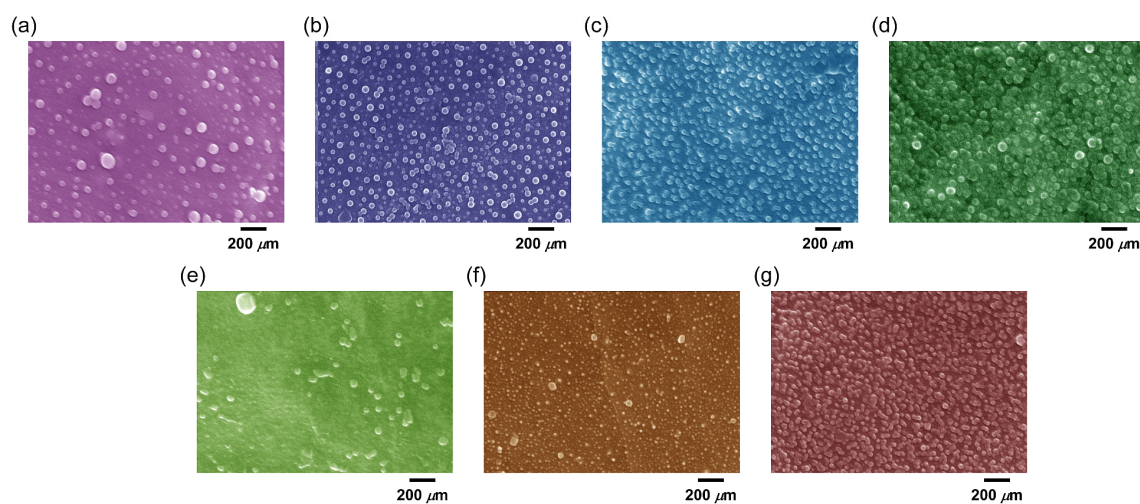


Figure 14. SEM images of polymer nanospheres. (a) **P1**, (b) **P2**, (c) **P3**, (d) **P4**, (e) **P5**, (f) **P6**, and (g) **P7**.

Morphology of Polymer Nanospheres. The morphology of the polymer nanospheres was observed using scanning electron microscopy (SEM). Figure 14 shows the SEM images of **P1–P7** nanospheres, which indicate that all polymers form spherical aggregates with an average particle size of 20–70 nm in diameter. The size distribution was also estimated using the SEM images, as summarized in Table 4.

Photoswitching Behavior in Absorption and Fluorescence of Polymer Nanospheres. Figure 15 shows the ultraviolet–visible (UV–Vis) absorption and PL spectra of nanosphere solutions of **P1–P7** in the open state. Similar to both of the CHCl_3 solutions and the cast films, the nanosphere solutions showed absorption and fluorescence bands corresponding to the π – π^* and π^* – π transitions of the polymer conjugated backbones. Thus, the peak wavelengths in both absorption and fluorescence were red-shifted with the increase in the effective conjugated length of the polymer backbone in the order of **P1–P7**. Namely the fluorescence color gradually changed from blue to red. The absorption and fluorescence peak wavelengths are summarized in Tables 2 and 3.

Interestingly, the absorption peaks in the nanosphere solutions exhibited intermediate values between those of the solutions and the cast films. This result implies that the nanosphere solution represents an intermediate state between an isolated state and an aggregated state. At the same time, the fluorescence peak wavelengths were similar to those in the cast films. It is well known that the fluorescence of conjugated polymers involve quasi-localized chromophores in the polymer backbone.^{56, 57} In addition, the energy in the excited conjugated backbone transfers intra-molecularly and is finally trapped in low-transition-energy regions, the so-called "exciton traps". Thus, the fluorescence spectra tend to reflect the fluorescent property of the exciton traps rather than that of the average of the entire conjugated backbone.⁵⁸ Hence, these results indicate that **P1–P7** nanospheres have exciton traps similar to those of the cast films because the polymers exist in an aggregated state in both the nanosphere solutions and the cast films.

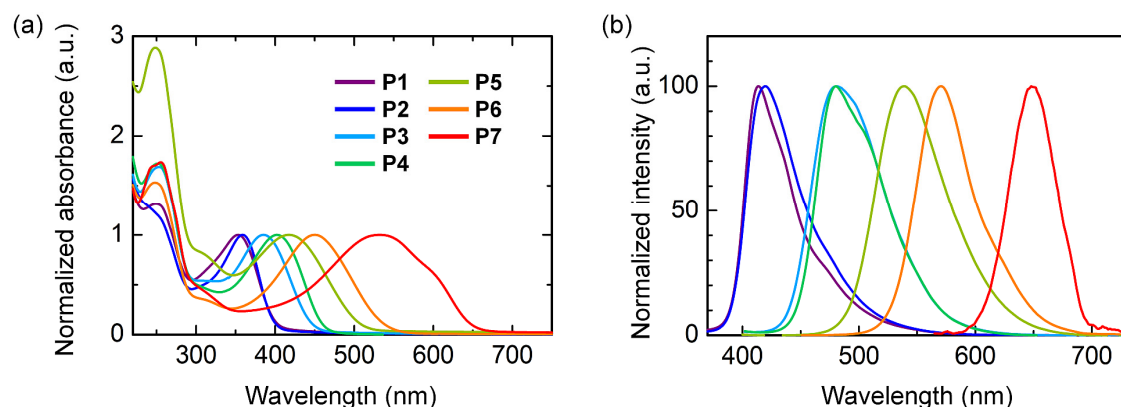


Figure 15. (a) UV-vis absorption and (b) normalized PL spectra of **P1–P7** nanosphere solutions in water.

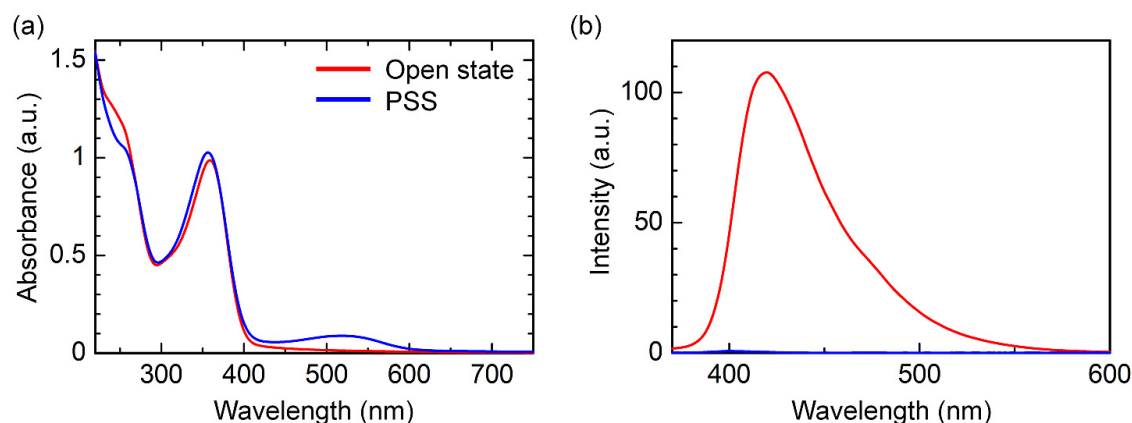


Figure 16. (a) UV-vis absorption and (b) PL spectra of polymer nanosphere solutions of **P2** in an open state and a PSS.

The photo-induced spectral changes in both absorption and fluorescence were also investigated. Figure 16a shows the absorption change of the **P2** nanosphere solution induced by external light stimuli. The absorption spectra show that the band at approximately 255 nm decreased in intensity with irradiation by UV light, whereas the bands at approximately 350 nm and 520 nm increased. This result indicates that the DE side chains photoisomerize from the open form to the closed form even in the polymer nanospheres. Subsequent irradiation by visible light regenerated the original absorption spectrum of **P2** in the open state through reverse photoisomerization of the DE moiety. Figure 16b shows the fluorescence change of the polymer nanosphere

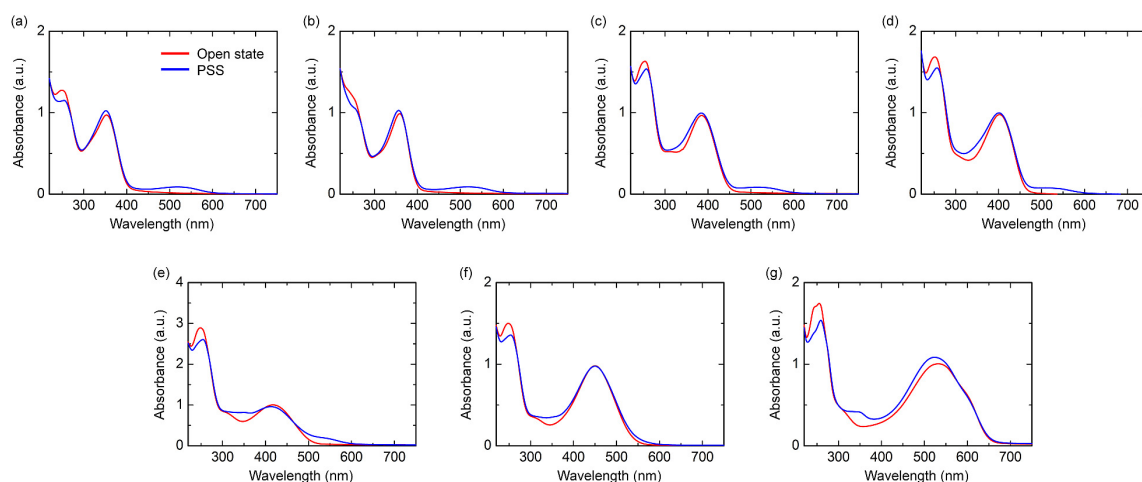


Figure 17. UV-vis absorption spectra of polymer nanosphere solutions of (a) **P1**, (b) **P2**, (c) **P3**, (d) **P4**, (e) **P5**, (f) **P6**, and (g) **P7** in an open state (red line) and a PSS (blue line).

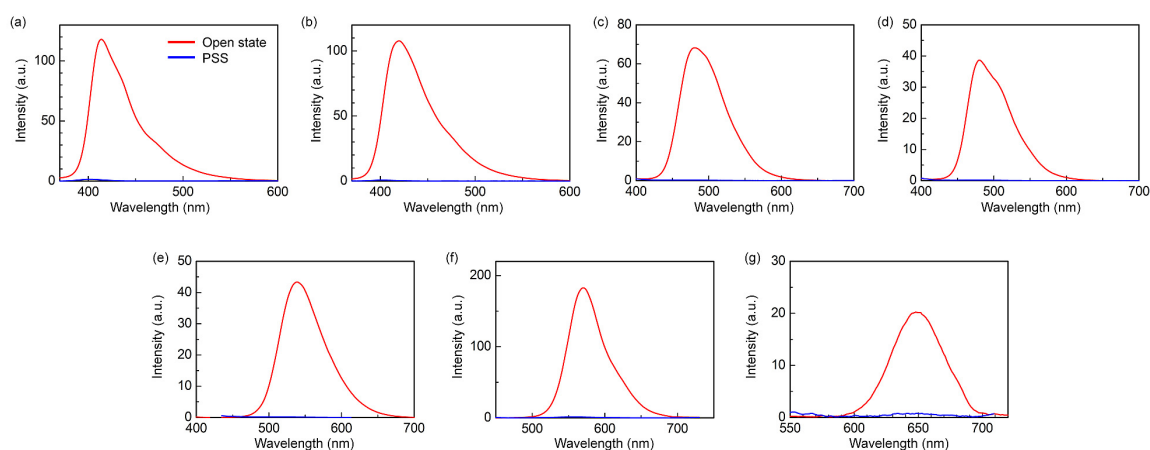


Figure 18. PL spectra of polymer nanosphere solutions of (a) **P1**, (b) **P2**, (c) **P3**, (d) **P4**, (e) **P5**, (f) **P6**, and (g) **P7** in an open state (red line) and a PSS (blue line).

solution. Similarly to the CHCl_3 solutions and the cast films, the fluorescence of **P2** nanospheres were quenched by UV irradiation and subsequently regenerated upon irradiation with visible light. The other nanosphere solutions of **P1** and **P3–P7** also exhibited the same behavior in both absorption and fluorescence regardless of the fluorescent colors (see Figures 3, 17, and 18). These results successfully demonstrated that the multi-colored fluorescence of the polymer nanospheres was

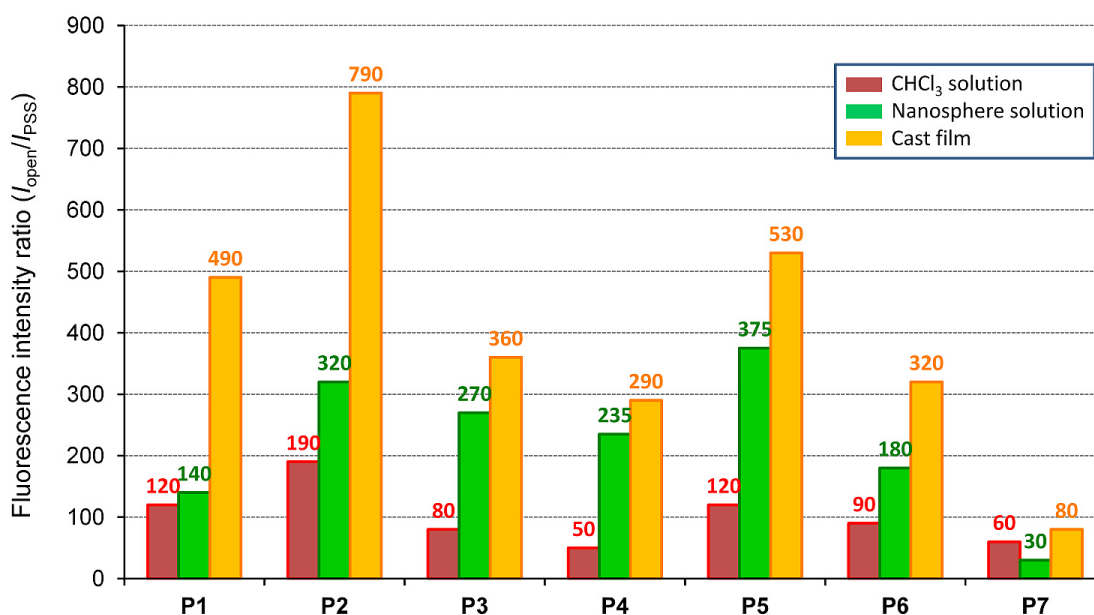


Figure 19. Fluorescence intensity ratios ($I_{\text{open}}/I_{\text{PSS}}$) in CHCl_3 solutions, nanosphere solutions, and cast films of **P1–P7**.

photoswitchable between emission and quenching using external light stimuli. In addition, the $I_{\text{open}}/I_{\text{PSS}}$ values were evaluated as 30–375, as summarized in Table 3, and represent intermediate values between those of the solutions and the cast films, except for **P7** (see Figure 19). This result also implies that the nanosphere solution is an intermediate state between an isolated state and an aggregated state.

It is worth noting that the red-colored fluorescence of **P7** nanosphere solution is unexpectedly weak in intensity, and therefore, it is difficult to visually observe the fluorescence photoswitching on a photo image (Figure 3). This is due to the high π -stacking feature of the PT backbone consisting only of thienylene rings with a planar structure, which causes a decrease in the fluorescence intensity in a solid state. In addition, the energy in the excited PT backbone is easily decayed due to the polarizable environment of the surrounding water solvent. The red-colored fluorescence of **P7** nanosphere solution is therefore too weak to be observed.

Mechanism of Fluorescence Quenching. As shown in Figure 10, the absorption band of the DE moiety **2** in a PSS overlaps the fluorescence bands of all the polymers although the absorption band of **2** in an open state does not. This is because the absorption band at 518 nm corresponding to the DE closed form extends over the visible region. It is therefore anticipated that the fluorescence of the polymers may be quenched through an energy transfer such as Förster resonance energy transfer (FRET) from the polymer conjugated backbone to the DE closed form, which requires the spectral overlap between the luminescence of donor (polymer conjugated backbone, herein) and the absorption of acceptor (DE closed form).

Furthermore, we investigated whether the energy transfer from the DE open form to the polymer conjugated backbone occurs or not. As mentioned above, the DE open form is partially degraded through the photoisomerization, which causes a decrease in intensity of the absorption band at around 250 nm even in CHCl_3 solution (see Figure 20). Thus, if there might be any energy transfer from the DE open form to the polymer conjugated backbone, the polymer fluorescence excited by UV light of $\lambda = 250$ nm also should decrease in intensity after the photoisomerization. If not, the polymer fluorescence intensity should keep unchanged. Hence we measured

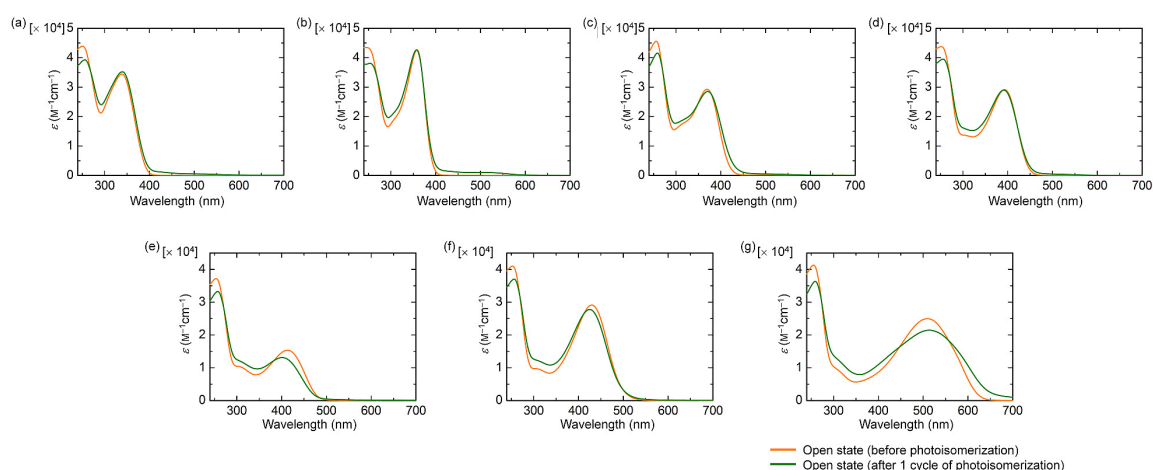


Figure 20. Spectral changes in UV–vis absorption of CHCl_3 solutions ($c = 4.0 \times 10^{-5}$ M) of (a) **P1**, (b) **P2**, (c) **P3**, (d) **P4**, (e) **P5**, (f) **P6**, and (g) **P7** in an open state before and after 1 cycle of photoisomerization. The photoisomerization cycle consists of irradiation of UV light ($\lambda = 254$ nm) for 50 s and then visible light ($\lambda > 400$ nm) for 3 min.

excitation spectra of CHCl_3 solutions of the polymers in an open state, and then compared the spectra before and after 1 cycle of the photoisomerization (Figure 21). The result of the excitation spectra of **P3–P6** showed that the PL intensity was kept unchanged even after the photoisomerization of the DE moiety (see, black arrows in Figure 21). This indicates that the PL intensity is not affected by the decrease in relative amount of DE open form, i.e., there is no energy transfer from the DE open form to the polymer conjugated backbone. Because the DE open form shows no

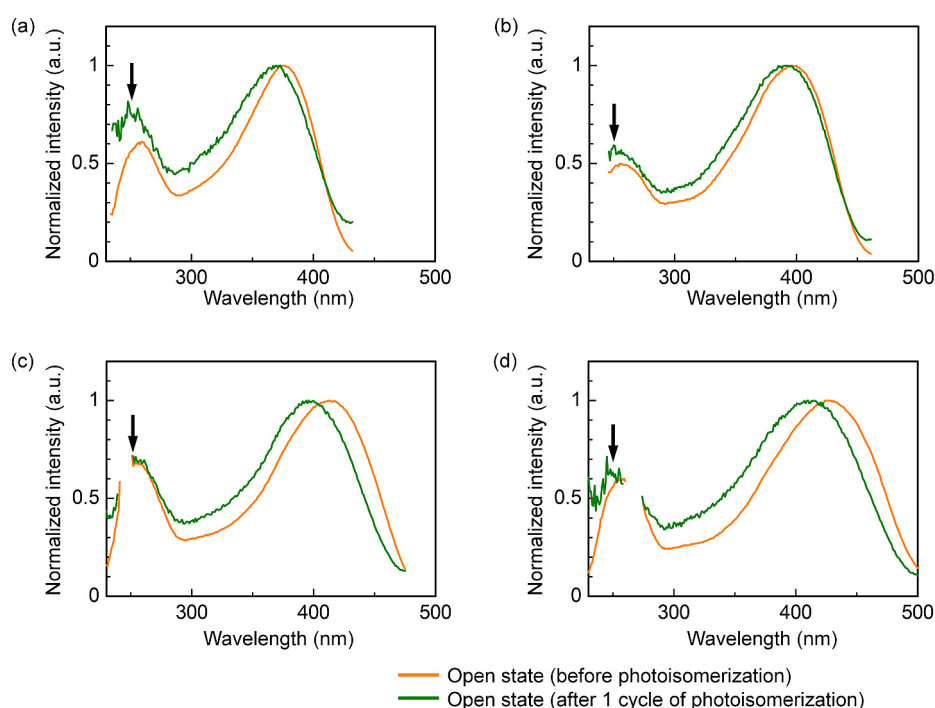


Figure 21. Changes in excitation spectra of CHCl_3 solutions ($c = 4.0 \times 10^{-5}$ M) of (a) **P3**, (b) **P4**, (c) **P5**, and (d) **P6** in an open state before and after 1 cycle of photoisomerization. The photoisomerization cycle consists of irradiation of UV light ($\lambda = 254$ nm) for 50 s and then visible light ($\lambda > 400$ nm) for 3 min. The intensity is normalized using the excitation peaks of the polymer conjugated backbones as a standard. Black arrows depicted in the spectra represent the excitation peak at 250 nm. Note that the PL intensity of **P1**, **P2**, and **P7** in an open state substantially decreased after 1 cycle of the photoisomerization, and therefore the excitation spectra of **P1**, **P2**, and **P7** were removed.

luminescence, this result implies that the energy transfer between the polymer conjugated backbone and the DE moiety may occur through the FRET mechanism, suggesting the fluorescence quenching process via FRET. However, it should be emphasized that the distance between the polymer conjugated backbone and the DE moiety is estimated to be 4–6 Å by using molecular mechanics calculation. Hence, Dexter type energy transfer, which can occur at a short distance within 10 Å via an electron-exchange process, is also regarded as an alternative mechanism of the energy transfer from the polymer backbone to the DE closed form. The detail mechanism of the fluorescence quenching still remains unclear and needs further investigation.

