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Synthesis of Aromatic-Ring-Layered Polymers

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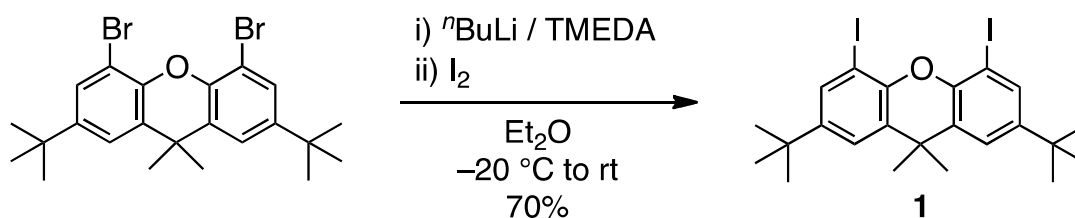
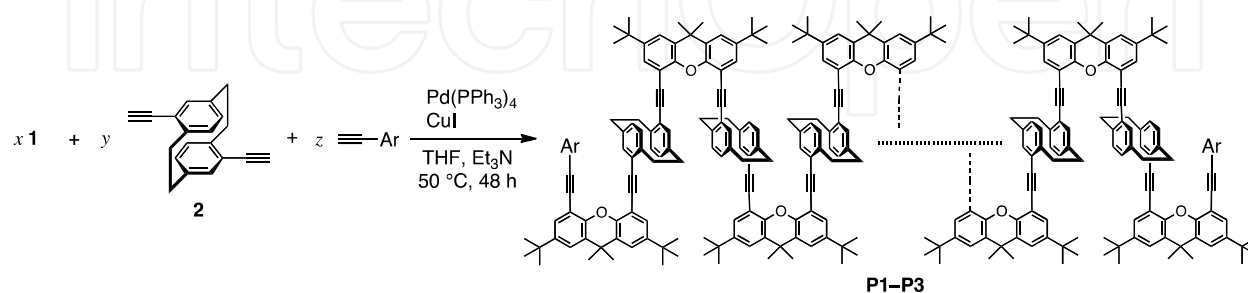
1. Introduction

In the fields of polymer and material chemistry, conjugated polymers (Skotheim et al., 2006) are an important class of polymers for next-generation optoelectronic materials due to their intriguing conductivity, photoluminescence, electroluminescence, and liquid crystallinity. Numerous conjugated polymers have been synthesized thus far, and a variety of unique conjugation systems have been incorporated into conjugated polymer backbones. One of the current research topics in this field focuses on the construction of layered and/or π -stacked structures. Layered π -electron systems are commonly found in both nature and artificial materials; for example, light-harvesting antenna complexes in photosynthetic systems, such as chlorophylls and bacteriochlorophylls, consist of layered π -electron systems. In optoelectronic materials, charges are delocalized in some layers and transferred from one electrode to the opposite one through the layered π -electron systems. Despite the importance of the layered structures of the π -electron systems, the synthesis of polymers comprising layered-aromatic rings and π -electron systems in a single polymer chain has rarely been studied (Morisaki & Chujo, 2006; Morisaki & Chujo, 2008a; Morisaki & Chujo, 2009d; Nakano, 2010).

To achieve the construction of the desired layered structure, xanthene, anthracene, and naphthalene compounds can be employed as scaffolds. The rotary motion of two aromatic units substituted at the 4,5-positions of xanthene, 1,8-positions of anthracene, and 1,8-positions of naphthalene is restricted due to steric hindrance, leading to a face-to-face structure. Thus, this review presents a summary of the syntheses and properties of a new class of aromatic ring-layered polymers, as well as oligomers containing xanthene, anthracene, and naphthalene scaffolds. Due to the vast number of studies on xanthene-, anthracene-, and naphthalene-based face-to-face dimeric systems, the polymers and oligomers (i.e., three or more face-to-face aromatic rings) are drawn.

2. Xanthene-based polymers

The 4,5-positions of xanthene can be readily functionalized by the treatment of xanthene compounds with alkyllithium reagents to yield the corresponding 4,5-dilithiated xanthenes due to the lithium-oxygen interaction, as shown in Scheme 1 (Morisaki & Chujo, 2005). The reaction of the 4,5-dilithiated xanthenes with halogens such as iodine results in the formation of diiodoxanthene derivative **1**, which is used in the palladium-catalyzed coupling reactions.

