Notes

Polymeric Oligothiophene Fluorophores Spatially Isolated by Spirobifluorene and Their Emission Properties

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1. Introduction

Since the first report about the polymer-based light-emitting diode (PLED) using poly(*p*-phenylenevinylene) (PPV) by the Cambridge group,[1] many polymeric materials such as poly(*p*-phenylene) and polyfluorene were successively produced. Polymers have advantages over low molecular weight materials in that the devices could be fabricated in the low cost process because the polymer solutions are easily spin cast on the substrate to obtain thin films with good quality and mechanical flexibility. However, they have shortcomings, such as the irregular effective conjugation length and the contamination by structural defects. The excimer formation triggered by the chain aggregation is also the matter of discussion to realize the polymer-based optoelectronic materials. In the PLED devices operated in the solid state, these problems become serious because the excited energy migrates from higher to lower energy fluorophore between polymer chains to result in the unexpected emission color or the quenching of the fluorescence.[2] To overcome this drawback, the fluorescent segment was chemically fixed in the matrix by thermally cross-linking the terminal vinyl group.[3] The attachment of a bulky side group onto the polymer was also effective to avoid chain aggregation to obtain stable blue and green emissions.[4] On the other hand, the introduction of spirobifluorene, having rectangular two fluorenes, into the polymer backbone is another technique to realize the stable light emission from purple to green color.[5] We herein investigate the polymeric oligothiophene fluorophore spatially isolated by spirobifluorene in order to shift the emission color to the longer wavelength region. The polymer preparation and their optical properties in both solution and film states are discussed. Since oligothiophene and polythiophene have a large tendency to form complex or regular π-stacked structures,[6] the attempt to insulate the intermolecular interaction of this kind of materials seems to be a challenging issue.

2. Experimental Section

2.1. Materials. All reactions were performed under nitrogen. Dry diethyl ether (ether) and tetrahydrofuran (THF) were purchased from Aldrich and Kanto Chemical Co., respectively. Tetrakis(triphenylphosphine)palladium(0) was purchased from TCI. 9,9-Dihexylfluorene-2,7-bis(trimethyleneborate) and dichlorobis(triphenylphosphine)palladium(II) were purchased from Aldrich. Iron(III) chroride was purchased from Kishida Chemical Co. ^{n}BuLi and ^{t}-BuLi were purchased from Kanto Chemical Co. *n*-Hexane and $CHCl_3$ were dried according to the standard procedure and distilled under nitrogen. 2,2′-Dibromo-9,9′-spirobifluorene (2,2′-BrSBF) and 2,7-dibromo-9,9′-spirobifluorene (2,7-BrSBF) were synthesized according to a previous report.[7] Sodium 4-hexyl-2-thienylboronate (STB) was synthesized according to previous reports.[8] 2,5-Bis(tri-*n*-butylstannyl)thiophene (BST) was synthesized according to previous reports.[9]

2.2. Instrumentation. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 200 FT-NMR spectrometer using tetramethylsilane (^{1}H NMR, δ 0.00) or $CDCl_3$ (^{13}C NMR, δ 77.0) as internal reference peaks. Infrared (IR) spectra were recorded on a Nicolet Impact 400D FT-IR spectrophotometer. Melting points (mp) were determined on a YANAGIMOTO micro melting point apparatus MP-J3. Gel permeation chromatographic (GPC) analyses were carried out on a Tosoh DP-8020 using tandem TSK Multipore H_{XL}-M columns (THF as an eluent, flow rate = 1.0 mL/min, 40 °C) equipped with a refractive index detector (RI-8010) on the basis of standard polystyrene samples. Ultraviolet (UV−vis) and photoluminescence (PL) spectra were recorded on a Shimadzu UV-1650PC spectrophotometer and a Shimadzu RF-5300PC spectrofluorometer, respectively, using an 1 cm quartz cell. Quantum yields in the solution state were determined relative to quinine sulfate in 0.1 N H_2SO_4 with a quantum yield of 0.55. A rough estimation of the fluorescence quantum yields in the solid state was achieved by comparing the thin film of the polymer with a thin film of poly(9,9-dihexylfluorene) as a reference standard (0.55). Differential scanning calorimetric (DSC) analyses were carried out using a Seiko SSC5000 equipped with DSC100 at a scanning rate of 10 °C/min under nitrogen. Thermogravimetric analyses (TGA) were carried out using a Seiko TG/DTA200 instrument at a scanning rate of 10 °C/min under nitrogen.