Conclusion.

Full-colored fluorescent conjugated copolymers with photoswitchable emissions were synthesized by combining phenylene- and thienylene-based main chains with photochromic DE side chains. The CHCl_3 solutions and cast films of the polymers exhibited various colored fluorescence in visible wavelengths of 400–700 nm corresponding to their main chain structures. The fluorescence was reversibly photoswitched between emission and quenching via DE photoisomerization using external UV and visible light stimuli. The reprecipitation method with ultrasonication enabled the polymers to form spherical aggregates with diameters of 20–70 nm in water. After investigating and comparing the optical properties, the resulting nanosphere solutions were estimated to exist in an intermediate state between an isolated state in solution and an aggregated state in cast film from the viewpoint of the luminescent properties. The fluorescence photoswitching behavior was also observed in the nanosphere solutions, except for the PT derivative. The current study demonstrated that the visible fluorescence of conjugated polymers were reversibly switchable between emission and quenching using the photoisomerizing DE side chain regardless of the fluorescent color and polymer chain aggregation. It is expected that the polymers synthesized in this work will be useful for creating photoresponsive optoelectronic devices.

Experimental Section

1. Measurements. NMR spectra were measured with JEOL EX-270, JEOL AL-400, and JEOL EX-400 spectrometers. Chemical shifts were represented in parts per million downfield from tetramethylsilane (TMS) as an internal standard. High-resolution mass spectra (HRMS) were obtained by using JEOL JMS-SX102A mass spectrometer. Elemental analyses were performed by Yanako CHN Corders (MT-3, MT-5 and MT-6), JSL JM-10, Mitsubishi chemical analytech AQF-100, and Dionex ICS-1500.

UV-vis absorption spectra were measured with JASCO V-570 UV/VIS/NIR spectrophotometer, and PL spectra were measured with JASCO FP-750 spectrofluorometer. All optical measurements were performed using a quartz cell or a quartz substrate. SEM was performed with JEOL JSM-7500F. The samples were coated with Pt-Pd alloy by using JEOL JFC-1600 ion coater before measurements of SEM. GPC was performed at 40 °C with a system consisting of Agilent Technologies PLgel 5 μ m MIXED-D column, JASCO CO-2065 Plus column oven, JASCO UV-2070 Plus UV/VIS detector, and JASCO PU-2080 Plus HPLC pump, where the instrument was calibrated by polystyrene standard. THF was used as an eluent and the flow rate was 1.0 mL/min. Photoirradiation was carried out at room temperature by using a UV mercury lamp ($\lambda = 254$ nm, 4 W) or a visible lamp ($\lambda > 400$ nm, 100 W) as the light source. The level of DE conversion from the open form to the closed form, which is defined as $\{[\text{closed form}]/([\text{open form}] + [\text{closed form}])\} \times 100$, was confirmed through ^1H NMR measurement in CDCl_3 . Ratio of the open form and the closed form was determined by using the integration values of CH_2 protons neighboring a thienylene ring of DE. The relative fluorescence quantum yield (Φ) was evaluated by using quinine sulfate in 1.0 M sulfuric acid as a standard. Ultrasonication was carried out using SONICS VCX 130.

2. Materials. All chemicals were used as purchased. Diisopropyl azodicarboxylate (40 wt % in toluene, ca. 1.9 M; DIAD), DCC, and DMAP were purchased from Tokyo Chemical Industry Co., Ltd. Triphenylphosphine (TPP) was purchased from Wako Pure Chemical Industries, Ltd. 2,5-Dibromobenzoic acid, 2-hexyl-1-decanol,

4,4'-biphenyldiboronic acid bis(neopentyl glycol) cyclic ester, 9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) cyclic ester, $\text{Pd}_2(\text{dba})_3$, $(2\text{-furyl})_3\text{P}$ and $\text{Pd}(\text{PPh}_3)_4$ were purchased from Aldrich Co., Ltd. Methyl 4-hydroxybenzoate, sodium carbonate (Na_2CO_3), potassium hydroxide (KOH), THF, dichloromethane (CH_2Cl_2), CHCl_3 and methanol (MeOH) were purchased from Nacalai Tesque, Inc. THF was freshly dried and distilled over sodium benzophenone ketyl under Ar. CH_2Cl_2 was distilled over CaCl_2 under argon atmosphere. MERCK silica gel 60 (particle size 0.063–0.200 mm) was used to purify compounds by column chromatography.

DE derivative **2** was synthesized according to previous literature.^{59, 60} Compounds **1**, **3**, **M1**, 2,5-dibromo-3-thenoic acid, and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene were prepared according to our previous works.^{49, 61} 4,4'-Biphenyldiboronic acid bis(1,3-propanediol) cyclic ester was synthesized by esterification of 4,4'-biphenyldiboronic acid with 1,3-propanediol. 9,9-Dihexylfluorene-2,7-diboronic acid bis(pinacol) cyclic ester was prepared according to previous literature.⁶² Photoresponsive polymers **P5** and **P6** were synthesized and reported in our previous work.⁴⁹

3. Synthesis. All syntheses were carried out under argon atmosphere.

4-(2-Hexyldecyloxy)benzoic acid (1). [Route A]: To a mixture of 2-hexyl-1-decanol (9.70 g, 40.0 mmol), TPP (11.5 g, 44.0 mmol), and methyl *p*-hydroxybenzoate (6.70 g, 44.0 mmol) in THF (70 mL) was added dropwise a solution of DIAD (23.2 mL, 44.1 mmol) in THF (20 mL) via a dropping funnel at 0 °C. The reaction mixture was stirred overnight at room temperature. After removing THF under reduced pressure, the residue was purified by column chromatography (silica gel; CHCl_3) to give methyl 4-(2-hexyldecyloxy)benzoate as yellow oil. The oil was dissolved in MeOH (250 mL), mixed with a solution of KOH (11.2 g, 200 mmol) in water (40 mL), and then stirred for 12 h at 50 °C. After removing MeOH under reduced pressure, HCl was added into the aqueous solution at 0 °C. The crude product was extracted with CHCl_3 , washed with a saturated NaCl aqueous solution, and then dried over anhydrous Na_2SO_4 . The precipitate was removed by filtration

and the filtrate was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel; CHCl_3) to give **1** as light yellow oil (12.8 g, 88 %): ^1H NMR (400 MHz, CDCl_3 , TMS): δ = 0.88 (m, 6H; $(\text{CH}_2)_5\text{CH}_3$ and $(\text{CH}_2)_7\text{CH}_3$), 1.27–1.44 (m, 24H; $\text{OCH}_2\text{CH}(\text{CH}_2)_5\text{CH}_3$ and $\text{OCH}_2\text{CH}(\text{CH}_2)_7\text{CH}_3$), 1.79 (m, 1H; $\text{OCH}_2\text{CH}(\text{C}_6\text{H}_{13})\text{C}_8\text{H}_{17}$), 3.90 (d, J = 5.9 Hz, 2H; OCH_2CH), 6.93 (d, J = 8.8 Hz, 2H; Ph-*H ortho* to $\text{OCH}_2\text{CH}(\text{C}_6\text{H}_{13})\text{C}_8\text{H}_{17}$), 8.06 ppm (d, J = 8.8 Hz, 2H; Ph-*H meta* to $\text{OCH}_2\text{CH}(\text{C}_6\text{H}_{13})\text{C}_8\text{H}_{17}$); ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ = 14.1, 22.7, 26.82, 26.85, 29.3, 29.6, 29.7, 30.0, 31.32, 31.34, 31.86, 31.93, 37.9, 71.2, 114.3, 121.4, 132.3, 164.0, 172.1 ppm; HRMS (ESI, m/z): $[\text{M} - \text{H}^+]$ calcd for $\text{C}_{23}\text{H}_{38}\text{O}_3$: 361.2748; Found: 361.2754; Anal. calcd for $\text{C}_{23}\text{H}_{38}\text{O}_3$: C 76.20, H 10.57; Found: C 76.09, H 10.69. [Route **B**]: **1** was synthesized by using the same procedure with our previous study.⁴⁹

1-{5-(2,5-Dibromo-3-thenoyloxymethyl)-2-methyl-3-thienyl}-2-(5-hydroxymethyl-2-methyl-3-thienyl)-3,3,4,4,5,5-hexafluorocyclopentene (4). To a mixture of **2** (2.50 g, 5.84 mmol), TPP (1.70 g, 6.48 mmol), and 2,5-dibromo-3-thenoic acid (1.67 g, 5.84 mmol) in THF (100 mL) was added dropwise a solution of DIAD (3.4 mL, 6.46 mmol) in THF (20 mL) via a dropping funnel at 0 °C. The reaction mixture was stirred overnight at room temperature. After removing the solvent under reduced pressure, the residue was purified by column chromatography (silica gel; CHCl_3) to give **4** as a pale yellow solid (1.88 g, 46 %): ^1H NMR (400 MHz, CDCl_3 , TMS): δ = 1.87 (s, 3H; thienyl- CH_3), 1.92 (s, 3H; thienyl- CH_3), 4.75 (s, 2H; CH_2OH), 5.35 (s, 2H; COOCH_2), 6.95 (s, 1H; thienyl-*H* in DE), 7.08 (s, 1H; thienyl-*H* in DE), 7.34 ppm (s, 1H; thienyl-*H*); ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ = 14.46, 14.48, 59.9, 60.9, 111.7, 119.9, 124.3, 124.6, 124.8, 128.4, 131.1, 131.6, 135.5, 142.2, 142.4, 143.6, 160.3 ppm; HRMS (ESI, m/z): $[\text{M} + \text{Na}^+]$ calcd for $\text{C}_{22}\text{H}_{14}\text{Br}_2\text{F}_6\text{O}_3\text{S}_3$: 718.8248; Found: 718.8226; Anal. calcd for $\text{C}_{22}\text{H}_{14}\text{Br}_2\text{F}_6\text{O}_3\text{S}_3$: C 37.95, H 2.03, Br 22.95, S 13.81; Found: C 37.85, H 2.08, Br 22.88, S 13.67.

1-{5-(2,5-Dibromo-3-thenoyloxymethyl)-2-methyl-3-thienyl}-2-[5-{4-(2-hexyloxy)benzoyloxymethyl}-2-methyl-3-thienyl]-3,3,4,4,5,5-hexafluorocyclopentene (M2). A solution of **1** (1.15 g, 3.17 mmol), **4** (1.66 g, 2.38 mmol), DCC (0.641 g, 3.11 mmol), and DMAP (0.324 g, 2.65 mmol) in CH_2Cl_2 (80 mL) was

stirred for 60 h at room temperature. The precipitate was removed by filtration and the filtrate was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel; hexane/ethyl acetate = 19:1) to give **M2** as colorless oil (2.30 g, 93 %): ^1H NMR (400 MHz, CDCl_3 , TMS): δ = 0.87 (m, 6H; $(\text{CH}_2)_5\text{CH}_3$ and $(\text{CH}_2)_7\text{CH}_3$), 1.27–1.43 (m, 24H; $\text{OCH}_2\text{CH}(\text{CH}_2)_5\text{CH}_3$ and $\text{OCH}_2\text{CH}(\text{CH}_2)_7\text{CH}_3$), 1.79 (m, 1H; $\text{OCH}_2\text{CH}(\text{C}_6\text{H}_{13})\text{C}_8\text{H}_{17}$), 1.87 (s, 3H; thienyl- CH_3), 1.88 (s, 3H; thienyl- CH_3), 3.88 (d, J = 5.8 Hz, 2H; OCH_2CH), 5.34 (s, 2H; COOCH_2), 5.37 (s, 2H; COOCH_2), 6.90 (d, J = 8.8 Hz, 2H; Ph- H *ortho* to $\text{OCH}_2\text{CH}(\text{C}_6\text{H}_{13})\text{C}_8\text{H}_{17}$), 7.09 (s, 2H; thienyl- H in DE), 7.33 (s, 1H; thienyl- H), 7.97 (d, J = 8.8 Hz, 2H; Ph- H *meta* to $\text{OCH}_2\text{CH}(\text{C}_6\text{H}_{13})\text{C}_8\text{H}_{17}$); ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ = 14.1, 14.4, 22.7, 26.80, 26.82, 29.3, 29.6, 29.7, 30.0, 31.29, 31.31, 31.8, 31.9, 37.9, 60.5, 60.9, 71.2, 111.6, 114.2, 119.9, 121.6, 124.3, 124.5, 127.6, 128.2, 131.1, 131.6, 131.7, 135.6, 136.9, 143.2, 143.7, 160.3, 163.5, 166.0 ppm; HRMS (ESI, m/z) [$\text{M} + \text{NH}_4^+$] calcd for $\text{C}_{45}\text{H}_{50}\text{Br}_2\text{F}_6\text{O}_5\text{S}_3$: 1058.1409; Found: 1058.1389; Anal. calcd for $\text{C}_{45}\text{H}_{50}\text{Br}_2\text{F}_6\text{O}_5\text{S}_3$: C 51.93, H 4.84, Br 15.35, S 9.24; Found: C 52.08, H 4.79, Br 15.31, S 9.21.

Photoresponsive poly(*para*-phenylene) derivative (P1). To a solution of **M1** (130 mg, 0.13 mmol), 4, 4'-biphenyldiboronic acid bis(neopentyl glycol) cyclic ester (47.2 mg, 0.13 mmol), and $\text{Pd}(\text{PPh}_3)_4$ (1.5 mg, 1.3 μmol) in THF (2 mL) was added 40 % Na_2CO_3 aqueous solution (2 mL) and then the mixture was stirred overnight at 60 $^\circ\text{C}$. The reaction mixture was poured into a large amount of water (300 mL) and vigorously stirred for 1 h. The resulting precipitate was collected by filtration, dissolved in minimum amount of THF (3 mL), and reprecipitated by stirring in methanol (300 mL) for 1 h. After filtration, the product was dried under vacuum to give white powder (115 mg, 89 %): ^1H NMR (400 MHz, CDCl_3 , TMS): δ = 0.89 (m, 6H, $(\text{CH}_2)_5\text{CH}_3$ and $(\text{CH}_2)_7\text{CH}_3$), 1.18 (m, 24H, $\text{OCH}_2\text{CH}(\text{CH}_2)_5\text{CH}_3$ and $\text{OCH}_2\text{CH}(\text{CH}_2)_7\text{CH}_3$), 1.33 (m, 1H, $\text{OCH}_2\text{CH}(\text{C}_6\text{H}_{13})\text{C}_8\text{H}_{17}$), 1.71 (s, 3H, thienyl- CH_3), 1.76 (s, 3H, thienyl- CH_3), 3.78 (d, 2H, J = 5.6 Hz, OCH_2CH), 5.15 (s, 2H, COOCH_2), 5.27 (s, 2H, COOCH_2), 6.81 (d, 2H, J = 8.2 Hz, Ph- H *ortho* to $\text{OCH}_2\text{CH}(\text{C}_6\text{H}_{13})\text{C}_8\text{H}_{17}$), 6.92 (s, 1H thienyl- H in DE), 6.98 (s, 1H, thienyl- H in DE),

7.16–7.77 (m, 10H, Ph-*H* in main chain), 7.88 (d, 2H, $J = 8.2$ Hz, Ph-*H meta* to $\text{OCH}_2\text{CH}(\text{C}_6\text{H}_{13})\text{C}_8\text{H}_{17}$), 8.07 (m, 1H, Ph-*H* in main chain).

Photoresponsive poly(fluorene phenylene) derivative (P2). The same procedure with **P1** was employed by using **M1** (172.0 mg, 0.17 mmol), 9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) cyclic ester (83.5 mg, 0.17 mmol), $\text{Pd}(\text{PPh}_3)_4$ (1.96 mg, 1.7 μmol), THF (2 mL), and 40 % Na_2CO_3 aqueous solution (2 mL). The product was obtained as white powder (184 mg, 92 %): ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta = 0.69$ (m, 6H, $\text{C}((\text{CH}_2)_5\text{CH}_3)_2$), 0.80 (m, 6H, $(\text{CH}_2)_5\text{CH}_3$ and $(\text{CH}_2)_7\text{CH}_3$), 1.02 (m, 16H, $\text{C}(\text{CH}_2(\text{CH}_2)_4\text{CH}_3)_2$), 1.20 (m, 24H, $\text{OCH}_2\text{CH}(\text{CH}_2)_5\text{CH}_3$ and $\text{OCH}_2\text{CH}(\text{CH}_2)_7\text{CH}_3$), 1.33 (m, 1H, $\text{OCH}_2\text{CH}(\text{C}_6\text{H}_{13})\text{C}_8\text{H}_{17}$), 1.72 (s, 3H, thienyl- CH_3), 1.74 (s, 3H, thienyl- CH_3), 1.98 (m, 4H, $\text{C}(\text{CH}_2\text{C}_5\text{H}_{11})_2$), 3.79 (d, 2H, $J = 6.0$ Hz, OCH_2CH), 5.09 (s, 2H, COOCH_2), 5.28 (s, 2H, COOCH_2), 6.82 (d, 2H, $J = 8.8$ Hz, Ph-*H ortho* to $\text{OCH}_2\text{CH}(\text{C}_6\text{H}_{13})\text{C}_8\text{H}_{17}$), 6.88 (s, 1H thienyl-*H* in DE), 7.00 (s, 1H, thienyl-*H* in DE), 7.16–7.79 (m, 8H, Ph-*H* and fluorene-*H* in main chain), 7.89 (d, 2H, $J = 8.8$ Hz, Ph-*H meta* to $\text{OCH}_2\text{CH}(\text{C}_6\text{H}_{13})\text{C}_8\text{H}_{17}$), 8.05 (m, 1H, Ph-*H* in main chain).

Photoresponsive poly(biphenylene thiophene) derivative (P3). The same procedure with **P1** was employed by using **M2** (136 mg, 0.13 mmol), 4,4'-biphenyldiboronic acid bis(1,3-propanediol) cyclic ester (42.0 mg, 0.13 mmol), $\text{Pd}(\text{PPh}_3)_4$ (1.50 mg, 1.30 μmol), THF (20 mL), and 40 % Na_2CO_3 aqueous solution (12 mL). The product was obtained as yellow powder (130 mg, 97 %): ^1H NMR (400 MHz, CDCl_3 , TMS): $\delta = 0.87$ (m, 6H, $(\text{CH}_2)_5\text{CH}_3$ and $(\text{CH}_2)_7\text{CH}_3$), 1.25 (m, 24H, $\text{OCH}_2\text{CH}(\text{CH}_2)_5\text{CH}_3$ and $\text{OCH}_2\text{CH}(\text{CH}_2)_7\text{CH}_3$), 1.36 (m, 1H, $\text{OCH}_2\text{CH}(\text{C}_6\text{H}_{13})\text{C}_8\text{H}_{17}$), 1.83 (s, 3H, thienyl- CH_3), 1.86 (s, 3H, thienyl- CH_3), 3.85 (d, 2H, $J = 5.6$ Hz, OCH_2CH), 5.30 (s, 2H, COOCH_2), 5.35 (s, 2H, COOCH_2), 6.87 (d, 2H, $J = 8.8$ Hz, Ph-*H ortho* to $-\text{OCH}_2\text{CH}(\text{C}_6\text{H}_{13})\text{C}_8\text{H}_{17}$), 7.07 (s, 2H thienyl-*H* in DE), 7.68 (m, 8H, Ph-*H* in main chain), 7.79 (s, 1H, thienylene-*H* in main chain), 7.96 (d, 2H, $J = 8.8$ Hz, Ph-*H meta* to $-\text{OCH}_2\text{CH}(\text{C}_6\text{H}_{13})\text{C}_8\text{H}_{17}$).