Scheme 1. Synthesis of monomer **1**Scheme 2. Synthesis of polymers **P1-P3**

entry	Mono-ethynylarene	Feed ratio $x : y : z$	Polymer	Yield (%)	M_n (calcd.)	M_n (found by $^1\text{H NMR}$)
1		10 : 9 : 2	P1a	79	5956	4100
2		5 : 4 : 2	P1b	65	3082	3100
3		3 : 2 : 1	P1c	50	1933	2100
4		10 : 9 : 2	P2a	70	5896	7500
5		5 : 4 : 2	P2b	50	3022	4200
6		3 : 2 : 1	P2c	65	1872	2600
7		10 : 9 : 2	P3a	76	5786	5750
8		5 : 4 : 2	P3b	59	2912	3000
9		3 : 2 : 1	P3c	56	1762	1700

Table 1. Polymerization results

As shown in Scheme 2, the Sonogashira-Hagihara coupling (Tohda et al., 1975; Sonogashira, 2002) of diiododioxanthene **1** with either a diethynylarene, such as pseudo-*p*-diethynyl[2.2]paracyclophane **2**, or mono-ethynylarenes **3-5** proceeded smoothly to produce [2.2]paracyclophane-layered polymers (Morisaki et al., 2008b; Morisaki et al., 2009b). The results are summarized in Table 1. In the presence of mono-ethynylarenes **3-5**, aromatic groups were introduced as end-capping units. Polymers **P1**, **P2**, and **P3** possess [2.2]paracyclophane, anthracene, and nitrobenzene as the end-capping units, respectively. Their molecular weights were controlled by the molar ratios of the monomers, as shown in Table 1. For example, in the case of a molar ratio ($x:y:z$) of 9:10:2, the number average molecular weights (M_n) of **P1a**, **P2a**, and **P3a** were 4100, 7500, and 5750 (entries 1, 4, and 7), respectively, which were calculated from their respective $^1\text{H NMR}$ spectra.

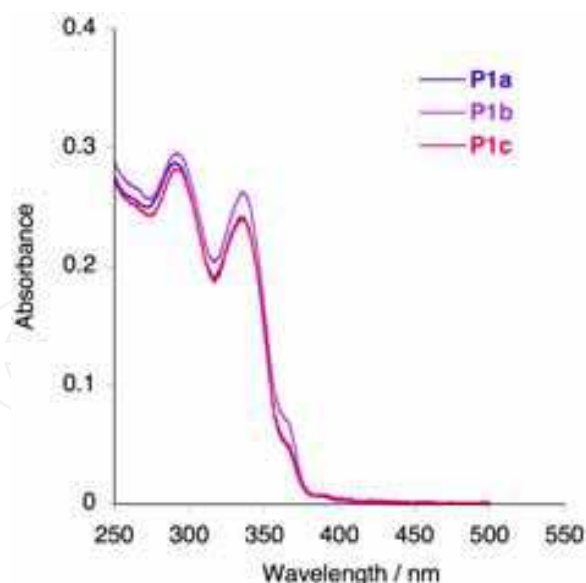


Fig. 1. UV-vis absorption (UV) spectra of polymers **P1a-c** in CHCl_3 (1.0×10^{-5} M).

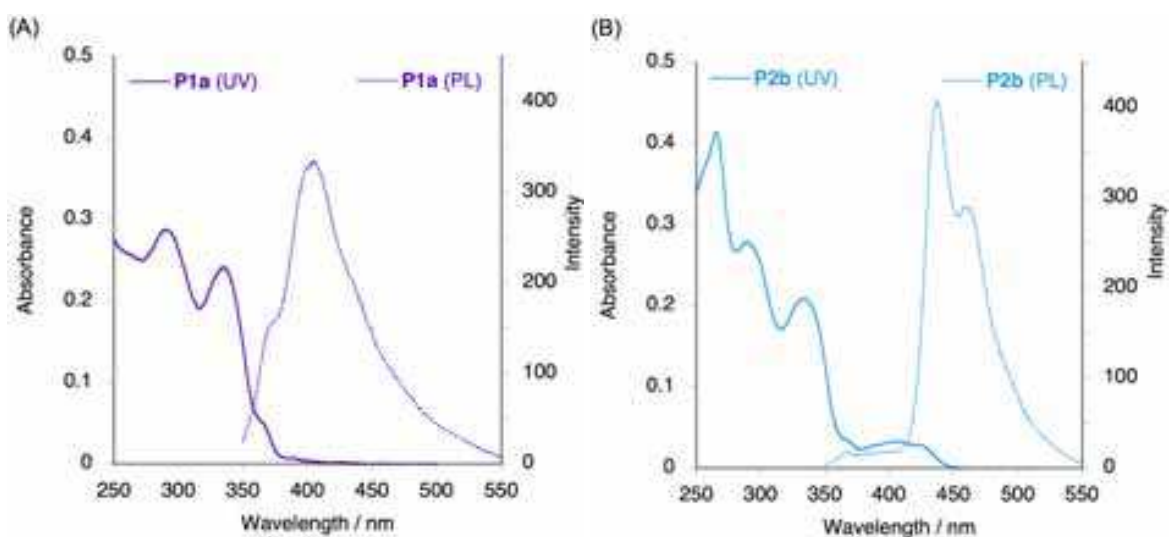


Fig. 2. (A) UV-vis absorption spectra in CHCl_3 (1.0×10^{-5} M) and photoluminescence (PL) spectra in CHCl_3 (5.0×10^{-7} M) of **P1a**. (B) UV-vis absorption spectra in CHCl_3 (1.0×10^{-5} M) and PL spectra in CHCl_3 (5.0×10^{-7} M) of **P2b**.