2.3. Monomer Synthesis. The synthesis of oligothiophene-substituted spirobifluorene derivatives started from 2,2′-dibromo-9,9-spirobifluorene (2,2′-BrSBF) or 2,7-dibromo-9,9-spirobifluorene (2,7-BrSBF) by the repetitive Suzuki coupling and bromination reactions. Detailed experimental procedures are described in the Supporting information.

2.4. Polymerization. The polymerizations were performed by Stille coupling and oxidation coupling reaction. The experimental procedures are as follows.

Poly(spirobifluorene-2,2′-diyl-*alt*-thiophene) (Poly-2,2′-SBFTh). To a flask containing 2,2′-BrSBF (0.59 g, 1.24 mmol) and BST (0.82 g, 1.24 mmol) in THF (11 mL) was added $PdCl_2(PPh_3)_2$ (0.026 g, 0.037 mmol). The mixture was heated to reflux for 9 h and filtered to remove the THF-insoluble part. The filtrate was rinsed with 2 N aqueous HCl and poured into MeOH to obtain a yellow solid (0.25 g, 56.8% yield): ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 7.78−7.82 (4H), 7.48−7.57 (2H), 7.33−7.36 (2H), 7.02−7.09 (2H), 6.87−7.00 (4H), 6.66−6.78 (2H); IR (KBr disk) (cm^{-1}) 3066, 2927, 2925, 1607, 1449, 1418, 1260, 1095, 1013, 804, 757, 729.

Poly(spirobifluorene-2,2′-diyl-*alt*-bithiophene) (Poly-2,2′-SBFBTh). To a $CHCl_3$ (55 mL) solution of $FeCl_3$ (0.45 g, 2.77 mmol) was slowly added a $CHCl_3$ (10 mL) solution of 2,2′-ThSBF (0.45 g, 0.69 mmol) from a dropping funnel at 0 °C. The mixture was reacted at room temperature for 24 h and then at 50 °C for 12 h.

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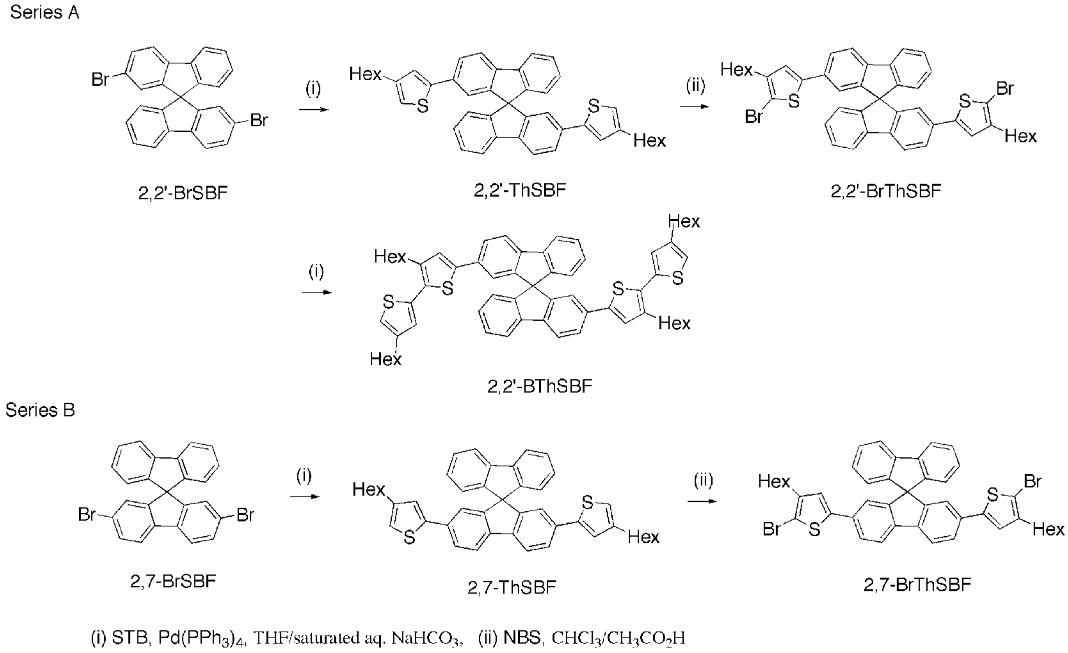
Scheme 1. Synthetic Route of Monomers