Photoresponsive poly(fluorene thiophene) derivative (P4). The same procedure with **P1** was employed by using **M2** (117 mg, 0.11 mmol), 9,9-dihexylfluorene-2,7-diboronic acid bis(pinacol) cyclic ester (66.0 mg, 0.11 mmol), $\text{Pd}(\text{PPh}_3)_4$ (1.27 mg,

1.1 μ mol), THF (20 mL), and 40 % Na_2CO_3 aqueous solution (12 mL). The product was obtained as yellow powder (122 mg, 89 %): ^1H NMR (400 MHz, CDCl_3 , TMS): δ = 0.77 (m, 6H, $\text{C}((\text{CH}_2)_5\text{CH}_3)_2$), 0.87 (m, 6H, $(\text{CH}_2)_5\text{CH}_3$ and $(\text{CH}_2)_7\text{CH}_3$), 1.11 (m, 16H, $\text{C}(\text{CH}_2(\text{CH}_2)_4\text{CH}_3)_2$), 1.26 (m, 24H, $\text{OCH}_2\text{CH}(\text{CH}_2)_5\text{CH}_3$ and $\text{OCH}_2\text{CH}(\text{CH}_2)_7\text{CH}_3$), 1.38 (m, 1H, $\text{OCH}_2\text{CH}(\text{C}_6\text{H}_{13})\text{C}_8\text{H}_{17}$), 1.85 (s, 3H, thienyl- CH_3), 1.87 (s, 3H, thienyl- CH_3), 2.06 (m, 4H, $\text{C}(\text{CH}_2\text{C}_5\text{H}_{11})_2$), 3.86 (d, 2H, J = 5.2 Hz, OCH_2CH), 5.29 (s, 2H, COOCH_2), 5.36 (s, 2H, COOCH_2), 6.89 (d, 2H, J = 8.4 Hz, Ph- H *ortho* to $\text{OCH}_2\text{CH}(\text{C}_6\text{H}_{13})\text{C}_8\text{H}_{17}$), 7.07 (s, 1H thienyl- H in DE), 7.10 (s, thienyl- H in DE), 7.45–7.79 (m, 7H, fluorene- H and thienylene- H in main chain), 7.96 (d, 2H, J = 8.4 Hz, Ph- H *meta* to $\text{OCH}_2\text{CH}(\text{C}_6\text{H}_{13})\text{C}_8\text{H}_{17}$).

Photoresponsive polythiophene derivative (P7). A solution of **M2** (104 mg, 0.10 mmol), $\text{Pd}_2(\text{dba})_3$ (0.92 mg, 1.00 μ mol), and (2-furyl) $_3\text{P}$ (0.93 mg, 4.00 μ mol) in THF (2 mL) was stirred at 50 $^\circ\text{C}$ for 30 min, followed by addition of 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (49.2 mg, 0.10 mmol). After stirred at 50 $^\circ\text{C}$ for 25 h, the reaction mixture was poured into a large amount of methanol (100 mL) containing HCl and then vigorously stirred for 3 h. The resulting precipitate was collected by filtration, dissolved in minimum amount of THF (3 mL), and reprecipitated by stirring in methanol (100 mL) for 30 min. After filtration, the product was dried under vacuum to give dark red powder (90 mg, 86 %): ^1H NMR (400 MHz, CDCl_3 , TMS): δ = 0.85 (t, J = 6.6 Hz, 6H; $(\text{CH}_2)_5\text{CH}_3$ and $(\text{CH}_2)_7\text{CH}_3$), 1.24–1.42 (m, 24H; $\text{OCH}_2\text{CH}(\text{CH}_2)_5\text{CH}_3$ and $\text{OCH}_2\text{CH}(\text{CH}_2)_7\text{CH}_3$), 1.74 (m, 1H; $\text{OCH}_2\text{CH}(\text{C}_6\text{H}_{13})\text{C}_8\text{H}_{17}$), 1.89 (br, 6H; thienyl- CH_3), 3.82 (d, J = 5.2 Hz, 2H; OCH_2CH), 5.34 (br, 4H; COOCH_2), 6.78 (br, 2H; thienylene- H in main chain), 6.86 (d, J = 8.8 Hz, 2H; Ph- H *ortho* to $\text{OCH}_2\text{CH}(\text{C}_6\text{H}_{13})\text{C}_8\text{H}_{17}$), 7.11 (br, 2H; thienyl- H in DE), 7.21 (br, 3H; thienylene- H in main chain), 7.95 (d, J = 8.8 Hz, 2H; Ph- H *meta* to $\text{OCH}_2\text{CH}(\text{C}_6\text{H}_{13})\text{C}_8\text{H}_{17}$).

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Chapter 6

Photochemically Color-Tunable White Fluorescence Illuminants Consisting of Conjugated Polymer Nanospheres

Introduction

Aromatic conjugated polymers have semi-conducting and luminescent properties, which can be utilized in organic light-emitting diodes, organic field-effect transistors, photovoltaic cells, and chemical biosensors.^{1–8} Such conjugated polymers can fluoresce various colors in the visible region through changing the conjugated backbones. It is of particular interest to dynamically control the luminescence of conjugated polymers by using external light stimulus. Dithienylethene (DE)^{9–12} is one of the most promising candidates for photochromic materials due to its good fatigue resistance, thermal stability, and an ability to undergo conformational changes between open and closed forms via photoisomerization. DE derivatives are also known to show luminescent color changes through photoisomerization.^{12–22} Similarly, conjugated polymers containing DE moieties in the polymer backbones exhibit photochromism attributed to structural changes of the main chains.^{12,23–26} Such photoresponsive conjugated polymers are essential for the next-generation of optoelectronic materials.

Meanwhile, by introducing the DE moiety into side chains of an aromatic conjugated polymer, the author and coworkers dynamically controlled the fluorescence through various colors via photoisomerization of DE moiety in solution and cast film.^{27,28} However, the red fluorescent polymer [e.g., poly(thiophene) derivative] produced extremely weak fluorescence due to the fact that it easily forms π -stacking structure owing to high coplanarity, which decreased the fluorescence quantum yield. The level of fluorescence quenching for the red fluorescent polymer was lower than for the other fluorescent polymers (e.g., blue–green fluorescent polymers), which impeded perfect photoswitching with red fluorescence. Therefore, the author developed a new type of red fluorescent conjugated polymer²⁹ with a fluorene block and a very small

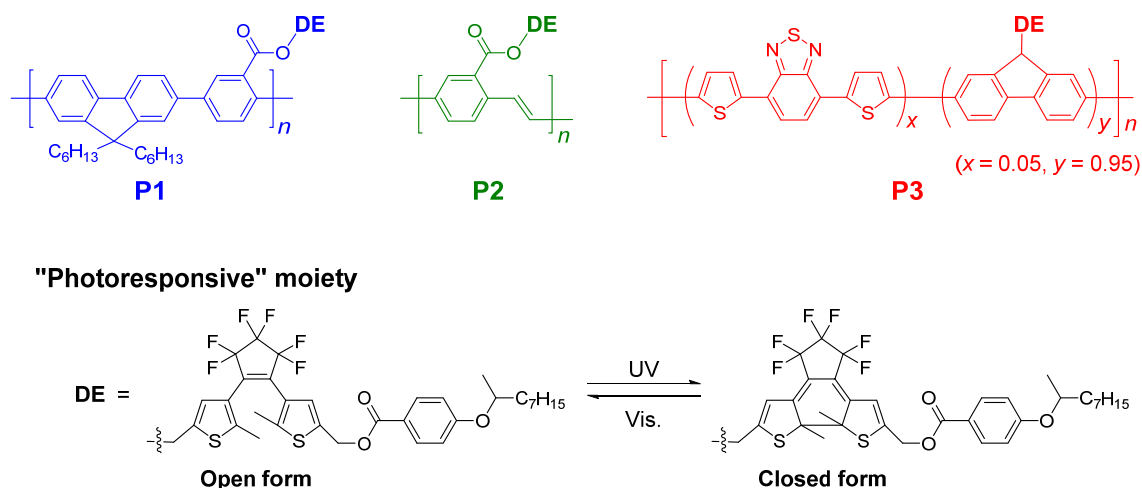
level of 4,7-di(2-thienyl)-2,1,3-benzothiadiazole (DBT) block in the main chain, which yields reddish purple fluorescence in a chloroform solution and red fluorescence with a relatively high fluorescence quantum yield in the aggregated state, such as in a nanosphere solution and cast film.

The nanosphere of the polymer was prepared to obtain the aggregated state of the polymer. The nanosphere can be considered an intermediate state between solution and film because the polymer nanoparticles are uniformly dispersed in the solvent, similar to the solution state, and also aggregate with each other, similar to the film state. Such bilateral character of the nanosphere causes the polymer to exhibit high processability and fluidity as well as aggregation effects. Moreover, the individual nanoparticles can inhibit the energy transfer between different polymers, so that white fluorescence may be achieved by casting the mixture of RGB-colored fluorescent nanospheres that are free from intermolecular energy transfer.

Herein, the author shows photoswitching between white emission and quenching as well as reversible change in fluorescent colors between white and red, green, or blue (RGB) for a mixture of photoresponsive conjugated polymer nanospheres in both a nanosphere solution and film state, except white-to-green film. The author designs and synthesizes photoresponsive conjugated polymers with RGB fluorescence by introducing DE moieties at the side chains. The polymers aggregate into nanospheres with 200–300 nm diameters through precipitating the polymers in water under ultrasonication.³⁰ In the nanosphere solution and film state, the polymer fluorescence can switch between emission and quenching using external light, which generates DE moiety photoisomerization.^{9–11} By mixing the RGB-fluorescent nanospheres, the white fluorescence photoswitches in both the nanosphere solution and film state. In addition, the color-tunable fluorescence system is constructed by replacing a photoresponsive polymer with a non-photoresponsive polymer analogue, which generated a fluorescent color that switches between white and RGB. Our results demonstrate that the individual nanospheres can inhibit energy transfer between different polymers, and hence, white fluorescence is generated by suspending or casting the RGB-colored fluorescent nanosphere mixture. The systems herein may be used as “photoresponsive polymer illuminants” with a photochemically color-tunable white fluorescence.

Results and Discussion

Photoresponsive polymer synthesis. The photoresponsive conjugated polymers **P1–P3** were synthesized by introducing DE moieties at the side chains (Scheme 1). The synthesis routes of **P1–P3** are shown in Experimental Section. The conjugated backbones of **P1** and **P2**, which comprise poly(fluorene phenylene) and poly(*para*-phenylene vinylene) derivatives, respectively, were designed to produce blue and green fluorescence in a nanosphere solution. **P3** is a poly(fluorene) derivative with a 5 mol% of a 4,7-(2-dithienyl)-2,1,3-benzothiadiazole moiety in the main chain, which was designed to generate red fluorescence in a nanosphere solution.²⁹ The synthesized polymers were soluble in organic solvents, such as tetrahydrofuran (THF), toluene, and chloroform (CHCl₃). The polymer molecular weights are shown in Table 1.



Scheme 1: Chemical structures of photoresponsive conjugated polymers. **P1** and **P2** are poly(fluorene phenylene) and poly(*para*-phenylene vinylene) derivatives, respectively. **P3** is a poly(fluorene) derivative with a 5 mol% of a 4,7-(2-dithienyl)-2,1,3-benzothiadiazole moiety in the main chain. All the polymers have photoresponsive DE moieties in the side chains.

Table 1. Molecular weights and photoswitching properties of **P1–P3** nanosphere solutions.

Polymer	M_n^a	M_w^a	M_w/M_n	DP ^b	I_{op}/I_{PSS}^c	Φ_{PL}^d (%)		Φ_{open}/Φ_{PSS}^e
						open	PSS	
P1	94,000	180,100	1.9	85	473.2	44.2	0.34	130.0
P2	5,300	7,800	1.5	7	850.7	39.7	0.66	60.2
P3	17,200	48,300	2.8	21	98.9	15.1	0.84	18.0

^a Number- (M_n) and weight-average (M_w) molecular weights evaluated with a polystyrene standard.

^b Degree of polymerization.

^c The fluorescence intensity ratio in nanosphere solutions.

^d Fluorescence quantum yield in nanosphere solutions evaluated by using an integral sphere.

^e Ratio of fluorescence quantum yields in open state and PSS of nanosphere solutions.

Photoswitching behavior in cast film and solution. A cast film for each polymer was prepared through spin-casting the corresponding polymer $CHCl_3$ solution. The UV–vis absorption and photoluminescence (PL) spectra for the cast film and solution are shown in Figure 1–3. Similar to **P1**, **P2**, and **P3** in solution, the cast films showed reversible photoisomerization between the open state and PSS. The cast films show fluorescence at longer wavelengths compared with the corresponding polymer solutions. Reversible photoresponsive emission and quenching were observed in the cast films and in solution (see Figure 1–3). Furthermore, the fluorescence quantum yields also decreased concomitant with photoisomerization of DE moiety upon conversion from the open to closed forms (see Table 2). Note that the excitation wavelengths ($\lambda = 350$ – 380 nm) were determined such that the maximum fluorescence intensity for each polymer and DE moiety in the open form was not affected by the excitation light at the wavelength range used.

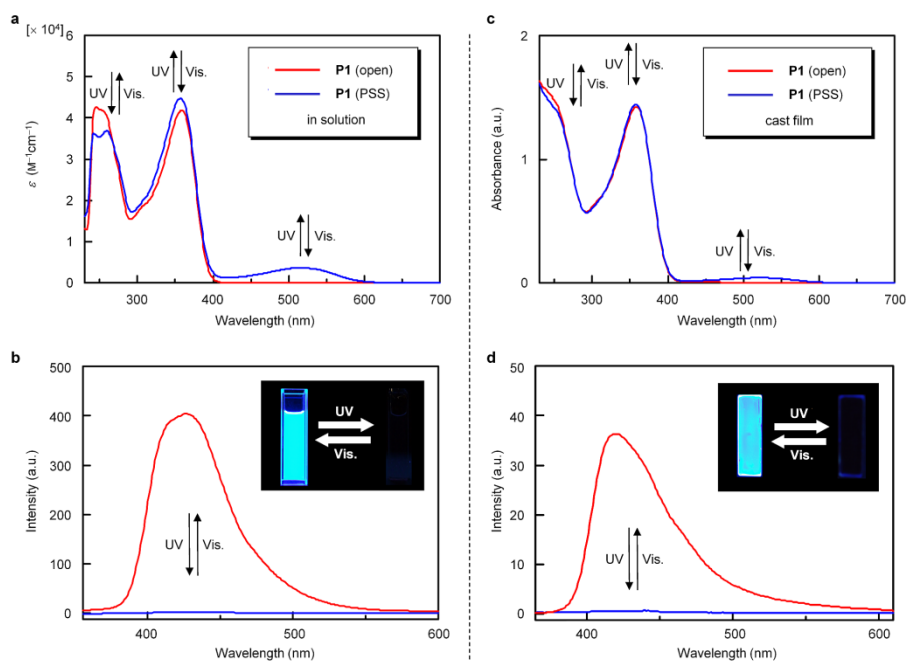


Figure 1. (a) UV–vis absorption and (b) PL spectra of **P1** in CHCl_3 (5.0×10^{-5} M) and (c, d) those in cast film. Inserts show photographs of the open state and the PSS of the polymer (excitation wavelength: $\lambda = 365$ nm).

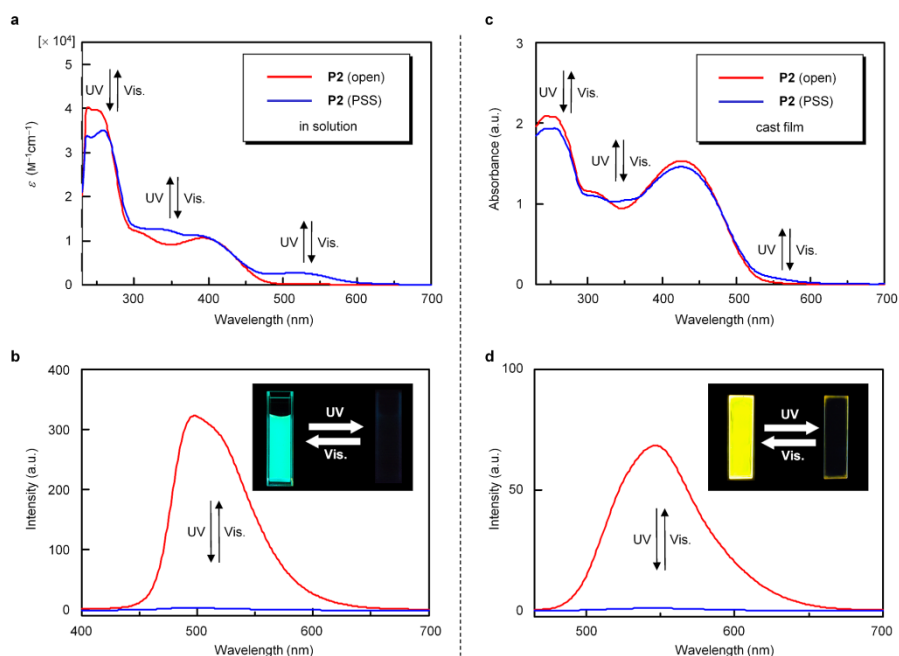


Figure 2. (a) UV–vis absorption and (b) PL spectra of **P2** in CHCl_3 (5.0×10^{-5} M) and (c, d) those in cast film. Inserts show photographs of the open state and the PSS of the polymer (excitation wavelength: $\lambda = 365$ nm).

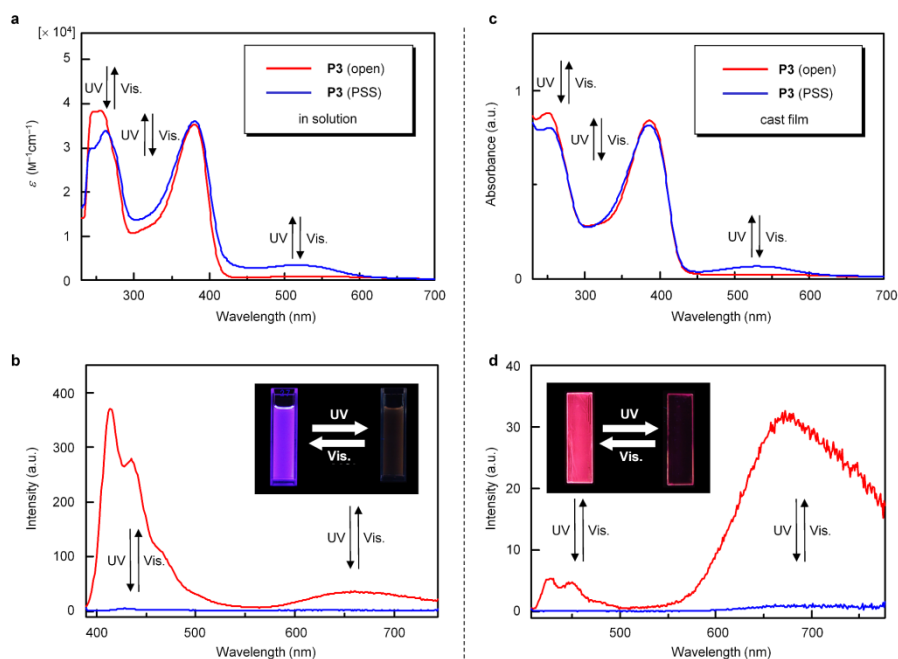


Figure 3. (a) UV–vis absorption and (b) PL spectra of **P3** in CHCl₃ (5.0×10^{-5} M) and (c, d) those in cast film. Inserts show photographs of the open state and the PSS of the polymer (excitation wavelength: $\lambda = 365$ nm).

Table 2. Fluorescence quantum yields (Φ_{PL} , %) of **P1–P3** in CHCl₃, nanosphere solution, and cast film.^a

Polymer	in CHCl ₃ ^b			nanosphere solution ^b			cast film		
	open	PSS	$\Phi_{\text{open}}/\Phi_{\text{PSS}}$	open	PSS	$\Phi_{\text{open}}/\Phi_{\text{PSS}}$	open	PSS	$\Phi_{\text{open}}/\Phi_{\text{PSS}}$
P1	71.6	2.69	26.6	44.2	0.34	130.0	43.9	0.90	48.8
P2	53.8	1.32	40.8	39.7	0.66	60.2	23.0	0.16	143.8
P3	42.2	0.76	55.5	15.1	0.84	18.0	12.3	1.41	8.7

^a Fluorescence quantum yield was evaluated by using an integral sphere.

^b Concentrations of the polymers are 5.0×10^{-5} M.

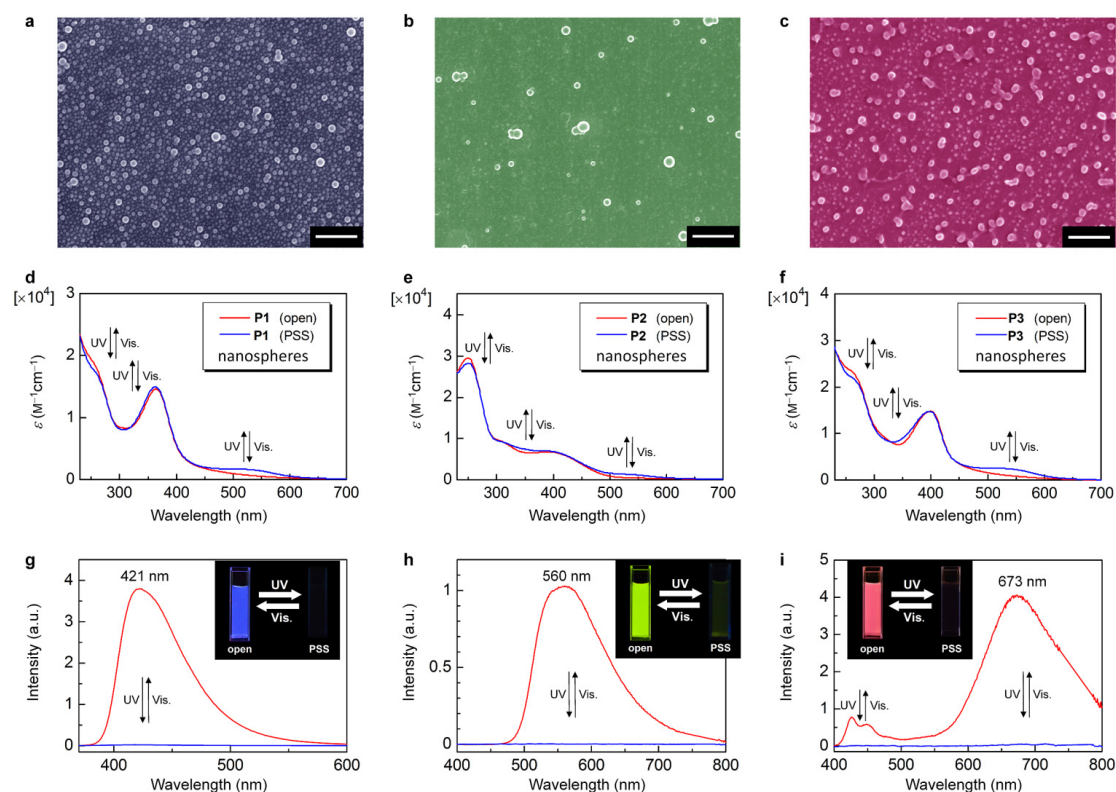


Figure 4. Morphology and photoresponsive behavior of P1–P3 nanospheres. (a–c) SEM images for **P1** (a), **P2** (b), and **P3** (c) nanospheres. Scale bar: 400 nm. (d–i) The changes on optical properties of **P1** (d, g), **P2** (e, h), and **P3** (f, i) nanosphere solutions in open state (red line) and PSS (blue line). They present UV–vis absorption (d–f) and PL spectra (g–i) for the **P1**, **P2**, and **P3** nanospheres dispersed in water ($c = 5.0 \times 10^{-5}$ M). The inserts show the fluorescence change of the nanosphere solutions in open state and PSS (excitation wavelength: $\lambda = 365$ nm).

Morphology and optical properties of polymer nanospheres. The polymer nanospheres were prepared as described in the Methods Section. A scanning electron microscopy (SEM) showed that **P1**, **P2**, and **P3** form spherical aggregates with a diameter of several hundred nanometers (Figure 4a–c). The results herein are consistent with the average sphere sizes of 365.3 ± 116.7 nm, 245.6 ± 116.5 nm, and 174.0 ± 81.3 nm for **P1**, **P2**, and **P3**, respectively, which were determined using dynamic light scattering (see Figure 5).

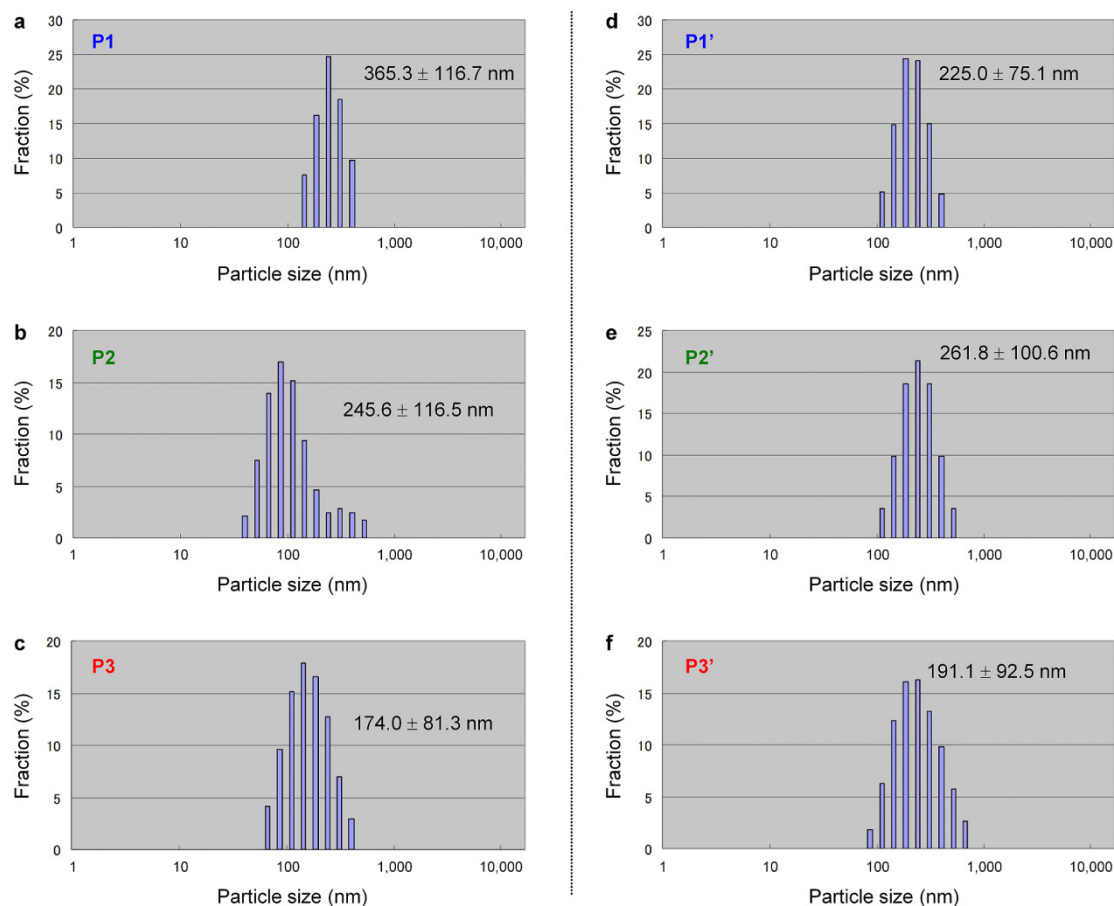


Figure 5. Particle size distribution graphs of (a) **P1**, (b) **P2**, (c) **P3**, (d) **P1'**, (e) **P2'**, and (f) **P3'** nanospheres in water, evaluated by dynamic light scattering.

The polymer nanospheres photoswitched between fluorescence and quenching, which was similar in both the polymer solutions and films. Figure 4d–i show the UV–vis absorption and photoluminescence (PL) spectra for the polymer nanospheres in water. **P1**, **P2**, and **P3** showed absorption bands at 364, 392, and 399 nm, respectively, which correspond to the π – π^* transitions of the conjugated backbones. The absorption band at approximately 250 nm, which corresponds to the open form of DE moiety, had decreased intensity upon irradiation with UV light ($\lambda = 254$ nm) for 30 s. Simultaneously, the shoulder bands at approximately 350 and 550 nm, which correspond to the closed form of DE moiety, gradually increased in intensity. Photoisomerization of the DE moiety from the open to closed forms generated the

changes in UV–vis spectra. The percent conversion from the open to closed forms in the photostationary states (PSS) of **P1**, **P2**, and **P3** were 38%, 50%, and 28%, respectively. PSS is an equilibrium state between the open and closed forms of DE moiety under UV irradiation. The spectra were recovered through subsequent irradiation with visible light for 3 min, as shown in Figure 4d–f, which indicates reconversion of DE moiety from the closed to open forms.

When the DE moiety is in the open form, the **P1**, **P2**, and **P3** nanospheres produced PL bands at 421, 560, and 673 nm under UV excitation of $\lambda = 350, 380,$ and 380 nm, respectively. Accordingly, **P1–P3** generated blue, green, and red fluorescence, as shown in Figure 4g–i. Upon irradiation with UV light ($\lambda = 254$ nm) for 30 s to photoisomerize DE moieties from open to closed forms, the fluorescent intensities drastically decreased, which quenched the fluorescence. The fluorescence intensity ratios between the open state and PSS ($I_{\text{open}}/I_{\text{PSS}}$) of the polymers were estimated at 473, 851, and 99 for the **P1**, **P2**, and **P3** nanospheres, respectively (Table 1). Furthermore, the fluorescence quantum yield also decreased concomitant with photoisomerization of DE moiety upon conversion from the open to closed forms. The fluorescence quantum yield ratios between the open state and PSS ($\Phi_{\text{open}}/\Phi_{\text{PSS}}$) were 130, 60, and 18 for the **P1**, **P2**, and **P3** nanospheres, respectively (Table 1). Therefore, fluorescence might be quenched due to efficient energy transfer from the polymer backbone in an excited state to the DE moiety in the closed form. The DE moiety releases energy via a nonradiative transition, which quenches the fluorescence. The fluorescence was subsequently regenerated through irradiation with visible light for 3 min. In each polymer nanosphere, photoswitching was observed over 10 cycles (see Figure 6). Inserts in Figure 4g–i show photoswitching images for the RGB-fluorescent nanospheres of **P1**, **P2**, and **P3** under UV excitation of $\lambda = 365$ nm.

Comparison of fluorescence quantum yields. The author found that fluorescence quantum yields of the polymer films had substantially smaller absolute values than the polymers in solution (Table 2), which may result from the level of quenching in the film. This result is due to the interchain distance between fluorescent polymers, which is shorter in film than in solution; hence, the fluorescent moiety tends to transfer

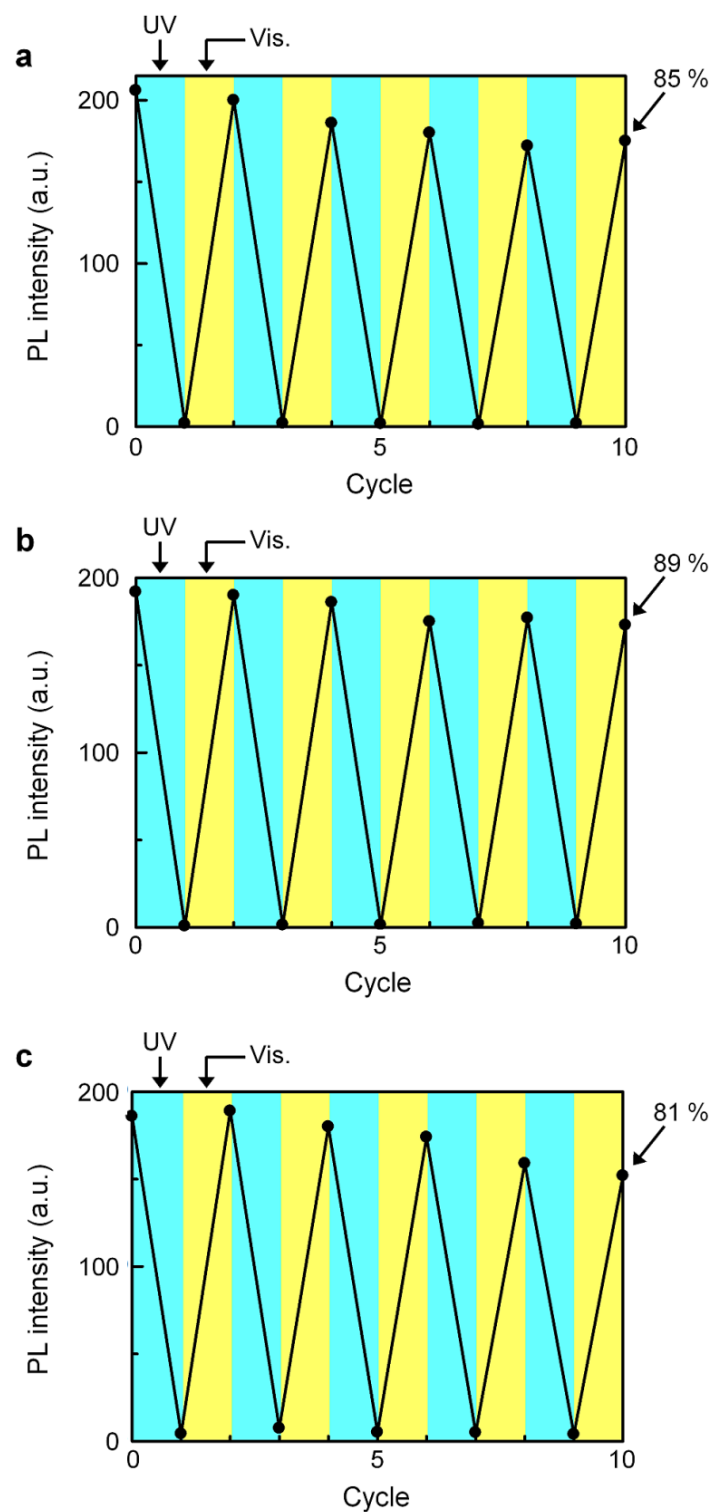


Figure 6. Reversible changes in PL intensity of (a) **P1**, (b) **P2**, and (c) **P3** nanospheres in water upon alternating irradiations of UV ($\lambda = 254$ nm, blue area) and visible (yellow area) lights.

energy through Förster resonance and Dexter energy transfers to the non-fluorescent moiety, which quenches the fluorescence. In addition, the nanosphere fluorescence quantum yields (15–44 %) generated intermediate values, which were between the values produced by the solution (42–72 %) and film (12–44 %), indicating that the nanosphere form may be an intermediate aggregation state between the solution and film forms. This result is expected because the nanospheres' dispersion states in water were similar to the solution states, whereas the polymer aggregation in nanospheres yields high levels of fluorescence quenching, which is similar to the film state.

Fluorescent property of P3. It is interesting that **P3** exhibits characteristic fluorescence behavior; namely, in the CHCl₃ solution, **P3** produces two PL bands. One band is a strong, sharp, blue emission band at approximately 414 nm that corresponds to the polyfluorene backbone. The other is a weak, broad, red emission band at approximately 657 nm that corresponds to 4,7-di(2-thienyl)-2,1,3-benzothiadiazole (DBT) moiety in the polymer backbone, which yields purple fluorescence (see Figure 3b). However, in the film and nanosphere forms, the blue emission band was dramatically less intense, whereas the red emission band showed greater intensity and produced red fluorescence. This result may be due to the narrow bandgap for the DBT moiety, which acts as an exciton trapping site, facilitates efficient intramolecular energy transfer from the polyfluorene backbone to the DBT moiety, and yields red fluorescence.

Photoswitching between white fluorescence and quenching. The author investigated photoswitching of white fluorescence in a mixed system composed of **P1–P3** nanospheres. Nanospheres composed of **P1**, **P2**, and **P3** in water were mixed at a molar ratio of 1:6:12. The molar ratio for mixing was experimentally determined to produce white fluorescence using the Commission Internationale de l'Éclairage (CIE) coordinates³¹. The SEM analysis (Figure 7a) showed that the polymer spherical aggregates separated from each other even after mixing, which indicates that the **P1–P3** nanospheres were uniformly mixed without morphology changes and aggregation of nanospheres. In addition, the photoresponsive behavior was maintained after mixing

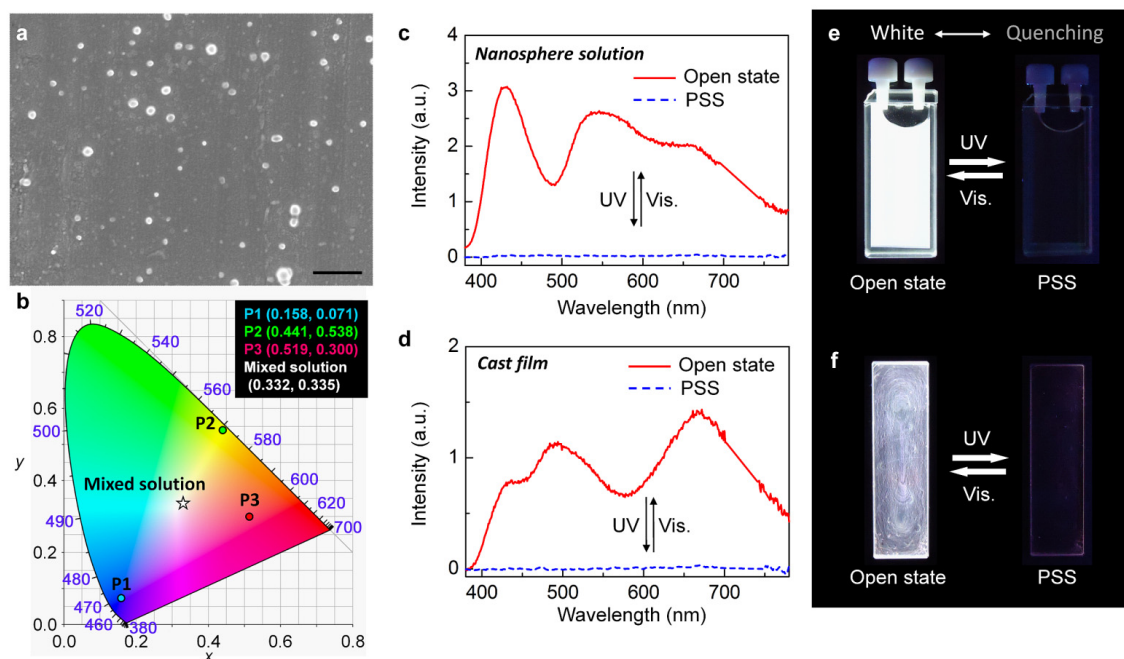


Figure 7. Reversible photoswitching of white fluorescence between emission and quenching. (a) SEM image for the **P1–P3** nanosphere mixture. Scale bar: 400 nm. (b) CIE coordinates for the **P1–P3** nanospheres and the mixed solution. (c) PL spectra for the mixed solution of **P1**, **P2**, and **P3** nanospheres (1:6:12 mol/mol/mol) in open state (solid line) and PSS (dashed line) under UV irradiation of $\lambda = 360$ nm. (d) PL spectra for the cast film prepared from the mixed solution of **P1**, **P2**, and **P3** nanospheres (4:1:32 mol/mol/mol) in open state (solid line) and PSS (dashed line) under UV irradiation of $\lambda = 360$ nm. (e, f) Photographs of white fluorescence photoswitching between emission and quenching in a nanosphere solution (e) and a cast film (f). Excitation wavelength: $\lambda = 365$ nm.

the nanospheres of **P1–P3**. The PL spectra were measured in the mixed solution under UV excitation of $\lambda = 360$ nm (Figure 7c). The mixed solution generated three emission bands around 430, 545, and 660 nm, which correspond to **P1**, **P2**, and **P3**, respectively; the bands extended throughout the visible region. The fluorescent colors for the **P1–P3** nanospheres and mixed solution are depicted in the CIE color space, as shown in Figure 7b. The CIE coordinates of **P1**, **P2**, and **P3** nanospheres in water were $(x, y) = (0.158, 0.071)$, $(0.441, 0.538)$, and $(0.519, 0.300)$, respectively. The CIE

coordinates of the mixed solution were estimated at (0.332, 0.335), which is similar to those of the white light [i.e., $(x, y) = (0.333, 0.333)$]. Similar to the individual **P1–P3**, the three emission bands generated by the mixed solution had substantially decreased intensities upon UV light irradiation ($\lambda = 254$ nm) for 30 s, which quenched the white fluorescence (Figure 7c and e). Fluorescence intensity ratio ($I_{\text{open}}/I_{\text{pss}}$) of the mixed solution was estimated to be 177, 134, and 77 at 430, 545, and 660 nm, respectively. The fluorescence quantum yield also decreased from 16.8 to 0.6 % after photoisomerization of DE moiety from the open to closed forms. The fluorescence intensity ratio and quantum yield indicate clear photoswitching for the white fluorescence. The quenched white fluorescence was regenerated through irradiation with visible light for 3 min.