The solution was concentrated and poured into MeOH. The obtained solid was dissolved in THF and precipitated in aqueous NH_3. The crude product was further purified by washing with acetone to obtain a yellow solid (0.16 g, 36.6% yield): ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 6.26−7.99 (16H), 2.23−2.56 (4H), 0.48−1.66 (22H); IR (KBr disk) (cm^{-1}) 3059, 2925, 2855, 1461, 825, 769, 754, 730.

Poly(spirobifluorene-2,2′-diyl-*alt*-terthiophene) (Poly-2,2′-SBFTTh). The polymer was synthesized from 2,2′-BrThSBF and BST by a procedure similar to that of Poly-2,2′-SBFTh in 86.3% yield: ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 7.85 (4H), 7.61 (2H), 7.38 (2H), 7.14 (2H), 6.97 (6H), 6.74 (2H), 2.45−2.69 (4H), 1.40−1.70 (4H), 1.15−1.43 (12H), 0.71−0.92 (6H); IR (KBr disk) (cm^{-1}) 3060, 2925, 2851, 1461, 1259, 1099, 1027, 826, 799, 758, 728.

Poly(spirobifluorene-2,2′-diyl-*alt*-quaterthiophene) (Poly-2,2′-SBFQTh). The polymer was synthesized from 2,2′-BThSBF by a procedure similar to that of Poly-2,2′-SBFBTh in 41.1% yield: ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 6.65−7.98 (18H), 2.32−2.83 (8H), 0.61−1.88 (44H); IR (KBr disk) (cm^{-1}) 3051, 2925, 2855, 1445, 1414, 824, 753, 729.

Poly(spirobifluorene-2,7-diyl-*alt*-bithiophene) (Poly-2,7-SBFBTh). The polymer was synthesized from 2,7-ThSBF by a procedure similar to that of Poly-2,2′-SBFBTh in 31.1% yield: ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 7.88 (2H), 7.80 (2H), 7.57 (2H), 7.40 (2H), 7.13 (2H), 6.95 (2H), 6.88 (2H), 6.79 (2H), 2.33−2.40 (4H), 1.41−1.46 (4H), 1.15−1.26 (12H), 0.75−0.86 (6H); IR (KBr disk) (cm^{-1}) 3051, 2925, 2855, 1496, 1445, 816, 757, 734, 643.

Poly(spirobifluorene-2,7-diyl-*alt*-terthiophene) (Poly-2,7-SBFTTh). The polymer was synthesized from 2,7-BrThSBF by a procedure similar to that of Poly-2,2′-SBFTTh in 78.5% yield: ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 7.69−7.92 (4H), 7.37−7.63 (4H), 6.67−7.20 (10H), 2.40−2.75 (4H), 1.42−1.72 (4H), 1.08−1.39 (12H), 0.64−0.91 (6H); IR (KBr disk) (cm^{-1}) 3060, 2925, 2851, 1461, 1259, 1099, 1028, 826, 799, 758, 728.

3. Results and Discussion

3.1. Preparation. The synthesis of thiophene-substituted spirobifluorene derivatives started from 2,2′-dibromo-9,9-spirobifluorene (2,2′-BrSBF) or 2,7-dibromo-9,9-spirobifluorene (2,7-BrSBF) (Scheme 1). Those having a thiophene and bromothiophene group were obtained by Stille coupling with STB and the following bromination with NBS. A monomer 2,2′-BThSBF having a bithiophene group was synthesized by the second Stille coupling between 2,2′-BrThSBF and STB. Although 2,2′-BrSBF included regioisomers such as a 2,3′-dibromo counterpart, monomers of series A could be isolated as a sole product by purifying with SiO_2 column chromatography. The structures of monomers were characterized by ^{1}H NMR spectra, and peaks could be fully assigned. The melting points were always narrow, supporting the purity of these monomers, except for 2,2′-BThSBF, having a bithiophene segment and two long hexyl chains.

Subsequently, polymers having odd- and even-numbered thiophene rings were synthesized by Stille and oxidation coupling polymerization, respectively (Figure 1). Poly-2,7-SBFTh without any alkyl chain precipitated at the early stage of the polymerization, and the integral ratio of the obtained product did not agree with the ideal structure. Poly-2,2′-SBFTh also had a poor solubility and the number-averaged molecular weight (M_n) was 1100 (Table 1). Other polymers showed a good solubility in many solvents such as $CHCl_3$, THF, and toluene. Polymers of series A having a nonconjugated main chain had better solubility than those of the fully conjugated series B. The isolated yields of polymers with even-numbered thiophene rings were below 40%, because of the complex isolation process to separate them from metallic impurities. A representative ^{1}H NMR spectrum of Poly-2,2′-SBFQTh is shown in Figure 2. The methylene proton signals adjacent to the thiophene ring were bimodal due to the difference in the magnetic environment of the two kinds of thiophene in the polymer backbone. The integral ratio of polymers in the ^{1}H NMR spectra agreed with the theoretical value, confirming the polymer structure. The linkage pattern of two hexylthiophene rings present at the border of the repeating unit in Poly-2,2′-SBFBTh, Poly-2,2′-SBFQTh, and Poly-2,7-SBFBTh obtained by the oxidation polymerization is believe to be head-to-head according to the previous reports.

The temperatures at which the polymer lost 5 wt % from the original mass (T_{d5}) were above 450 °C, except for Poly-2,2′-SBFTh, which reflected the thermal stability of the spirobifluorene unit (Table 2). The glass transition temperature (T_g) of Poly-2,2′-SBFBTh was 153 °C and the temperature decreased in proportion to the elongation of the oligothiophene segment. On the other hand, T_g was not observed in Poly-2,2′-SBFTh.