To prepare a white fluorescent cast film, the **P1–P3** nanospheres in water were mixed at a molar ratio of 4:1:32. Similarly to the nanosphere solution, the molar ratio was experimentally determined using the CIE coordinates. Note that, in film state, energy transfer of excited conjugated backbones partially occurred from **P1** and **P3** to **P2**. Therefore, the mixed film requires higher molar concentrations of **P1** and **P3** than those in the mixed solution to produce white fluorescence. After adding a small amount of ethanol to efficiently evaporate the solvent, the mixed solution was heated on a quartz substrate at 60 °C to form a cast film. PL spectra of the cast film were measured under UV excitation of $\lambda = 360$ nm, as shown in Figure 7d. CIE coordinates of the cast film were estimated to be $(x, y) = (0.334, 0.336)$. The almost pure white fluorescence colour in the cast film is attributed to individual aggregation of the polymers, which inhibit energy transfer between different polymers. This is also supported by the fact that red fluorescence, but not white one, was observed in a cast film prepared from CHCl_3 solution of the polymer mixture with the same mixing ratio (Figure 8) where the polymers aggregated each other. The white fluorescence successfully photoswitched through irradiation with UV and visible light (Figure 7d and f); the fluorescence quantum yields were 16.7 % in open form and 0.4 % in PSS. Figure 7e and f show photoswitching images of white fluorescence for the nanosphere solution and cast film. Thus, the author demonstrated the reversible control of white fluorescence emission and quenching for conjugated polymers in both nanosphere solution and film state, as summarized in Table 3.

Table 3. Fluorescent properties of mixtures of **P1–P3** nanospheres.

	CIE coordinates (x, y)	Φ_{PL}^a (%)		$\Phi_{\text{open}}/\Phi_{\text{PSS}}$
		open	PSS	
in water	(0.332, 0.335)	16.8	0.61	27.5
cast film	(0.334, 0.336)	16.7	0.38	44.0

^a Fluorescence quantum yields evaluated by using an integral sphere.

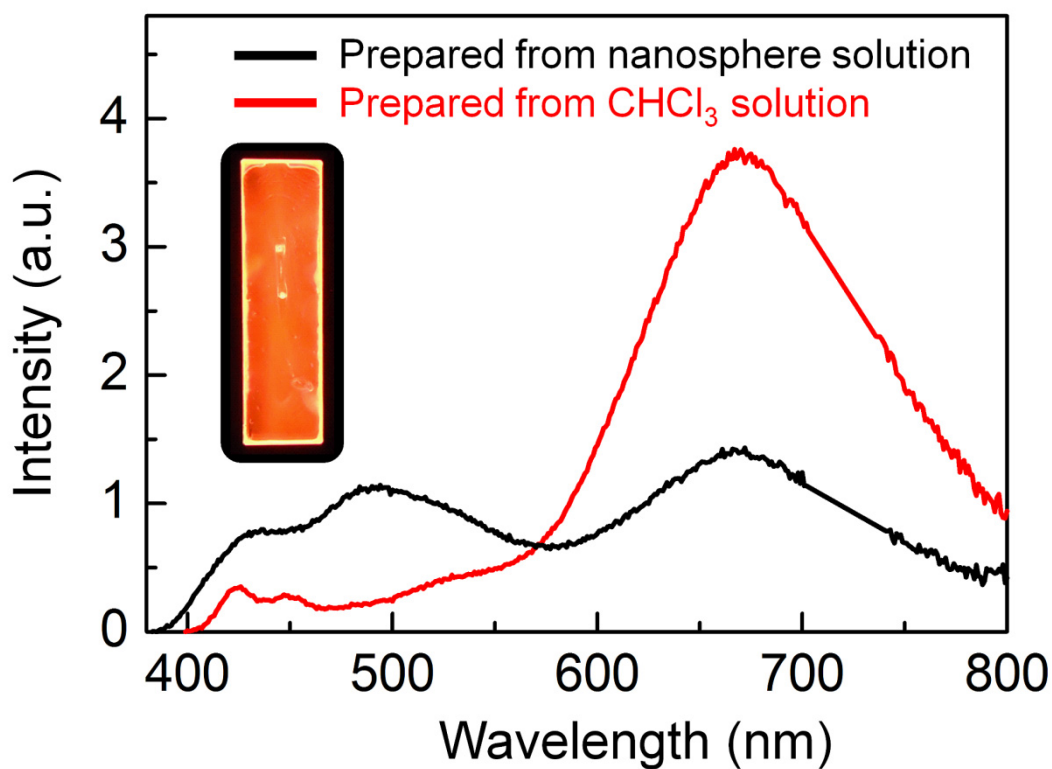


Figure 8. PL spectra of **P1–P3** mixed cast films prepared from nanosphere solution and CHCl_3 solution, in which the mixing molar ratio of **P1–P3** was kept constant (**P1:P2:P3** = 4:1:32 mol/mol/mol). Insert shows a photograph of the cast film prepared from CHCl_3 solution under irradiation of UV light ($\lambda = 365$ nm).

Photoswitching between white and RGB fluorescence. The author investigated photoswitching from white to RGB fluorescence by replacing a photoresponsive polymer with a non-photoresponsive conjugated polymer. **P1'–P3'** are the analogous polymers for **P1–P3** that include the same conjugated backbones without DE moieties in the side chains (see Experimental Section and Table 4). The **P1'–P3'** nanospheres were prepared using the same method used for **P1–P3**, and formed spherical aggregates as shown in Figure 9. The results are consistent with the DLS measurements, which showed average sphere sizes at 225.0 ± 75.1 nm for **P1'**, 261.8 ± 100.6 nm for **P2'**, and 191.1 ± 92.5 nm for **P3'**, respectively (see Figure 5d–f). Similar to **P1–P3**, the nanosphere solutions of **P1'–P3'** in water exhibited blue, green, and red fluorescence, respectively. The PL spectra and fluorescence quantum yields for **P1'–P3'** are in Figure 10 and Table 4.

Table 4. Molecular weights and fluorescence quantum yields of **P1'–P3'**.

Polymer	M_n^a	M_w^a	M_w/M_n	DP ^b	Φ_{PL}^c (%)
P1'	38,400	88,800	2.3	66	26.3
P2'	15,800	84,000	5.3	58	25.0
P3'	26,700	98,500	3.7	68	16.6

^a Number- (M_n) and weight-average (M_w) molecular weights were evaluated with a polystyrene standard.

^b Degree of polymerization.

^c Fluorescence quantum yields in nanospheres evaluated by using an integral sphere.

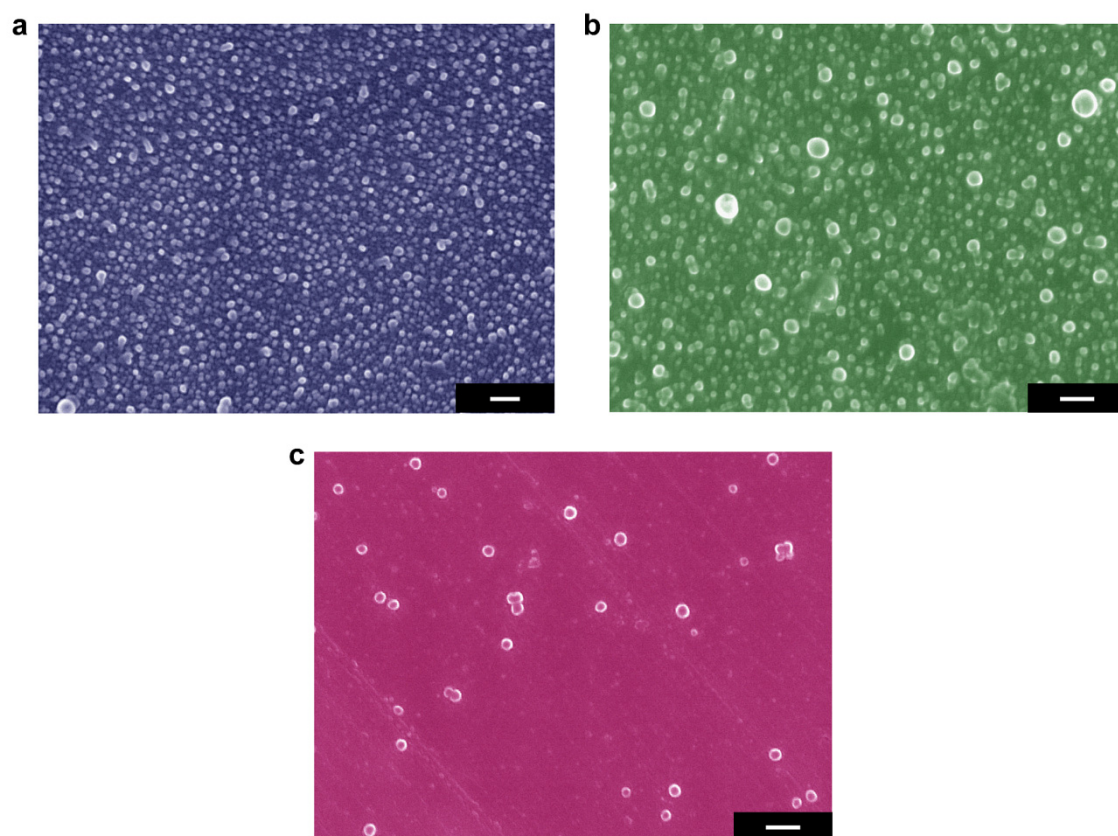


Figure 9. SEM images of the nanospheres of (a) **P1'**, (b) **P2'**, and (c) **P3'**. Scale bar: 200 nm.

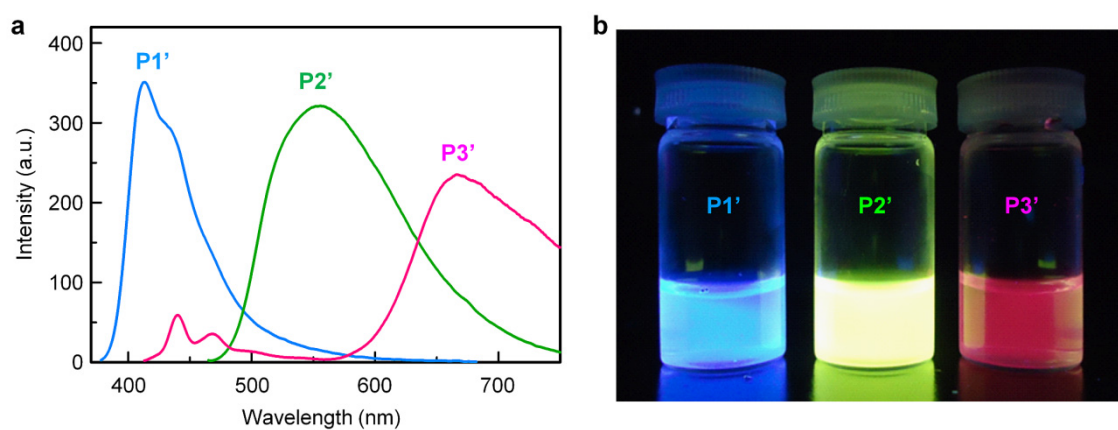


Figure 10. (a) PL spectra of the nanospheres of non-photoresponsive polymers, **P1'**–**P3'**. (b) Photographs of nanosphere solutions of **P1'**–**P3'** under UV irradiation of $\lambda = 365$ nm.

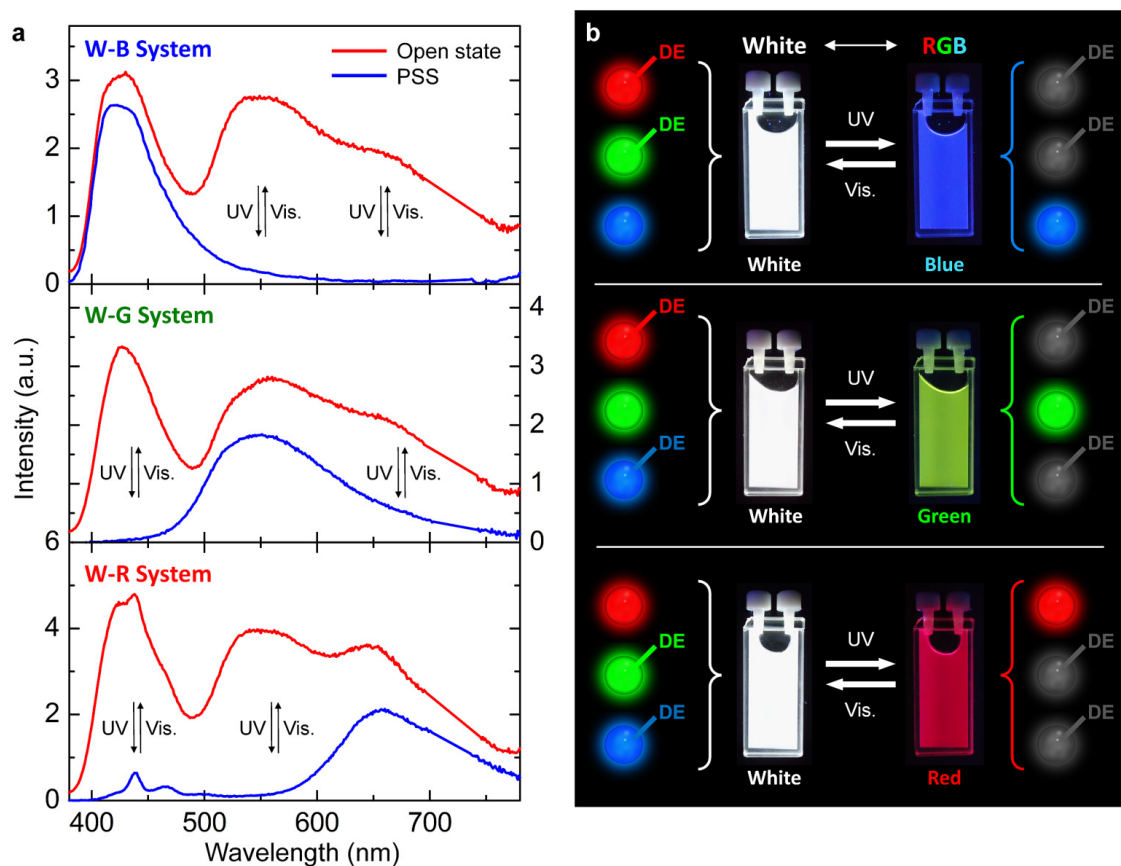


Figure 11. Reversible photoswitching between white and RGB in mixed nanosphere solutions. (a) PL spectra for the white-to-blue (W-B), white-to-green (W-G), and white-to-red (W-R) systems under UV irradiation of $\lambda = 360$ nm. In the systems, one of the photoresponsive polymers (**P1**–**P3**) is replaced by a corresponding polymer analogue, **P1'**–**P3'**, which have no DE moiety in the side chains. (b) Photographs of photoswitching between white and RGB-colored fluorescence in mixed nanosphere solutions in water. Excitation wavelength: $\lambda = 365$ nm.

Three types of mixtures were prepared by mixing the polymer nanospheres as follows: **P1'**, **P2**, and **P3** for white-to-blue (W-B); **P1**, **P2'**, and **P3** for white-to-green (W-G); and **P1**, **P2**, and **P3'** for white-to-red (W-R). Each system includes three RGB-fluorescent nanospheres, in which two polymers include DE moieties at the side chains, while the other does not. In each system, the three polymers were mixed at the appropriate ratio, and PL spectra of the mixed solutions were measured under UV excitation of $\lambda = 360$ nm. As shown in Figure 11, the mixtures generated white

Table 5. Fluorescent properties of W-B, W-G, and W-R systems in open state and PSS.

System		CIE coordinates (x, y)		Φ_{PL}^a (%)	
		open	PSS	open	PSS
White-to-Blue (W-B)	in water	(0.333, 0.340)	(0.169, 0.093)	19.3	6.1
	cast film	(0.338, 0.329)	(0.196, 0.156)	13.5	3.7
White-to-Green (W-G)	in water	(0.340, 0.333)	(0.405, 0.522)	20.9	8.6
	cast film	(0.335, 0.333)	(0.336, 0.419)	17.8	0.4
White-to-Red (W-R)	in water	(0.337, 0.330)	(0.509, 0.282)	26.7	7.8
	cast film	(0.336, 0.338)	(0.511, 0.276)	29.3	14.9

^a Fluorescence quantum yields evaluated by using an integral sphere.

fluorescence with blue, green, and red emission bands when the DE moiety is in the open form. The CIE coordinates of W-B, W-G, and W-R systems were (x, y) = (0.333, 0.340), (0.340, 0.333), and (0.337, 0.330), respectively (see Table 5). These coordinates are similar to the pure white fluorescence coordinates of (x, y) = (0.333, 0.333). Upon irradiating each system with UV light ($\lambda = 254$ nm) for 30 s, the fluorescence that corresponds to the photoresponsive polymers **P1–P3** had a drastically decreased intensity due to photoisomerization of DE moiety. Fluorescence for the non-photoresponsive polymers **P1'–P3'** remained after the UV irradiation because the DE moiety was absent. Therefore, for the W-B, W-G, and W-R systems, the white fluorescence switched to blue, green, and red fluorescence, respectively, via the UV irradiation (Figure 11). Interestingly, in all mixed systems of **P1–P3** and **P1'–P3'**, the PL intensities for the non-photoresponsive polymers **P1'–P3'** slightly decreased after photoisomerization of DE moiety in **P1–P3**, which indicates fluorescence re-absorption or partial energy transfer. With photoisomerization of DE moiety from the open to closed forms, the fluorescence quantum yields also decreased from 19.3 to 6.1 % for the W-B system, 20.9 to 8.6 % for the W-G system, and 26.7 to 7.8 % for the W-R system (see Table 5). The fluorescence quantum yield decrease in each system was due to fluorescence quenching from the 2 photoresponsive polymers bearing the DE moiety. For each system, the RGB fluorescence was then converted to white fluorescence

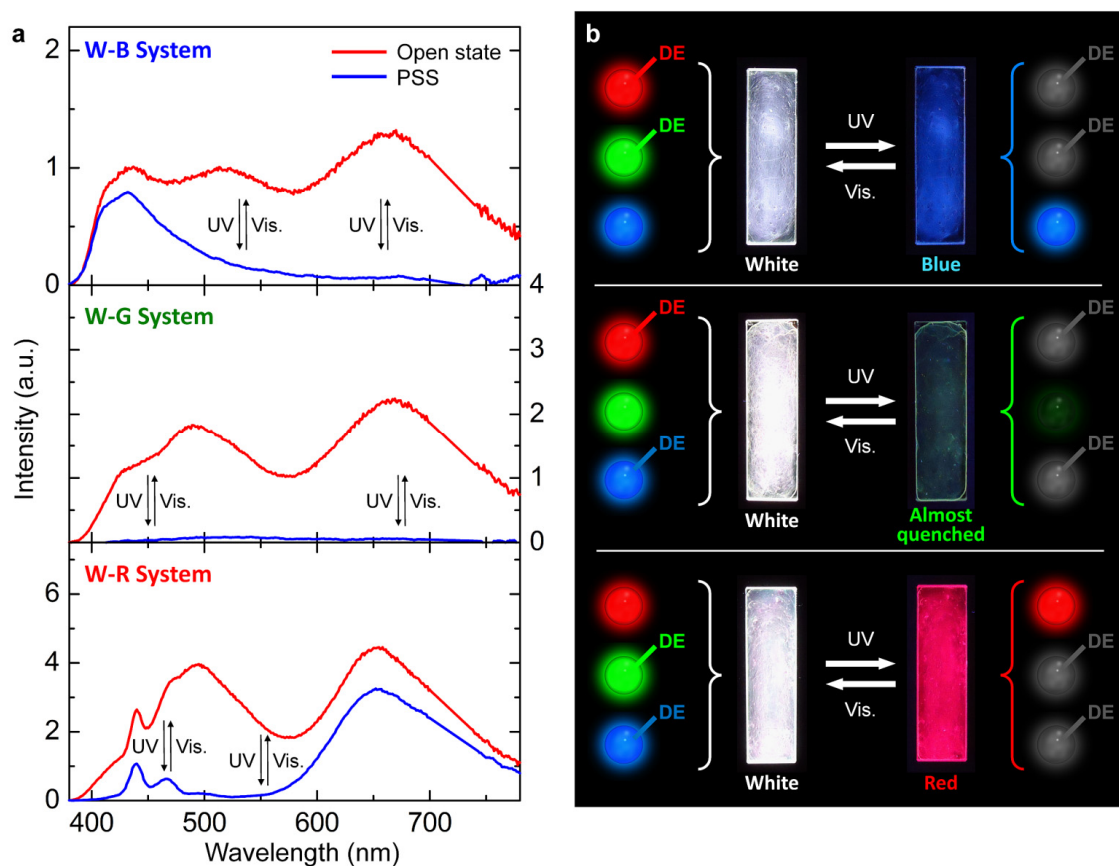


Figure 12. Reversible photoswitching between white and RGB in cast films. (a) PL spectra for the white-to-blue (W-B), white-to-green (W-G), and white-to-red (W-R) cast films under UV irradiation of $\lambda = 360$ nm. The cast films were prepared by heating the mixture of polymer nanosphere solutions on a quartz substrate at 60 °C. In the cast films, one of the photoresponsive polymers (**P1–P3**) is replaced by a corresponding polymer analogue, **P1'–P3'**, which have no DE moiety in the side chains. Similarly to the corresponding systems, the W-B and W-R cast films showed white fluorescence in the open state and blue- or red-colored fluorescence in PSS. Although green fluorescence in the W-G cast film was visually observed in PSS, its intensity was too weak to be evidently detected in fluorescence spectrum, resulting in an almost quenched situation from the spectroscopic point of view. (b) Photographs of photoswitching between white and RGB-colored fluorescence in the mixed cast films. Excitation wavelength: $\lambda = 365$ nm.

through irradiation with visible light for 3 min. Hence, the author generated reversible photoswitching between white and RGB fluorescence.