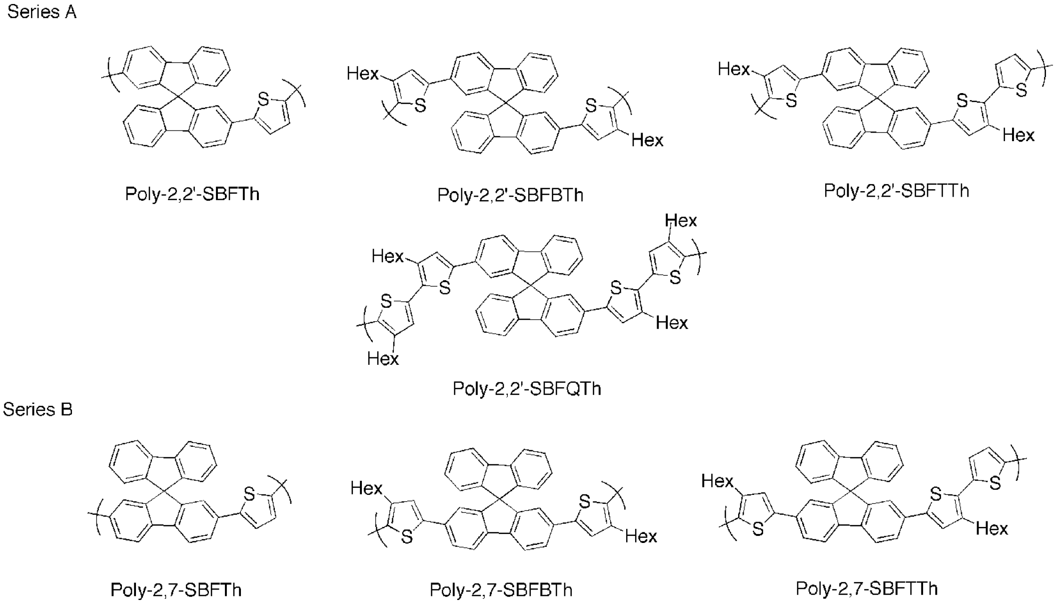


Figure 1. Chemical structure of polymers.

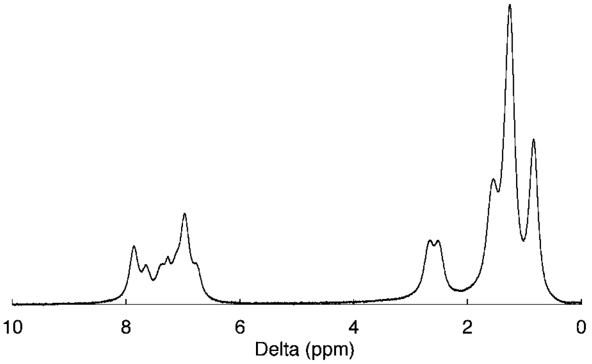


Figure 2. ^{1}H NMR spectrum of Poly-2,2′-SBFQTh (200 MHz, $CDCl_3$).

Table 1. Polymerization Results

polymer code	yield (%)[a]	M_n[b]	PDI[b]
Poly-2,2-SBFTh	56.8	1000	1.7_8
Poly-2,2-SBFBTh	36.6	3700	1.5_2
Poly-2,2-SBFTTh	86.3	3400	1.8_9
Poly-2,2-SBFQTh	31.1	11500	2.6_2
Poly-2,7-SBFBTh	41.1	5800	1.5_8
Poly-2,7-SBFTTh	78.5	3000	1.5_5

[a] Isolated yield. [b] GPC (THF system, PSt std).

Table 2. TGA and DSC Data of Polymers

polymer code	T_{d5} (°C)[a]	T_g (°C)[b]
Poly-2,2-SBFTh	430	NA
Poly-2,2-SBFBTh	455	153
Poly-2,2-SBFTTh	457	147
Poly-2,2-SBFQTh	457	115
Poly-2,7-SBFBTh	453	163
Poly-2,7-SBFTTh	457	153

[a] Temperature at which the polymer lost 5 wt % from the original mass. [b] Glass transition temperature.

The polymers of series B had higher glass transition temperatures than those of series A.

3.2. Optical Properties. The UV and PL spectra of polymers and monomers were obtained in the $CHCl_3$ solution under the concentration of 10^{-5} M (repeating unit). Figure 3a shows the UV spectra of the polymers. The absorption spectra of polymers of series B were observed at a longer wavelength region than those of series A having the same oligothiophene segment, which stems from the fully conjugated structure of series B. The red-shift from the corresponding monomer to polymer was smaller in series A due to the same reason. For example, the absorption maximum wavelength of Poly-2,2′-SBFTTh (403 nm) shifted as much as 68 nm from that of 2,2′-BrThSBF, while that of Poly-2,7-SBFTTh (433 nm) shifted as much as 73 nm

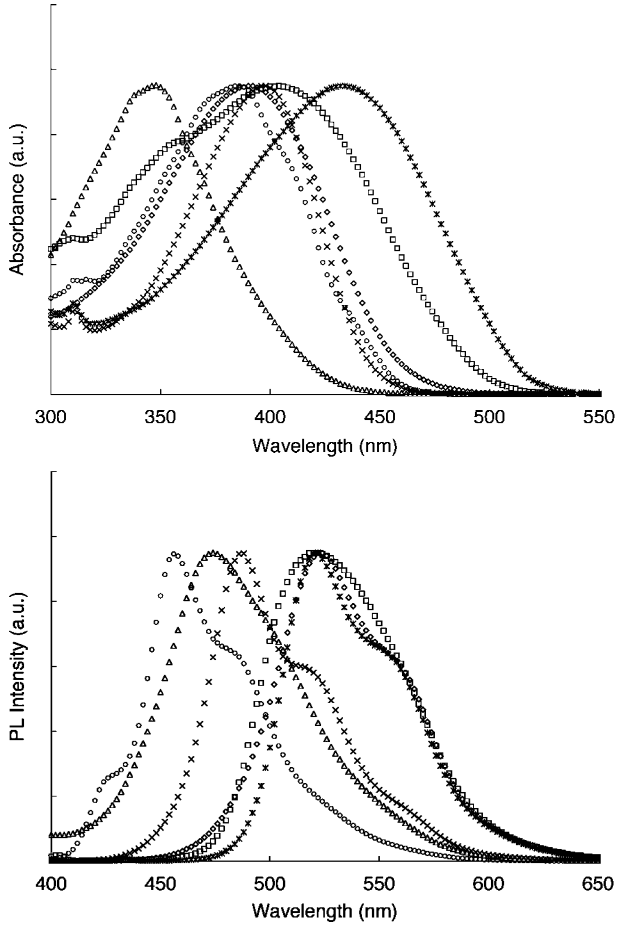


Figure 3. UV (upper) and PL (lower) spectra of polymers in $CHCl_3$ solution (10^{-5} M) (circle, Poly-2,2′-SBFTh; triangle, Poly-2,2′-SBFBTh; square, Poly-2,2′-SBFTTh; diamond, Poly-2,2′-SBFQTh; cross, Poly-2,7-SBFBTh; and star, Poly-2,7-SBFTTh).

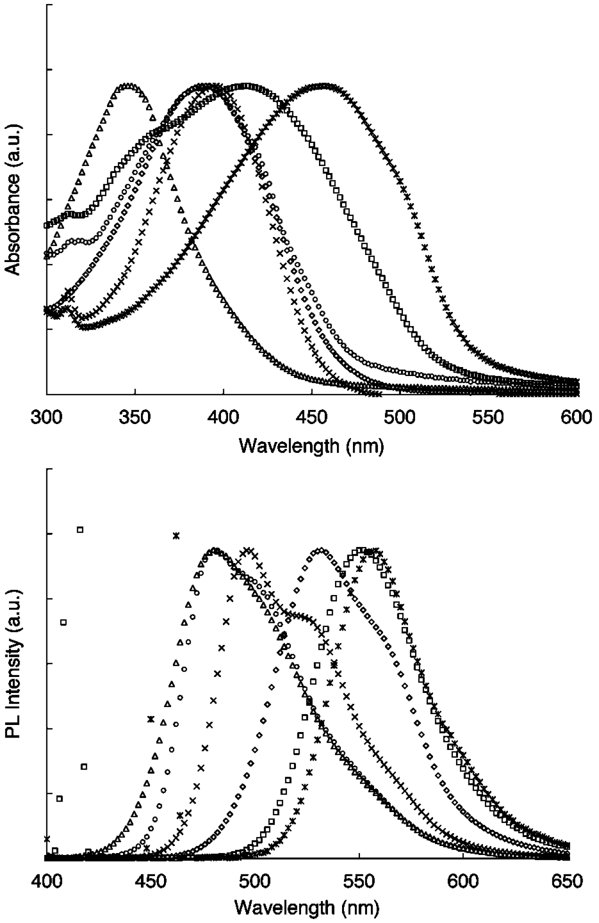
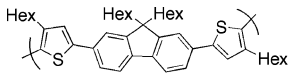