The reversible photoswitching between white and RGB fluorescence was also demonstrated in cast films. The W-B, W-G, and W-R cast films were prepared in the same manner as the white fluorescent cast film of **P1–P3**. As shown in Figure 12, all cast films in the open state exhibited white fluorescence under UV excitation of $\lambda = 360$ nm. Similarly to the corresponding systems, the W-B and W-R cast films showed blue- and red-colored fluorescence in PSS after UV irradiation of $\lambda = 254$ nm for 15–30 s. The fluorescence quantum yields also decreased from 13.5 to 3.7 % for the W-B cast film and 29.3 to 14.9 % for the W-R cast film (Table 5). On the other hand, although green fluorescence in the W-G cast film was visually observed in PSS, its intensity was too weak to be evidently detected in fluorescence spectrum, resulting in an almost quenched situation from the spectroscopic point of view (see Figure 12a). This was also confirmed by the fluorescence quantum yields which were 17.8 % in open state and 0.4 % in PSS. This should be due to the fact that the DE moieties in closed forms of **P1** and **P3** have an absorption band at 550 nm and hence they absorb the green fluorescence around 550 nm of **P2'** in the cast film. Therein, the polymer nanospheres cannot be separated from each other owing to aggregation of **P1**, **P2'**, and **P3** nanospheres. This is in sharp contrast to the nanosphere solution. Nevertheless, in all cast films, the white fluorescence was regenerated through the visible light irradiation. The CIE coordinates and fluorescence quantum yields of the cast films are summarized in Table 5.

The W-B, W-G, and W-R systems can be easily constructed by mixing the photoresponsive polymers with the non-photoresponsive polymers. Therefore, these systems combined should be attractive for a tunable fluorescent system application.

Conclusion

In summary, the author has successfully constructed multiplex fluorescent systems consisting of photoresponsive polymer nanospheres. The reversible control of the emission and quenching of RGB fluorescence in conjugated polymers are achieved in both nanosphere solution and film states. Photoresponsive conjugated polymers with RGB fluorescence, **P1–P3**, are synthesized by introducing DE moieties into side chains of specific conjugated backbones. The fluorescence of the polymers is quenched by UV light and subsequently regenerated by visible light via the photoisomerization of the DE moieties in the side chains. Polymer nanospheres with several hundred nanometers in diameter are prepared by a reprecipitation method.

White fluorescence is obtained by mixing the RGB fluorescent polymer nanospheres in the appropriate ratio. The white fluorescence is photoswitchable between emission and quenching upon irradiation with UV and visible light in both nanosphere solution and film states. Photoswitching between white fluorescence and RGB fluorescence is also achieved by replacing one of the photoresponsive polymers with a non-photoresponsive conjugated polymer analogue, except the W-G cast film. The present systems with photochemically color-tunable white fluorescence herein can be used as photoresponsive polymer illuminants.

Experimental Section

1. Measurements. NMR spectra were obtained with JEOL AL-400 or JEOL EX-400. Chemical shifts are represented in parts per million downfield from tetramethylsilane (TMS) as internal standards. Elemental analyses were performed by Yanako CHN Corders (MT-3, MT-5 and MT-6), JSL JM-10, Mitsubishi chemical analytech AQF-100, and Dionex ICS-1500. High-resolution mass spectra (HRMS) were obtained by using Thermo Fisher Scientific EXACTIVE (ESI, APCI) and Thermo Fisher Scientific MALDI DUO orbitrapXL (MALDI).

Gel permeation chromatography (GPC) result was obtained with a system consisting of a JASCO CO-2065 Plus column oven and a JASCO UV-2070 Plus detector, where the instrument was calibrated by polystyrene standard at 40 °C. Tetrahydrofuran (THF) was used as an eluent and the flow rate was 1.0 mL/min. Ultraviolet–visible (UV–vis) absorption spectra were measured with JASCO V-570 UV/VIS/NIR spectrophotometer. Photoluminescence (PL) spectra were measured with JASCO FP-6500 spectrofluorometer. All optical measurements were performed using a quartz cell or substrate. Scanning electron microscopy (SEM) was performed with JEOL JSM-7500F. The samples were coated with Pt-Pd alloy using JEOL JFC-1600 ion coater before measurements of SEM. Dynamic light scattering (DLS) measurements were performed using Otsuka Electronics ELSZ-1000S. Ultrasonication was carried out using SONICS VCX 130. The CIE coordinates were calculated by using the method of colour matching functions (CMFs)³¹.

2. Materials. All the chemicals were commercially available and used as received. All the chemicals were purchased from Aldrich Chemical Co. Ltd., Tokyo Kasei Co. Ltd. and Wako Co. Ltd. Solvents were dried and distilled before use.

3. Synthesis. Compound **1** was prepared according to the previous study.²⁷ XPhosPd is a XPhos-coordinated palladium precatalyst³² reported by S. L. Buchwald *et al.* in 2010. The synthetic routes are shown in Schemes 2 and 3.

1-{5-(2,5-Dibromobenzoyloxymethyl)-2-methyl-3-thienyl}-2-(5-hydroxymethyl-2-methyl-3-thienyl)-3,3,4,4,5,5-hexafluorocyclopentene (2). To a mixture of **1** (2.01 g, 4.69 mmol), triphenylphosphine (TPP, 1.35 g, 5.15 mmol), and 2,5-dibromobenzoic

acid (1.31 g, 4.68 mmol) in THF (50 mL) was added dropwise a solution of diethyl azodicarboxylate (DEAD, 0.98 g, 40 wt % in toluene, 5.63 mmol) in THF (20 mL) via a dropping funnel at 0 °C under argon atmosphere. The reaction mixture was stirred at room temperature overnight. The crude product was extracted with chloroform, washed with saturated NaCl aqueous solution, dried over anhydrous sodium sulfate, and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, chloroform) to give **2** as a yellow transparent solid (2.23 g, 69 %): ¹H NMR (400 MHz, CDCl₃, TMS): δ = 1.87 (s, 3H; thienyl-CH₃), 1.93 (s, 3H; thienyl-CH₃), 4.75 (d, 2H, *J* = 5.6 Hz; CH₂OH), 5.41 (s, 2H; COOCH₂), 6.95 (s, 1H; thienyl-*H*), 7.12 (s, 1H; thienyl-*H*), 7.46 (dd, 1H, *J* = 8.4 Hz and 2.4 Hz; phenyl-*H*), 7.53 (d, 1H, *J* = 8.4 Hz; phenyl-*H*), 7.88 ppm (d, 1H, *J* = 2.4 Hz; phenyl-*H*); ¹³C NMR (100 MHz, CDCl₃, TMS): δ = 14.5, 59.9, 61.5, 120.6, 121.1, 124.3, 124.7, 124.8, 128.8, 133.1, 133.6, 134.20, 134.25, 135.2, 135.83, 135.85, 142.2, 142.4, 143.8, 164.5 ppm; HRMS (ESI, *m/z*): [M+Cl⁻] calcd for C₂₄H₁₆Br₂F₆O₃S₂: 724.8485; Found: 724.8502; Anal calcd for C₂₄H₁₆Br₂F₆O₃S₂: C 41.76, H 2.34, S 9.29; Found: C 42.02, H 2.53, S 9.30.

Ethyl 4-(2-nonoxy)benzoate (3). To a mixture of ethyl 4-hydroxybenzoate (1.66 g, 10.0 mmol), TPP (2.89 g, 11.0 mmol), and 2-nonanol (1.59 g, 11.0 mmol) in THF (30 mL) was added dropwise a solution of DEAD (1.92 g, 40 wt % in toluene, 11.0 mmol) in THF (10 mL) via a dropping funnel at 0 °C under argon atmosphere. The reaction mixture was stirred at room temperature for 5 h. After evaporating the solvent under reduced pressure, the residue was purified by column chromatography (silica gel, hexane/ethyl acetate = 15:1) to give **3** as a yellowish oil (2.64 g, 90 %): ¹H NMR (400 MHz, CDCl₃, TMS): δ = 0.88 (t, 3H, *J* = 6.8 Hz; (CH₂)₆CH₃), 1.27–1.44 (m, 16H; OCHCH₃, CH₂(CH₂)₅CH₃, and COOCH₂CH₃), 1.55–1.75 (dm, 2H; OCHCH₂), 4.34 (q, 2H, *J* = 7.2 Hz; COOCH₂CH₃), 4.43 (sext, 1H, *J* = 6.0 Hz; OCH(CH₃)C₇H₁₅), 6.88 (dt, 2H, *J* = 9.2 Hz and 2.4 Hz; Ar-*H*), 7.97 ppm (d, 2H, *J* = 9.2 Hz and 2.4 Hz; Ar-*H*); ¹³C NMR (100 MHz, CDCl₃, TMS): δ = 14.1, 14.4, 19.6, 22.7, 25.5, 29.2, 29.5, 31.8, 36.4, 60.5, 74.0, 115.0, 122.5, 131.6, 162.1, 166.5 ppm; HRMS (ESI, *m/z*): [M-H⁺] calcd for C₁₈H₂₈O₃: 291.1966; Found: 291.1971; Anal calcd for C₁₈H₂₈O₃: C 73.93, H 9.65; Found: C 73.81, H 9.85.

4-(2-Nonoxy)benzoic acid (4). **3** (2.44 g, 8.36 mmol) was hydrolyzed by NaOH (3.35 g, 83.7 mmol) in water (15 mL) and MeOH (150 mL) at 60 °C for 4 h. The solvent was then evaporated, and the crude product was dissolved in water. The mixture was acidified to pH = 1 with hydrochloric acid solution. The crude product was extracted with chloroform, washed with saturated NaCl aqueous solution, dried over anhydrous sodium sulfate, and evaporated under reduced pressure to give **4** as a white solid (2.19 g, 99 %): ^1H NMR (400 MHz, CDCl_3 , TMS): δ = 0.88 (t, 3H, J = 6.8 Hz; $(\text{CH}_2)_6\text{CH}_3$), 1.27–1.44 (m, 13H; OCHCH_3 and $\text{OCHCH}_2(\text{CH}_2)_5\text{CH}_3$), 1.56–1.76 (dm, 2H; OCHCH_2), 4.46 (sext, 1H, J = 6.0 Hz; $\text{OCH}(\text{CH}_3)\text{C}_7\text{H}_{15}$), 6.91 (d, 2H, J = 8.8 Hz; Ar- H), 8.05 (d, 2H, J = 8.8 Hz; Ar- H); ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ = 14.1, 19.6, 22.7, 25.5, 29.2, 29.5, 31.8, 36.3, 74.1, 115.1, 121.1, 132.4, 163.0, 172.0 ppm; HRMS (APCI, m/z): $[\text{M}+\text{H}^+]$ calcd for $\text{C}_{16}\text{H}_{24}\text{O}_3$: 265.1798; Found: 265.1793; Anal calcd for $\text{C}_{16}\text{H}_{24}\text{O}_3$: C 72.69, H 9.15; Found: C 72.41, H 9.23.

1-{5-(2,5-Dibromobenzoyloxymethyl)-2-methyl-3-thienyl}-2-[5-{4-(2-nonoxy)benzoyloxymethyl}-2-methyl-3-thienyl]-3,3,4,4,5,5-hexafluorocyclopentene (5). A mixture of **2** (1.06 g, 1.54 mmol), **4** (0.41 g, 1.55 mmol), N,N' -dicyclohexylcarbodiimide (DCC, 0.35 g, 1.70 mmol), and 4-dimethylaminopyridine (DMAP, 0.23 g, 1.88 mmol) in CH_2Cl_2 (40 mL) was stirred overnight under argon atmosphere at room temperature. The crude product was extracted with chloroform, washed with saturated NaCl aqueous solution, dried over anhydrous sodium sulfate and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, chloroform) to give **5** as a yellow viscous oil (0.83 g, 58 %): ^1H NMR (400 MHz, CDCl_3 , TMS): δ = 0.87 (t, 3H, J = 6.8 Hz; $(\text{CH}_2)_6\text{CH}_3$), 1.26–1.46 (m, 13H, OCHCH_3 and $\text{OCHCH}_2(\text{CH}_2)_5\text{CH}_3$), 1.54–1.79 (dm, 2H; OCHCH_2), 1.887 (s, 3H; thienyl- CH_3), 1.893 (s, 3H; thienyl- CH_3), 4.43 (sext, 1H, J = 6.0 Hz; $\text{OCH}(\text{CH}_3)\text{C}_7\text{H}_{15}$), 5.36 (s, 2H; COOCH_2), 5.40 (s, 2H; COOCH_2), 6.88 (dt, 2H, J = 9.2 Hz and 2.4 Hz; phenyl- H), 7.08 (s, 1H; thienyl- H), 7.13 (s, 1H; thienyl- H), 7.44 (dd, 1H, J = 8.4 Hz and 2.4 Hz; phenyl- H), 7.51 (d, 1H, J = 8.4 Hz; phenyl- H), 7.88 (d, 1H, J = 2.4 Hz; phenyl- H), 7.96 ppm (dt, 2H, J = 9.2 Hz and 2.4 Hz; phenyl- H); ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ = 14.1, 14.4, 19.6, 22.6, 25.5, 29.2, 29.5, 31.8, 36.3, 60.5, 61.5, 74.1, 115.1, 120.6, 121.1, 121.5, 124.3, 124.6, 127.5, 128.6, 131.8, 133.1, 134.3, 135.3, 135.80, 135.85, 136.9, 143.2, 143.8, 162.5, 164.4, 165.9

ppm; HRMS (ESI, m/z): $[M+Cl^-]$ calcd for $C_{40}H_{38}Br_2F_6O_5S_2$: 971.0105; Found: 971.0133; Anal calcd for $C_{40}H_{38}Br_2F_6O_5S_2$: C 51.29, H 4.09, S 6.85; Found: C 51.43, H 4.16, S 6.94.

1-{5-Hydroxymethyl-2-methyl-3-thienyl}-2-[5-{4-(2-nonoxy)benzoyloxymethyl}-2-methyl-3-thienyl]-3,3,4,4,5,5-hexafluorocyclopentene (6). To a mixture of **1** (1.02 g, 2.38 mmol), **4** (0.63 g, 2.38 mmol) and TPP (0.69 g, 2.63 mmol) in THF (50 mL) was added dropwise a solution of DEAD (0.50 g, 40 wt % in toluene, 2.87 mmol) in THF (20 mL) via a dropping funnel at 0 °C under argon atmosphere. The reaction mixture was stirred at room temperature overnight. The crude product was extracted with chloroform, washed with saturated NaCl aqueous solution, dried over anhydrous sodium sulfate, and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, chloroform) to give **9** as a yellow solid (0.95 g, 59 %): 1H NMR (400 MHz, $CDCl_3$, TMS): δ = 0.87 (t, 3H, J = 6.8 Hz; CH_3), 1.28–1.74 (m, 15H, $OCHCH_3$ and $OCH(CH_2)_6CH_3$), 1.87–1.94 (m, 6H; thienyl- CH_3), 4.44 (sext, 1H, J = 6.0 Hz; $OCH(CH_3)C_7H_{15}$), 4.74 (s, 2H; CH_2OH), 5.40 (s, 2H; $COOCH_2$), 6.88 (d, 2H, J = 9.2 Hz; *ortho* to $OCH(CH_3)C_7H_{15}$), 6.93 (s, 1H; thienyl- H), 7.05 (s, 1H; thienyl- H), 7.96 ppm (d, 2H, J = 9.2 Hz; *meta* to $OCH(CH_3)C_7H_{15}$); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 14.1, 14.4, 19.6, 22.7, 25.5, 29.3, 29.5, 31.8, 36.3, 52.7, 59.9, 61.5, 74.1, 115.1, 121.1, 121.5, 127.4, 128.6, 131.7, 135.8, 136.9, 143.9, 162.5, 165.9 ppm; HRMS (APCI, m/z): $[M+Cl^-]$ calcd for $C_{33}H_{36}F_6O_4S_2$: 709.1642; Found: 709.1663; Anal calcd for $C_{33}H_{36}F_6O_4S_2$: C 58.74, H 5.38, S 9.50; Found: C 58.65, H 5.33, S 9.45.

Ethyl 2,7-dibromo-9H-fluorene-9-carboxylate (7). To a solution of diisopropylamine (1.99 g, 19.8 mmol) in THF (50 mL) was added dropwise *n*-BuLi (1.26 g, 15 wt % in hexane, 19.8 mmol) via a dropping funnel at –78 °C under argon atmosphere, and the mixture was stirred for 30 min. Then, a solution of 2,7-dibromofluorene (3.05 g, 9.41 mmol) in THF (15 mL) was added dropwise to the mixture and stirred for another 30 min at –78 °C. Then, a solution of ethyl chlorocarbonate (1.03 g, 9.49 mmol) in THF (15 mL) was added dropwise to the mixture. After addition, the mixture was warmed to room temperature and stirred for 1 h. The crude product was extracted with chloroform, washed with saturated NaCl aqueous solution, dried over anhydrous sodium sulfate, and evaporated under reduced

pressure. The residue was recrystallized from hexane to give **7** as a yellow solid (2.94 g, 79 %): ^1H NMR (400 MHz, CDCl_3 , TMS): δ = 0.87 (t, 3H, J = 7.2 Hz; CH_3), 4.26 (q, 2H, J = 7.2 Hz; $\text{COOCH}_2\text{CH}_3$), 4.81 (s, 1H; fluorene-9-*H*), 7.55–7.57 (m, 4H; fluorene-*H*), 7.81 ppm (s, 2H; fluorene-*H*); ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ = 14.2, 53.0, 61.9, 121.3, 121.5, 129.1, 131.5, 139.4, 142.2, 169.3 ppm; HRMS (APCI, m/z): $[\text{M}+\text{NH}_4^+]$ calcd for $\text{C}_{16}\text{H}_{12}\text{Br}_2\text{O}_2$: 394.9112; Found: 394.9105; Anal calcd for $\text{C}_{16}\text{H}_{12}\text{Br}_2\text{O}_2$: C 48.52, H 3.05, Br 40.35; Found: C 48.37, H 2.94, Br 40.31.

2,7-Dibromo-9H-fluorene-9-carboxylic acid (8). To a solution of **7** (2.00 g, 5.05 mmol) in acetic acid (48 mL) was added a solution of sulfuric acid (98 %, 6 mL) in H_2O (36 mL). The reaction mixture was refluxed at 100 °C overnight. After cooling to room temperature, the precipitate was filtered and washed exhaustively with water. The residue was recrystallized from chloroform/hexane to give **8** as a white solid (1.23 g, 66 %): ^1H NMR (400 MHz, CD_3OD , TMS): δ = 4.84 (s, 1H; fluorene-9-*H*), 7.53–7.61 (m, 4H; fluorene-*H*), 7.84 ppm (s, 2H; fluorene-*H*); ^{13}C NMR (100 MHz, CD_3OD , TMS): δ = 53.4, 121.5, 121.5, 129.3, 131.5, 139.6, 142.9, 171.8 ppm; HRMS (APCI, m/z): $[\text{M}-\text{H}^+]$ calcd for $\text{C}_{14}\text{H}_8\text{Br}_2\text{O}_2$: 366.8798; Found: 366.8793; Anal calcd for $\text{C}_{14}\text{H}_8\text{Br}_2\text{O}_2$: C 45.69, H 2.19, Br 43.42; Found: C 45.52, H 2.16, Br 43.23.

1-[5-{(2,7-Dibromo-9H-fluorene-9-yl)methyl}-2-methyl-3-thienyl]-2-[5-{4-(2-nonyloxy)benzoyloxymethyl}-2-methyl-3-thienyl]-3,3,4,4,5,5-hexafluorocyclopentene (9). To a mixture of **6** (0.50 g, 0.74 mmol), **8** (0.27 g, 0.73 mmol), and TPP (0.21 g, 0.80 mmol) in THF (20 mL) was added dropwise a solution of DEAD (0.15 g, 40 wt % in toluene, 0.86 mmol) in THF (10 mL) via a dropping funnel at 0 °C under argon atmosphere. The reaction mixture was stirred at room temperature overnight. The crude product was extracted with chloroform, washed with saturated NaCl aqueous solution, dried over anhydrous sodium sulfate, and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, chloroform) to give **9** as a yellow solid (0.54 g, 71 %): ^1H NMR (400 MHz, CDCl_3 , TMS): δ = 0.87 (t, 3H, J = 7.2 Hz; CH_3), 1.28–1.82 (m, 21H, OCHCH_3 , $\text{OCH}(\text{CH}_2)_6\text{CH}_3$, and thienyl- CH_3), 3.42 (d, 2H, J = 6.0 Hz; fluorene-9- CH_2), 4.16 (t, 1H, J = 5.6 Hz; fluorene-9-*H*), 4.43 (sext, 1H, J = 6.0 Hz; $\text{OCH}(\text{CH}_3)\text{C}_7\text{H}_{15}$), 5.40 (s, 2H; COOCH_2), 6.60 (s, 1H; thienyl-*H*), 6.87 (d, 2H, J = 8.4 Hz; *ortho* to $\text{OCH}(\text{CH}_3)\text{C}_7\text{H}_{15}$), 7.04 (s, 1H; thienyl-*H*), 7.48–7.53 (m, 6H; fluorene-*H*), 7.95 ppm (d, 2H, J = 8.4 Hz; *meta* to $\text{OCH}(\text{CH}_3)\text{C}_7\text{H}_{15}$); ^{13}C NMR

(100 MHz, CDCl_3 , TMS): δ = 14.1, 14.2, 14.2, 19.6, 22.6, 25.4, 29.2, 29.5, 31.8, 33.0, 36.3, 47.9, 60.5, 74.0, 115.0, 121.1, 121.2, 121.4, 123.9, 124.3, 125.7, 127.3, 127.7, 130.8, 131.7, 136.5, 137.9, 139.2, 140.5, 143.1, 147.1, 162.3, 165.8 ppm; HRMS (APCI, m/z): $[\text{M}+\text{NH}_4^+]$ calcd for $\text{C}_{46}\text{H}_{42}\text{Br}_2\text{F}_6\text{O}_3\text{S}_2$: 998.1164; Found: 998.1130; Anal calcd for $\text{C}_{46}\text{H}_{42}\text{Br}_2\text{F}_6\text{O}_3\text{S}_2$: C 56.33, H 4.32, S 6.54; Found: C 56.26, H 4.21, S 6.48. Note that *unexpected CO_2 elimination occurred during the Mitsunobu reaction, resulting in the formation of direct C–C bond, instead of a typical ester bond.*

4,7-Dibromo-2,1,3-benzothiadiazole (10). To a solution of 2,1,3-benzothiadiazole (5.00 g, 36.72 mmol) in hydrobromic acid (47 %, 50 mL) was added dropwise a solution of Br_2 (17.61 g, 110.16 mmol) in hydrobromic acid (47 %, 50 mL) via a dropping funnel at room temperature. After total addition of Br_2 , the solution was refluxed at 100 °C for 6 h. After cooling to room temperature, saturated aqueous solution of NaHCO_3 was added to consume excess Br_2 . The precipitate was filtered, and washed exhaustively with water. The solid was then washed once with cold diethyl ether and recrystallized from chloroform to give **10** as a colorless solid (7.66 g, 71 %): ^1H NMR (400 MHz, CDCl_3 , TMS): δ = 7.73 ppm (s, 2H; benzothiadiazole-*H*); ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ = 113.9, 132.4, 153.0 ppm; HRMS (APCI, m/z): $[\text{M}+\text{H}^+]$ calcd for $\text{C}_6\text{H}_2\text{Br}_2\text{N}_2\text{S}$: 292.8378; Found: 292.8369; Anal calcd for $\text{C}_6\text{H}_2\text{Br}_2\text{N}_2\text{S}$: C 24.51, H 0.69, N 9.53, S 10.91; Found: C 24.59, H 0.76, N 9.59, S 10.85.

4,7-Di(2-thienyl)-2,1,3-benzothiadiazole (11). To a mixture of **10** (3.03 g, 10.31 mmol), 2-thiopheneboronic acid (2.87 g, 22.43 mmol), and XPhosPd (0.32 g, 0.41 mmol) in THF (70 mL) was added an aqueous solution of K_3PO_4 (0.5 M, 70 mL) under argon atmosphere, and then the mixture was stirred at 40 °C for 3 h. The crude product was extracted with diethyl ether, washed with saturated NaCl aqueous solution, dried over anhydrous sodium sulfate, and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, chloroform), and then recrystallized from chloroform/ethanol to give **11** as a red solid (2.80 g, 90 %): ^1H NMR (400 MHz, CDCl_3 , TMS): δ = 7.20 (dd, 2H, J = 5.1 Hz and 3.6 Hz; thienyl-*H*), 7.45 (dd, 2H, J = 5.1 Hz and 1.0 Hz; thienyl-*H*), 7.84 (s, 2H; benzothiadiazole-*H*), 8.10 ppm (dd, 2H, J = 3.6 Hz and 1.0 Hz; thienyl-*H*); ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ = 125.8, 126.0, 126.8, 127.5, 128.0, 139.4, 152.7 ppm; HRMS (APCI, m/z): $[\text{M}+\text{H}^+]$ calcd for

$C_{14}H_8N_2S_3$: 300.9922; Found: 300.9913; Anal calcd for $C_{14}H_8N_2S_3$: C 55.97, H 2.68, N 9.32, S 32.02; Found: C 55.93, H 2.56, N 9.33, S 31.74.

4,7-Bis(5-bromo-2-thienyl)-2,1,3-benzothiadiazole (12). A mixture of **11** (1.50 g, 4.99 mmol) and *N*-bromosuccinimide (NBS, 2.22 g, 12.47 mmol) in chloroform (100 ml) was stirred for 48 h under argon atmosphere at room temperature. Then, the precipitate was filtered and washed with chloroform. The residue was recrystallized from chloroform to give **12** as a red solid (0.69 g, 30 %): 1H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.16 (d, 2H, J = 4.0 Hz; thienyl-*H*), 7.80 (s, 2H; benzothiadiazole-*H*), 7.82 ppm (d, 2H, J = 4.0 Hz; thienyl-*H*); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 111.4, 127.8, 128.9, 129.4, 130.9, 140.6, 154.0 ppm; HRMS (APCI, m/z): $[M+H]^+$ calcd for $C_{14}H_6Br_2N_2S_3$: 458.8111; Found: 458.8099; Anal calcd for $C_{14}H_6Br_2N_2S_3$: C 36.70, H 1.32, N 6.11, S 20.99; Found: C 36.48, H 1.36, N 6.13, S 20.96.

***n*-Nonyl 2,5-dibromobenzoate (13).** To a mixture of TPP (2.06 g, 7.85 mmol) and 2,5-dibromobenzoic acid (2.00 g, 7.15 mmol) in THF (50 mL) was added dropwise a solution of DEAD (1.49 g, 40 wt % in toluene, 8.56 mmol) and 1-nonanol (1.03 g, 7.14 mmol) in THF (20 mL) via a dropping funnel at 0 °C under argon atmosphere. The reaction mixture was stirred at room temperature overnight. The crude product was extracted with chloroform, washed with saturated NaCl aqueous solution, dried over anhydrous sodium sulfate, and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, chloroform) to give **13** as a colorless oil (1.97 g, 62 %): 1H NMR (400 MHz, $CDCl_3$, TMS): δ = 0.88 (t, 3H, J = 6.8 Hz; CH_3), 1.28–1.47 (m, 12H; $COOCH_2CH_2(CH_2)_6CH_3$), 1.77 (quint, 2H, J = 6.8 Hz; $COOCH_2CH_2$), 4.33 (t, 2H, J = 6.8 Hz; $COOCH_2$), 7.43 (dd, 1H, J = 8.6 Hz and 2.4 Hz; Ar-*H*), 7.51 (d, 1H, J = 8.6 Hz; Ar-*H*), 7.89 ppm (d, 1H, J = 2.4 Hz; Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 14.1, 22.7, 26.0, 28.6, 29.2, 29.5, 31.9, 66.3, 120.3, 121.0, 134.0, 134.2, 135.3, 135.7, 165.0 ppm; HRMS (ESI, m/z): $[M+H]^+$ calcd for $C_{16}H_{22}Br_2O_2$: 407.0039; Found: 407.0035; Anal calcd for $C_{16}H_{22}Br_2O_2$: C 47.32, H 5.46, Br 39.35; Found: C 47.56, H 5.32, Br 39.36.

2,7-Dibromo-9,9-dioctylfluorene (14). To a solution of 2,7-dibromofluorene (1.50 g, 4.63 mmol) and benzyltriethylammonium chloride (catalyst) in DMSO (30 mL) were added an aqueous solution of sodium hydroxide (50 wt %, 5 mL), and subsequently 1-bromooctane (2.24 g, 11.57 mmol). The reaction mixture was stirred at room

temperature for 3 h under argon atmosphere. The crude product was extracted with diethyl ether, washed with saturated NaCl aqueous solution, dried over anhydrous sodium sulfate, and evaporated under reduced pressure. The residue was recrystallized from hexane to give **14** as a white solid (2.14 g, 84 %): ^1H NMR (400 MHz, CDCl_3 , TMS): δ = 0.58 (quint, 4H, J = 4.0 Hz; CH_2), 0.83 (t, 6H, J = 7.2 Hz; CH_2CH_3), 1.05–1.27 (m, 20H; CH_2), 1.88–1.93 (m, 4H; fluorene-9- $[\text{CH}_2(\text{CH}_2)_6\text{CH}_3]_2$), 7.44 (s, 2H, fluorene- H), 7.45 (dd, 2H, J = 8.0 Hz and 1.8 Hz; fluorene- H), 7.51 ppm (dd, 2H, J = 8.0 Hz and 0.8 Hz; fluorene- H); ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ = 14.1, 22.6, 23.6, 29.1, 29.2, 29.9, 31.8, 40.2, 55.7, 121.1, 121.5, 126.2, 130.2, 139.1, 152.6 ppm; HRMS (APCI, m/z): $[\text{M}^+]$ calcd for $\text{C}_{29}\text{H}_{40}\text{Br}_2$: 548.1473; Found: 548.1464; Anal calcd for $\text{C}_{29}\text{H}_{40}\text{Br}_2$: C 63.51, H 7.35, Br 29.14; Found: C 63.55, H 7.52, Br 28.49.

P1. To a solution of **5** (242 mg, 0.26 mmol), 9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (130 mg, 0.26 mmol), and XPhosPd (8.0 mg, 10.2 μmol) in THF (4 mL) was added an aqueous solution of K_3PO_4 (0.5 M, 4 mL) under argon atmosphere, and then the mixture was stirred at 40 $^\circ\text{C}$ for 48 h. The reaction mixture was poured into a large amount of H_2O (300 mL) and vigorously stirred for 2 h. The resulting precipitate was collected by filtration, dissolved in THF (15 mL), and stirred with an aqueous solution of NaCN (0.10 g in 10 mL) for 1 h at RT to give a yellowish precipitate. Then, the precipitate was dissolved in a small amount of THF and reprecipitated in methanol (400 mL). After filtration, the product was dried under vacuum to give **P1** as a white solid (148 mg, 52 %): ^1H NMR (400 MHz, CDCl_3 , TMS): δ = 0.74–1.43 (m, 40H, $\text{C}(\text{CH}_2\text{C}_5\text{H}_{11})_2$ and $\text{OCH}(\text{CH}_3)\text{C}_7\text{H}_{15}$), 1.79–1.83 (m, 6H; thienyl- CH_3), 2.04 (m, 4H, $\text{C}(\text{CH}_2\text{C}_5\text{H}_{11})_2$), 4.44 (sext, 1H, J = 8.0 Hz; $\text{OCH}(\text{CH}_3)\text{C}_7\text{H}_{15}$), 5.14 (s, 2H, COOCH_2), 5.34 (s, 2H, COOCH_2), 6.85 (d, 2H, J = 9.0 Hz; *ortho* to $\text{OCH}(\text{CH}_3)\text{C}_7\text{H}_{15}$), 6.95 (s, 1H thienyl- H), 7.07 (s, 1H, thienyl- H), 7.33–7.87 (m, 8H, phenyl- H), 7.96 (d, 2H, J = 8.0 Hz; *meta* to $\text{OCH}(\text{CH}_3)\text{C}_7\text{H}_{15}$), 8.12 (s, 1H, phenyl- H); ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ = 14.1, 14.3, 19.6, 22.6, 25.5, 29.2, 29.5, 31.6, 36.3, 55.2, 55.4, 60.5, 60.8, 74.1, 115.1, 119.7, 120.3, 121.5, 123.1, 124.4, 126.1, 127.4, 127.6, 127.7, 136.9, 140.7, 143.2, 143.3, 151.1, 151.2, 162.5, 165.9 ppm.

P2. A solution of **5** (235 mg, 0.25 mmol), *trans*-1,2-bis(tributylstannyl)ethylene (152 mg, 0.25 mmol), $\text{Pd}_2(\text{DBA})_3$ (2.35 mg, 2.57 μmol), and tri(2-furyl)phosphine (2.39 mg,

10.28 μmol) in DMF (4 mL) was stirred under argon atmosphere at 80 °C for 72 h. The reaction mixture was poured into a large amount of methanol (350 mL) containing HCl and vigorously stirred for 1 h. The resulting precipitate was collected by filtration, dissolved in THF (20 mL), mixed with an aqueous solution of NaCN (0.10 g/10 mL), and stirred for 40 min at RT. Then, the solution was reprecipitated in methanol (450 mL). After filtration, the product was dried under vacuum to give **P2** as an orange solid (121 mg, 60 %): ^1H NMR (400 MHz, CDCl_3 , TMS): δ = 0.85 (s, 3H; CH_3), 1.26–1.70 (m, 18H; $\text{OCH}(\text{CH}_3)\text{C}_7\text{H}_{15}$), 1.86 (s, 6H; thienyl- CH_3), 4.41 (s, 1H; $\text{OCH}(\text{CH}_3)\text{C}_7\text{H}_{15}$), 5.33 (s, 2H; COOCH_2), 5.44 (s, 2H; COOCH_2), 6.85 (d, 2H; J = 8.0 Hz; *ortho* to $\text{OCH}(\text{CH}_3)\text{C}_7\text{H}_{15}$), 7.07 (s, 1H; thienyl- H), 7.17 (s, 1H; thienyl- H), 7.72–8.03 ppm (m, 7H; phenyl- H , vinyl- H , and *meta* to $\text{OCH}(\text{CH}_3)\text{C}_7\text{H}_{15}$); ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ = 14.1, 14.3, 19.6, 22.6, 25.4, 29.2, 29.5, 31.8, 36.3, 60.5, 61.0, 74.1, 115.1, 121.4, 124.3, 124.5, 126.7, 127.5, 131.8, 136.2, 136.9, 143.6, 162.5, 165.9 ppm.

P3. To a solution of **9** (147 mg, 0.14 mmol), **12** (3.5 mg, 7.6 μmol), bis(pinacolato)diboron (38.5 mg, 0.15 mmol), and XPhosPd (4.7 mg, 6.0 μmol) in THF (2 mL) was added an aqueous solution of K_3PO_4 (0.5 M, 2 mL) under argon atmosphere, and then the mixture was stirred at 40 °C for 48 h. The reaction mixture was poured into a large amount of H_2O (300 mL) and vigorously stirred for 1 h. The resulting precipitate was collected by filtration, dissolved in minimum amount of THF (2 mL), and reprecipitated in methanol (300 mL) for 1 h. After filtration, the product was dried under vacuum to give **P3** as a purple solid (108 mg, 90 %): ^1H NMR (400 MHz, CDCl_3 , TMS): δ = 0.86 (br, 3H; $(\text{CH}_2)_6\text{CH}_3$), 1.27–1.71 (m, 21H; OCHCH_3 , $\text{OCH}(\text{CH}_2)_6\text{CH}_3$, and thienyl- CH_3), 3.64 (br, 2H; fluorene-9- CH_2), 4.40–4.41 (m, 2H; fluorene-9- H and $\text{OCH}(\text{CH}_3)\text{C}_7\text{H}_{15}$), 5.29 (s, 2H; COOCH_2), 6.71 (s, 1H; thienyl- H), 6.85 (d, 2H, J = 8.4 Hz; *ortho* to $\text{OCH}(\text{CH}_3)\text{C}_7\text{H}_{15}$), 7.01 (s, 1H; thienyl- H), 7.66–7.82 (m, 6H; fluorene- H), 7.94 ppm (d, 2H, J = 8.4 Hz; *meta* to $\text{OCH}(\text{CH}_3)\text{C}_7\text{H}_{15}$); ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ = 14.06, 14.14, 19.5, 22.6, 25.4, 29.2, 29.5, 31.7, 36.3, 48.1, 60.5, 74.0, 115.0, 120.3, 121.4, 123.1, 123.8, 124.3, 125.4, 126.8, 127.2, 131.6, 136.4, 138.9, 140.1, 143.3, 146.5, 162.3, 165.7 ppm; Anal calcd for $[(\text{C}_{46}\text{H}_{42}\text{F}_6\text{O}_3\text{S}_2)_{0.95} \cdot (\text{C}_{14}\text{H}_6\text{N}_2\text{S}_3)_{0.05}]_n$: C 66.75, H, 5.00, N 0.47, S 9.03; Found: C 66.23, H 5.02, N 0.28, S 8.14.

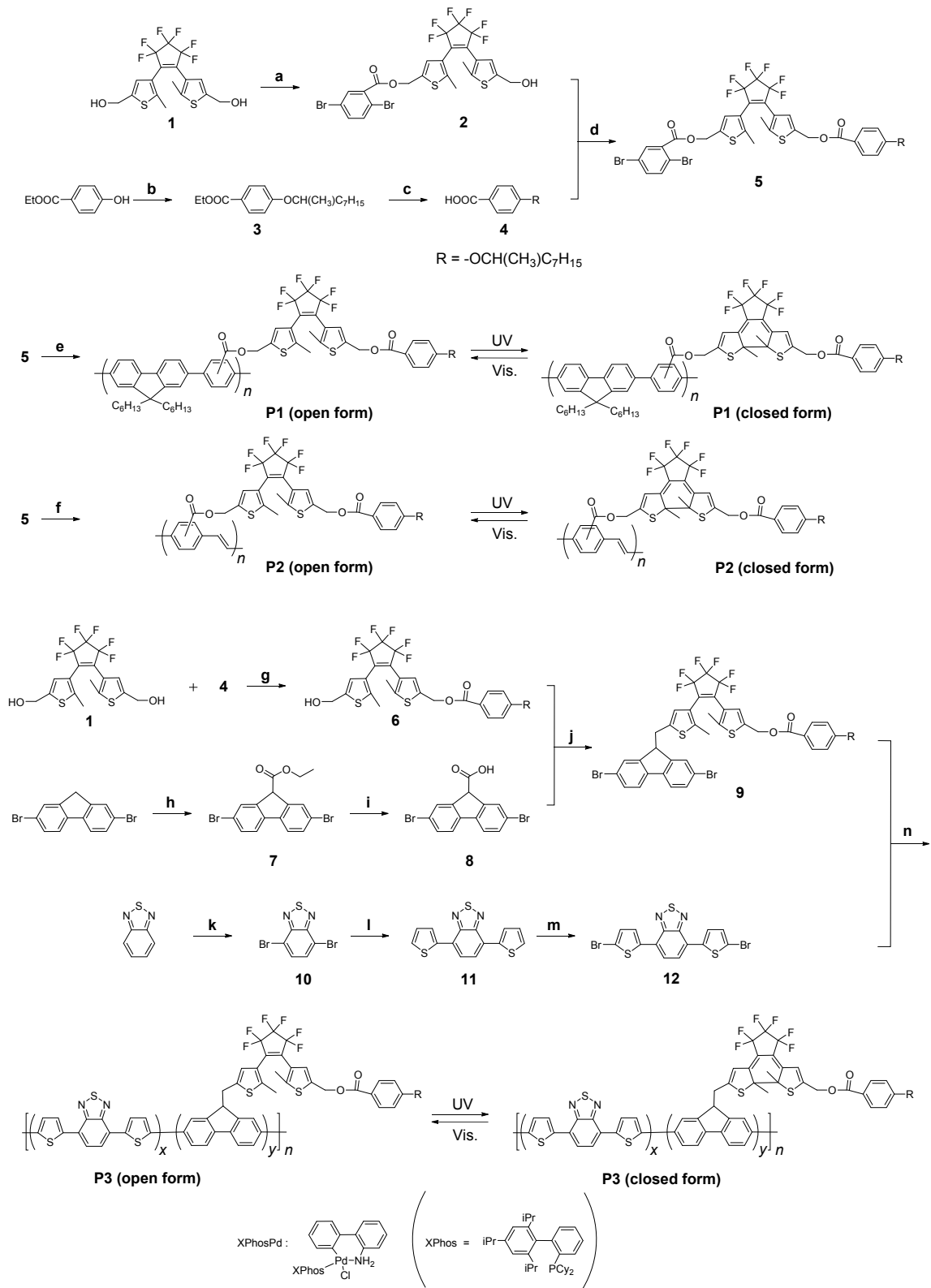
P1'. To a mixture of **13** (152 mg, 0.37 mmol), 9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (188 mg, 0.37 mmol), and XPhosPd (11.8 mg, 14.9 μ mol) in THF (2 mL) was added an aqueous solution of K_3PO_4 (0.5 M, 2 mL) under argon atmosphere, and then the mixture was stirred at 40 °C for 48 h. The reaction mixture was poured into a large amount of H_2O (300 mL) and vigorously stirred for 1 h. The resulting precipitate was collected by filtration, dissolved in minimum amount of THF (2 mL), and reprecipitated in methanol (300 mL) for 1 h. After filtration, the product was dried under vacuum to give **P1'** as a white solid (199 mg, 92 %): 1H NMR ($CDCl_3$): δ = 0.78–1.41 (m, 39H; $C(CH_2C_5H_{11})_2$ and $OCH_2C_8H_{17}$), 2.01 (s, 4H; $C(CH_2C_5H_{11})_2$), 4.08 (s, 2H; $OCH_2C_8H_{17}$), 7.39–8.13 (m, 9H; phenyl-*H*); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 14.1, 17.4, 22.7, 22.8, 23.9, 25.9, 28.5, 29.3, 29.8, 31.7, 31.9, 55.4, 55.5, 65.4, 119.4, 120.1, 121.4, 123.0, 126.0, 128.2, 129.4, 131.2, 132.3, 151.8, 151.9, 169.1 ppm.