Figure 4. UV (upper) and PL (lower) spectra of polymers in a thin film (circle, Poly-2,2′-SBFTh; triangle, Poly-2,2′-SBFBTh; square, Poly-2,2′-SBFTTh; diamond, Poly-2,2′-SBFQTh; cross, Poly-2,7-SBFBTh; and star, Poly-2,7-SBFTTh).

from that of 2,7-BrThSBF. In series A, the absorption maximum wavelength red-shifted in the order Poly-2,2′-SBFBTh (347 nm) < Poly-2,2′-SBFTh (385 nm) < Poly-2,2′-SBFQTh (390 nm) < Poly-2,2′-SBFTTh (403 nm), which disagrees with the length of the oligothiophene segment. Since Poly-2,2′-SBFBTh and Poly-2,2′-SBFQTh had a head-to-head bithiophene unit, nonplanar structures limit the elongation of the effective conjugation length. On the other hand, the emission maximum wavelength gradually red-shifted as the length of the oligothiophene segment increased both in series A and B (Figure 3b). The PL spectra of Poly-2,2′-SBFQTh, Poly-2,7-SBFBTh, and Poly-2,7-SBFTTh, with relatively long effective conjugation length, demonstrated a shoulder peak due to the vibronic structure. The quantum yields of polymers were relatively low (<0.38) because of the spin-orbital coupling by the heavy sulfur element. The visible color of the fluorescence ranged from blue (Poly-2,2′-SBFBTh) to greenish yellow (Poly-2,7-SBFTTh).

Subsequently, the electronic spectra of the thin film obtained by spin-coating a toluene solution of polymers (15 mg/mL) were recorded. The UV and PL spectra are shown in Figure 4. As compared with the data in the solution state, the absorption maximum wavelength of Poly-2,2′-SBFTh, Poly-2,2′-SBFTTh, and Poly-2,7-SBFTTh evidently red-shifted and the spectra became broad. These results are considered to originate from the planarization/chain aggregation of the oligothiophene segment. Neither the red-shift nor the spectral broadening was observed for Poly-2,2′-SBFBTh, Poly-2,2′-SBFQTh, and Poly-2,7-SBFBTh, having a head-to-head bithiophene unit. The spectral shifts from solution to film among these polymers were also confirmed in the PL spectra. The red-shifts of the PL spectra were obvious in Poly-2,2′-SBFTh (23 nm), Poly-2,2′-SBFTTh (29 nm), and Poly-2,7-SBFTTh (35 nm). The quantum yields of the polymer in the solid state were roughly estimated by using a film of poly(9,9-dihexylfluorene) as a standard. As a result, the quantum yield was the maximum for Poly-2,2′-SBFBTh (0.66) and that of Poly-2,7-SBFTTh demonstrated a minimum (0.12) because of the concentration quenching of the relatively planar polymer chain. The visible color of the fluorescence ranged from greenish blue (Poly-2,2′-SBFBTh) to orange (Poly-2,7-SBFTTh).



X

Figure 5. Chemical structure of reference polymer X.

At this point, the question whether the suppression of the spectral red-shift in some polymers arose from the head-to-head bithiophene unit or the spirobifluorene structure still remained. Accordingly, the influence of the spirobifluorene structure was discussed quantitatively by comparing the data with a reference polymer X[10] (Figure 5). The shift of the emission maximum wavelength from solution to film for X was reported to be 10 nm, which well-agreed with that for Poly-2,7-SBFBTh, having the same bithiophene unit. In sharp contrast, the shift for Poly-2,2′-SBFBTh was smaller by as much as 4 nm. The above results reveal that the chain aggregation and excimer formation of the oligothiophene segment could be suppressed not only by the head-to-head bithiophene unit but also by the twisted polymer structure induced by spirobifluorene. The oligothiophene segment is considered to be spatially isolated by the bulky spirobifluorene unit. The same trend was also observed between Poly-2,2′-SBFTTh and Poly-2,7-SBFTTh. Since, in the polymer-based light-emitting devices, the polymer morphology could be changed by the heat due to the current passage, to bring about the unexpected light emission, the polymer film on the quartz plate was annealed to further investigate the potential of the spirobifluorene unit for the isolation of the oligothiophene fluorophore. Even after the thermal annealing at 150 °C for 12 h, the spectral shape did not change at all, indicating the thermally stable nature of the emission of these polymers.