P2'. A solution of **13** (406 mg, 1.00 mmol), *trans*-1,2-bis(tributylstannyl)ethylene (607 mg, 1.00 mmol), $Pd_2(DBA)_3$ (9.20 mg, 10.0 μ mol), and tri(2-furyl)phosphine (9.41 mg, 40.5 μ mol) in DMF (4 mL) was stirred under argon atmosphere at 80 °C for 72 h. The reaction mixture was poured into a large amount of methanol (500 mL) containing HCl and vigorously stirred for 1 h. The resulting precipitate was collected by filtration, dissolved in THF (100 mL), mixed with an aqueous solution of NaCN (0.10 g/10 mL), and stirred for 40 min at 65 °C. Then, the solution was concentrated (ca. 50 mL) under reduced pressure and reprecipitated in methanol (400 mL). After filtration, the product was dried under vacuum to give **P2'** as an orange solid (241 mg, 88 %): 1H NMR (400 MHz, $CDCl_3$, TMS): δ = 0.85 (s, 3H; CH_3), 1.26–1.74 (m, 14H; $OCH_2(CH_2)_7CH_3$), 4.3 (s, 2H; $OCH_2(CH_2)_7CH_3$), 7.53–7.72 ppm (m, 5H; phenyl-*H*, vinyl-*H*); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 14.1, 22.6, 26.0, 28.5, 29.1, 29.4, 31.6, 66.0, 120.3, 127.6, 127.9, 130.9, 131.8, 143.5, 169.3 ppm.

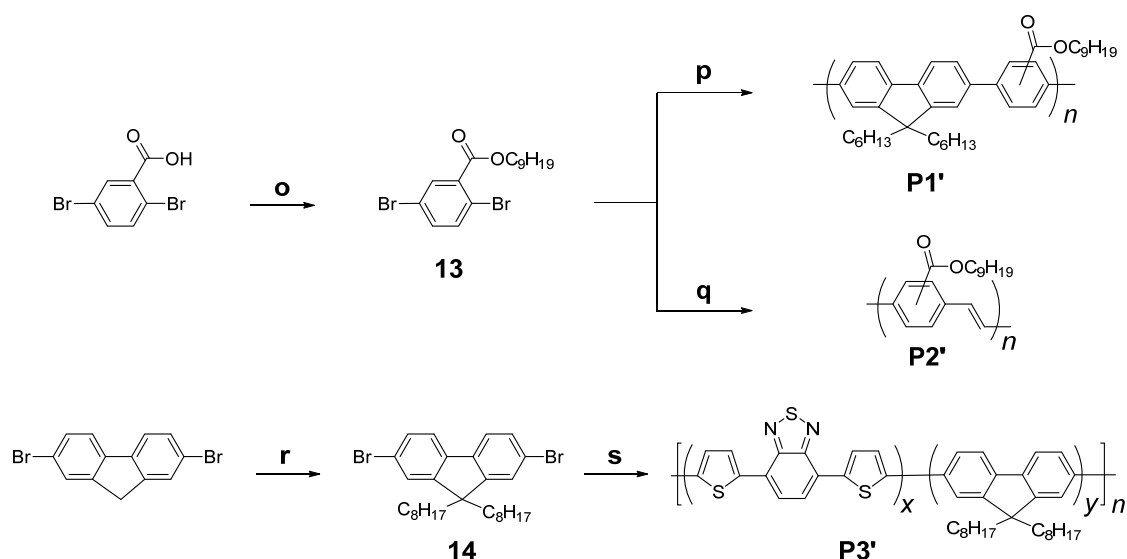
P3'. To a solution of **12** (6.6 mg, 14.4 μ mol), **14** (150 mg, 0.28 mmol), bis(pinacolato)diboron (73.1 mg, 0.29 mmol), and XPhosPd (9.1 mg, 11.6 μ mol) in THF (2 mL) was added an aqueous solution of K_3PO_4 (0.5 M, 2 mL) under argon atmosphere, and then the mixture was stirred at 40 °C for 48 h. The reaction mixture was poured into a large amount of H_2O (300 mL) and vigorously stirred for 1 h. The resulting precipitate was collected by filtration, dissolved in minimum amount of THF

(3 mL), and reprecipitated in methanol (300 mL) for 1 h. After filtration, the product was dried under vacuum to give **P3'** as a purple solid (89 mg, 86 %): ^1H NMR (400 MHz, CDCl_3 , TMS): δ = 0.82 (t, 10H, J = 6.8Hz; CH_2 and CH_2CH_3), 1.14–1.22 (m, 20H; CH_2), 2.12 (br, 4H; fluorene-9- $[\text{CH}_2(\text{CH}_2)_6\text{CH}_3]_2$), 7.68 (br, 4H; fluorene- H), 7.84 (br, 2H; fluorene- H), 8.19 ppm (br, 0.1 H; thienyl- H); ^{13}C NMR (100 MHz, CDCl_3 , TMS): δ = 14.1, 22.7, 24.0, 29.3, 30.1, 30.9, 31.9, 40.4, 55.4, 119.9, 121.4, 126.1, 140.0, 140.4, 151.7 ppm; Anal calcd for $[(\text{C}_{29}\text{H}_{40})_{0.95} \cdot (\text{C}_{14}\text{H}_6\text{N}_2\text{S}_3)_{0.05}]_n$: C 87.97, H 9.95; N 0.47, S 1.61; Found: C 86.51, H 9.90, N 0.41, S 1.40.

*Photochemically Color-Tunable White Fluorescence Illuminants
consisting of Conjugated Polymer Nanospheres*



Scheme 2. Synthetic routes of P1, P2, and P3. (a) 2,5-Dibromo benzoic acid, TPP, DEAD, THF, RT, overnight. (b) 2-Nonanol, TPP, DEAD, THF, RT, 1 h. (c) Sodium hydroxide, methanol, water, 60 °C, 4 h. (d) DCC, DMAP, CH₂Cl₂, RT, overnight. (e) 9,9-Dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester, XPhosPd, K₃PO₄, THF, water, 40 °C, 48 h. (f) 1,2-Bis(tributylstannyl)ethylene, Pd₂(DBA)₃, tri(2-furyl)phosphine, DMF, 80 °C, 72 h. (g) TPP, DEAD, THF, RT, overnight. (h) (i) lithium diisopropylamide (LDA), hexane, THF, -78 °C, 30 min; (ii) Ethyl chlorocarbonate, THF, -78 °C, 10 min; (iii) RT, 1 h. (i) Sulfuric acid, acetic acid, water, 100 °C, overnight. (j) TPP, DEAD, THF, RT, overnight. (k) Bromine, hydrobromic acid, 100 °C, 6 h. (l) 2-Thiopheneboronic acid, XPhosPd, K₃PO₄, THF, water, 40 °C, 3 h. (m) *N*-Bromosuccinimide (NBS), chloroform, RT, 48 h. (n) Bis(pinacolato)diboron, XPhosPd, K₃PO₄, THF, water, 40 °C, 48 h. TPP = Triphenylphosphine, DEAD = diethyl azodicarboxylate, DCC = *N,N'*-dicyclohexylcarbodiimide, DMAP = 4-dimethylaminopyridine, DBA = dibenzilideneacetone.



Scheme 3. Synthetic routes of P1', P2', and P3'. (o) 1-Nonanol, TPP, DEAD, THF, RT, overnight. (p) 9,9-Dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester, XPhosPd, K₃PO₄, THF, water, 40 °C, 48 h. (q) 1,2-Bis(tributylstannyl)ethylene, Pd₂(DBA)₃, tri(2-furyl)phosphine, DMF, 80 °C, 72 h. (r) 1-Bromooctane, benzotriethylammonium chloride, sodium hydroxide, DMSO, water, RT, 3 h. (s) **12**, bis(pinacolato)diboron, XPhosPd, K₃PO₄, THF, water, 40 °C, 48 h. TPP = Triphenylphosphine, DEAD = diethyl azodicarboxylate, DBA = dibenzilideneacetone.

4. Methods.

Photoisomerization and percent conversion of DE moiety: Photoisomerization of DE moiety was generated by irradiating with UV light ($\lambda = 254$ nm, 4 W, handy lamp) for 15–60 s and visible light (1.0 W, white LED lamp) for 3 min. The level of conversion, which is defined as $\{[\text{closed form}]/([\text{open form}] + [\text{closed form}])\} \times 100\%$ ^{9, 26–28}, was confirmed through ¹H NMR measurements in CDCl₃. The ratio of open and closed forms of DE moiety was determined by using the integration values of CH₂ protons neighboring a thiophene ring of DE.

Preparation method of polymer nanosphere solutions: The **P1**, **P2**, and **P3** nanosphere solutions were prepared in water via a reprecipitation method³⁰. First, the polymers (1 μ mol) were dissolved in THF (2–20 mL). Second, the solution was added

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dropwise to water (20 mL) during ultrasonication using an ultrasonic homogenizer (130 W, 20 kHz). THF was then removed under reduced pressure to generate the nanosphere solution in water (5×10^{-5} M).

References

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General Conclusion

In this thesis, the author has studied the higher-ordered structure and the advanced optical properties of aromatic conjugated polymers. Detailed findings are summarized below.

In *Chapter 1*, the author has synthesized various types of thiophene-based LC conjugated copolymers containing a chiral nonyloxy carbonyl group in the side chain. The polymers with three aromatic rings in the repeating unit showed bisignate Cotton effects in the CD spectra of solutions and films and formed a polymer assembly with an interchain helically π -stacked structure. The concentration and temperature dependence of the absorption and CD spectra indicated that the polymer assembly exists even at dilute concentrations at room temperature but dissociates into single polymers at high temperatures. These polymers exhibited RGB-colored fluorescence with quantum yields from 0.04–0.26 and also showed CPF both in solution and as a film. The films showed enhanced CPF signals because of the strengthening of the helical π -stacking in solid states. The annealed films demonstrated very high CPF with g_{lum} values up to 10^{-1} , which were due to the large interchain interactions achieved during self-ordering in the N*-LC phase. The author found that the hierarchical arrangement of the higher-order structure by chiral liquid crystallinity is promising for the evolution of CPF with a very high dissymmetry factor in the chiral conjugated polymers. Furthermore, when some of the polymers were mixed in the appropriate ratio, CPF was observed across most of the visible region, indicating circularly polarized white luminescence. These results suggest that the polymers synthesized here may be useful as advanced materials for creating unique optical devices, such as circularly polarized electroluminescence in next-generation polymer electronics.

In *Chapter 2*, the author synthesized poly(*para*-terphenylene) and poly(terthiophene) derivatives, **PPPs** and **PTs**, by introducing the racemic or optically-active (2-nonyloxy)carbonyl side chains and then collected the soluble parts by Soxhlet extraction. By investigating the chiroptical properties, the author found that **PPPs** and **PTs** existed as isolated chains in chloroform solution and showed no

circular polarization in both absorption and luminescence regardless of the presence or absence of chiral side chains. Meanwhile, it was also found that **PPPs** and **PTs** with optically-active side chains self-assembled into the interchain helically π -stacked structure in the aggregated state such as polymer nanospheres and furthermore that the chiral **PPPs** fluoresced the circularly polarized light. Thus it is clarified that the circular polarization of **PPPs** and **PTs** in absorption and luminescence arises from the interchain helicity in polymer aggregates. Subsequently the author successfully demonstrated that chirality transferred from the chiral polymer to the achiral polymer through the interchain π - π interaction by mixing these polymers into a polymer nanosphere. The mixed system consisting of (*rac*)-**PPP** and chiral **PT** showed a CD spectrum that coincided with the sum of the CD spectra of chiral **PPP** and chiral **PT** in the aggregated state. This indicates that not only **PT** but also **PPP** have the interchain π -stacked structure with same helical sense according to the side chain chirality of chiral **PT**. The same result was obtained in the mixed system of chiral **PPP** and (*rac*)-**PT**. As a result, it was successfully demonstrated that the interchain π - π interaction can play an important role in the appearance of circular polarization on ACP main chain and the chiral transfer between ACPs.

In *Chapter 3*, the author found that the mixture of a cationic poly(*para*-phenylene) derivative (**PPP**) and an anionic chiral binaphthyl derivative (**BNP**) forms a hierarchically self-organized assembly with an interchain helically π -stacked structure stabilized by the presence of both electrostatic and π - π interactions. The electrostatic and π - π interactions are essential to the stability of the π -stacked structure, resulting in large dissymmetry factors of $|10^{-2}|$ – $|10^{-1}|$ in absorption and luminescence. It was demonstrated that the polymer assemblies further gathered to form spherulites, which can be regarded as semi-crystalline nanospheres, and the spherulites exhibit circularly polarized blue luminescence. The fabricated spherulites could be useful as novel chiral nanomaterials for the next-generation of plastic optoelectronics.

In *Chapter 4*, the author presented a novel approach for preparing interchain helically π -stacked assemblies of ionic conjugated polymers with high dissymmetry

factors of 10^{-2} – 10^{-1} by utilizing both intermolecular electrostatic and π – π interactions. The author designed and synthesized cationic chiral PPP derivatives, **PPP1** and **PPP2**, with ammonium moieties linked with asymmetric centers in their side chains. In CD spectra, both **PPP1** and **PPP2** showed a bisignate Cotton effect corresponding to the exciton coupling between neighboring phenylene rings in the conjugated backbone, indicating the presence of intrachain helicity. This case is the first in which aromatic conjugated polymers with a linear main chain, such as PPP derivatives, are verified to exhibit intrachain helicity in solution. Upon the addition of an anionic aromatic additive, **SNap**, into the aqueous solution of **PPP1** or **PPP2**, chiral assemblies with interchain helically π -stacked structure were formed through electrostatic and π – π interactions between the cationic polymer and the anionic additive. Although the chiral assembly of **PPP1** was dissociated upon thermal heating, the helically π -stacked structure of the **PPP2** assembly was thermally reinforced. The annealed assembly of **PPP2**–**SNap** showed a large g_{lum} value of $|10^{-1}|$ even in a dispersion system such as aqueous solution, which is the same magnitude as the values achieved in LC conjugated polymers. The present approach based on the cooperative intermolecular electrostatic and π – π interactions is versatile and applicable for preparations of other types of polymer assemblies with chiroptical functions.

In **Chapter 5**, full-colored conjugated copolymers with photoswitchable emissions were synthesized by combining phenylene- and thienylene-based main chains with photochromic DE side chains. The CHCl_3 solutions and cast films of the polymers exhibited various colored fluorescence in visible wavelengths of 400–700 nm corresponding to their main chain structures. The fluorescence was reversibly photoswitched between emission and quenching via DE photoisomerization using external UV and visible light stimuli. The reprecipitation method with ultrasonication enabled the polymers to form spherical aggregates with diameters of 20–70 nm in water. After investigating and comparing the optical properties, the resulting nanosphere solutions were estimated to exist in an intermediate state between an isolated state in solution and an aggregated state in cast film. The fluorescence photoswitching behavior was also observed in the nanosphere solutions, except for the PT derivative. The current study demonstrated that the visible fluorescence of conjugated polymers

were reversibly switchable between emission and quenching using the photoisomerizing DE side chain regardless of the fluorescent color and polymer chain aggregation. It is expected that the polymers synthesized in this work will be useful for creating photoresponsive optoelectronic devices.

In *Chapter 6*, the author has successfully constructed multiplex fluorescent systems consisting of photoresponsive polymer nanospheres. The reversible control of the emission and quenching of RGB fluorescence in conjugated polymers are achieved in both nanosphere solution and film states. Photoresponsive conjugated polymers with RGB fluorescence, **P1–P3**, are synthesized by introducing DE moieties into side chains of specific conjugated backbones. The fluorescence of the polymers is quenched by UV light and subsequently regenerated by visible light via the photoisomerization of the DE moieties in the side chains. Polymer nanospheres with several hundred nanometers in diameter are prepared by a reprecipitation method. White fluorescence is obtained by mixing the RGB fluorescent polymer nanospheres in the appropriate ratio. The white fluorescence is photoswitchable between emission and quenching upon irradiation with UV and visible light in both nanosphere solution and film states. Photoswitching between white fluorescence and RGB fluorescence is also achieved by replacing one of the photoresponsive polymers with a non-photoresponsive conjugated polymer analogue, except the W-G cast film. The present systems with photochemically color-tunable white fluorescence herein can be used as photoresponsive polymer illuminants.

As a result, in Chapters 1–4, the author successfully demonstrated that ACPs with chirality self-assembled into supramolecular aggregates with the interchain helical π -stacking and further higher-ordered structures. The interchain structure clearly affords peculiar optoelectronic properties such as circularly polarized luminescence. In all case, the π – π interaction played an important role to construct their ordered assembly. Meanwhile, in Chapters 5 and 6, the author provided the photoswitchable fluorescence series of ACPs and color-tunable white fluorescence by combining ACPs with the photoresponsive DE moiety. Such a strategy is a promising way to realize advanced optoelectronic features.

List of Publications

Chapter 1

Helically π -Stacked Thiophene-Based Copolymers with Circularly Polarized Fluorescence: High Dissymmetry Factors Enhanced by Self-Ordering in Chiral Nematic Liquid Crystal Phase

Watanabe, K.; Osaka, I.; Yorozya, S.; Akagi, K. *Chem. Mater.* **2012**, *24*, 1011–1024.

Chapter 2

Chirality Transfer through Interchain Helically π -Stacking Interactions between Chiral and Achiral Aromatic Conjugated Polymers

Watanabe, K.; Notsu, K.; Yorozya, S.; Akagi, K. *to be submitted*.

Chapter 3

Circularly Polarized Blue Luminescent Spherulites Consisting of Hierarchically Assembled Ionic Conjugated Polymers with a Helically π -Stacked Structure

Watanabe, K.; Iida, H.; Akagi, K. *Adv. Mater.* **2012**, *24*, 6451–6456 (**Back cover**).

Chapter 4

Interchain Helically π -Stacked Assembly of Cationic Chiral Poly(*para*-phenylene) Derivatives Enforced by Anionic π -Conjugated Molecules through Both Electrostatic and π – π Interactions

Watanabe, K.; Sun, Z.; Akagi, K. *submitted to Chem. Mater.*

Chapter 5

Dynamic Control of Full-Colored Emission and Quenching of Photoresponsive Conjugated Polymers by Photostimuli

Watanabe, K.; Hayasaka, H.; Miyashita, T.; Ueda, K.; Akagi, K. *submitted to Adv. Funct. Mater.*

List of Publications

Chapter 6

Photochemically Colour-Tuneable White Fluorescence Illuminants Consisting of Conjugated Polymer Nanospheres

Bu, J.; Watanabe, K.; Hayasaka, H.; Akagi, K. *Nature Commun.* **2014**, *5*, 3799.

Other Publications

(1) Hierarchically Self-Assembled Helical Aromatic Conjugated Polymers

Watanabe, K.; Suda, K.; Akagi, K. *J. Mater. Chem. C* **2013**, *1*, 2797–2805.

(2) Helically Assembled π -Conjugated Polymers with Circularly Polarized Luminescence

Watanabe, K.; Akagi, K. *Sci. Technol. Adv. Mater.* **2014**, *15*, 044203 (Cover).

Books

(1) 技術シーズを活用した 研究開発テーマの発掘 (技術情報協会)

Chapter 8, Section 3: 導電性高分子を活用した研究開発テーマの発掘
渡辺和誉、松下哲士、赤木和夫 (2013)

(2) CSJ Current Review 13: キラル化学、日本化学会 編 (化学同人)

Part II 7 章: 不斉液晶反応場を用いたらせん状共役ポリマーの創出
赤木和夫、渡辺和誉 (2013)

List of Awards

- **Excellent Student Poster Award, 18th Iketani Conference**

Poster Presentation: K. Watanabe, H. Iida, and K. Akagi, "Synthesis of Lyotropic Liquid Crystalline and Water-Soluble Poly-*Para*-Phenylene Derivative"

18th Iketani Conference, International Conference on Control of Super-Hierarchical Structures and Innovative Functions of Next-Generation Conjugated Polymers, in Awaji, Hyogo, Japan (Oct. 21–23, 2008).

- **Young Researcher Poster Award, ICSM 2010**

Poster Presentation: K. Watanabe and K. Akagi, "Circularly Polarized Luminescence of Ionic Conjugated Polymers with Induced Chirality"

International Conference on Science and Technology of Synthetic Metals 2010 (ICSM2010), in Kyoto, Japan (Jul. 4–9, 2010).

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