Finally, the light emission from the polymer blend film was investigated. Namely, Poly-2,2′-SBFBTh and Poly-2,7-SBFTTh, having the maximum emission wavelength at 478 and 557 nm, respectively, were dissolved in toluene and the solution was spin-coated on a quartz plate. The weight percentage of Poly-2,7-SBFTTh relative to Poly-2,2′-SBFBTh varied from 0.5%, 1%, and 5%. When the concentration of Poly-2,7-SBFTTh was low (0.5 wt %), the maximum emission wavelength (481 nm) was comparable to that of Poly-2,2′-SBFBTh in the film state, and a small shoulder peak was observed (Figure 6). By increasing the content of Poly-2,7-SBFTTh, the longer wavelength emission became prominent and gradually red-shifted, which stem from the fluorescence resonance energy transfer (FRET) from Poly-2,2′-SBFBTh as donor to Poly-2,7-SBFTTh as acceptor. The greenish yellow emission from Poly-2,7-SBFTTh was almost detected when the content of Poly-2,7-SBFTTh reached to 5 wt %. However, the emission wavelength was 528 nm, which obviously blue-shifted as compared to that of Poly-2,7-SBFTTh in the film state (557 nm). Since the concentration of Poly-2,7-SBFTTh is relatively low (5 wt %), the Poly-2,7-SBFTTh fluorophores are well-dispersed in the Poly-2,2′-SBFBTh matrix

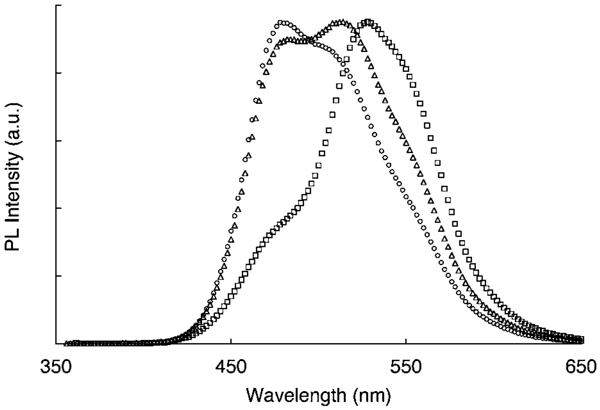


Figure 6. PL spectra of polymer blend films at various weight percentage of Poly-2,7-SBFTTh (circle, 0.5 wt %; triangle, 1 wt %; and square, 5 wt %).

and behave as if in solution. Actually, the emission wavelength of 528 nm was close to that in the solution state (522 nm). The achievement of longer wavelength emission by utilizing electron donor−acceptor interaction is in progress.

4. Conclusion

A family of polymers introducing the oligothiophene segment separated by spirobifluorene was synthesized by Stille coupling polymerization and oxidation polymerization. The polymers consisted of series A and B, where the attachments of the oligothiophene segment were the 2,2′ and 2,7 positions of spirobifluorene, respectively. The polymers bearing the hexyl group on the thiophene ring had good solubility and high heat resistance. The red-shift of the absorption maximum wavelength from monomer to polymer was larger in series B, having the fully conjugated main chain. In series A, the absorption maximum wavelength was influenced by not only the length of oligothiophene segment but also the regiochemistry of neighboring thiophenes. The quantum yields of polymers in $CHCl_3$ solution were constantly low (<0.38). The chain aggregation of oligothiophene fluorophore in the solid-state could be effectively suppressed by the twisted polymer structure (series A) induced by spirobifluorene. In the polymer blend films, fluorescence resonance energy transfer (FRET) occurred to obtain a longer wavelength emission from the minor fluorophore.

Supporting Information Available: Monomer syntheses and their characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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