As shown in the UV-vis absorption spectra (in CHCl_3 , 1.0×10^{-5} M) of polymers **P1a-c** (Figure 1), there were π - π^* absorption bands at around 290 and 330 nm. The absorption spectra of **P1a-c** were independent of the number of the layered [2.2]paracyclophanes. It is reported that neighboring [2.2]paracyclophane units in the polymer backbone have sufficient free space according to X-ray crystallographic analysis of the model compound (Morisaki et al., 2009a). Therefore, π - π interactions among [2.2]paracyclophane units in a single polymer chain are considered to be weak in the ground state.

The optical properties of polymers **P1a** ($M_n = 4100$) and **P2b** ($M_n = 4200$) were compared. Figures 2A and 2B show the UV-vis absorption and emission spectra of polymers **P1a** and **P2b**, respectively. As shown in Figure 2A (see also Figure 1), the π - π^* band of the layered [2.2]paracyclophane units was observed in the spectrum of **P1a**, whereas a sharp absorption peak at around 270 nm and a broad absorption peak at around 400 nm appeared in the

spectrum of **P2b** (Figure 2B). These new absorption bands were derived from the anthracene units at the polymer **P2b** chain ends.

Polymer **P1a** emitted blue light with a peak at around 400 nm after excitation at 334 nm (Figure 2A), which was attributed to emission from the layered [2.2]paracyclophane moieties. **P2b** exhibited a quite different photoluminescence spectrum with a peak at around 450 nm with a vibrational structure on the excitation wavelength of 334 nm (Figure 2B). This excitation wavelength excited only the layered [2.2]paracyclophane moieties because the end-capping anthracene units do not have an absorption band around 334 nm. Thus, **P2b** emitted from the terminal anthracenes instead of emitting from the layered [2.2]paracyclophanes. As shown in Figures 2A and 2B, the emission peak of the layered cyclophane units (at 400 nm in Figure 2A) efficiently overlapped with the absorption band of the anthracene moieties (at around 400 nm in Figure 2B). Time-resolved photoluminescence spectra of **P2b** are shown in Figure 3; these spectra indicate that emission from the cyclophane units decreased while that from the anthracene units increased. These results suggest that fluorescence resonance energy transfer (FRET) (Förster, 1946) from the cyclophane units to the end-capping anthracenes occurs.

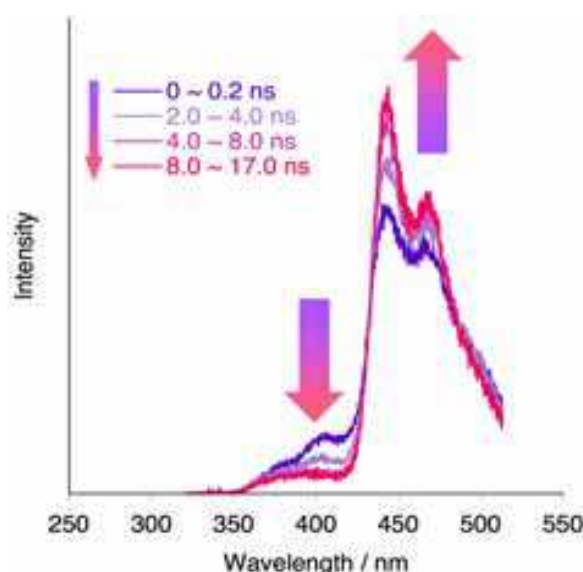


Fig. 3. Time-resolved PL spectra of polymer **P2b** in CHCl_3 .

The UV-vis absorption spectra of the nitrobenzene-end-capped polymers **P3a-c** (in CHCl_3 , 1.0×10^{-5} M) are shown in Figure 4A. These spectra exhibited broad absorption bands around 400 nm in addition to the π - π^* transition band of the layered [2.2]paracyclophanes; the absorbance around 400 nm increased as the M_n value decreased. This absorption band arises from the polymer chain ends that contain nitrophenyl groups as the concentration of the end-capping nitrophenyl groups increased with a decreasing M_n value. As can be expected, the emission from the [2.2]paracyclophane moieties was quenched by the introduction of the nitrophenyl units at the polymer chain ends due to the good overlap between the emission peak of the [2.2]paracyclophane moieties and the absorption band of the nitrophenyl moieties. As shown in Figure 4B, the photoluminescence peak intensities and the photoluminescence quantum efficiencies of **P3a-c** decreased relative to those of **P1a**. The end-capping nitrophenyl groups of **P3a-c** effectively quenched the photoluminescence from the layered [2.2]paracyclophane moieties by FRET. It is reported that the end-capping nitrophenyl group quenched photoluminescence 1.0×10^4 times more effectively than the addition of nitrobenzene to a **P1a** solution.

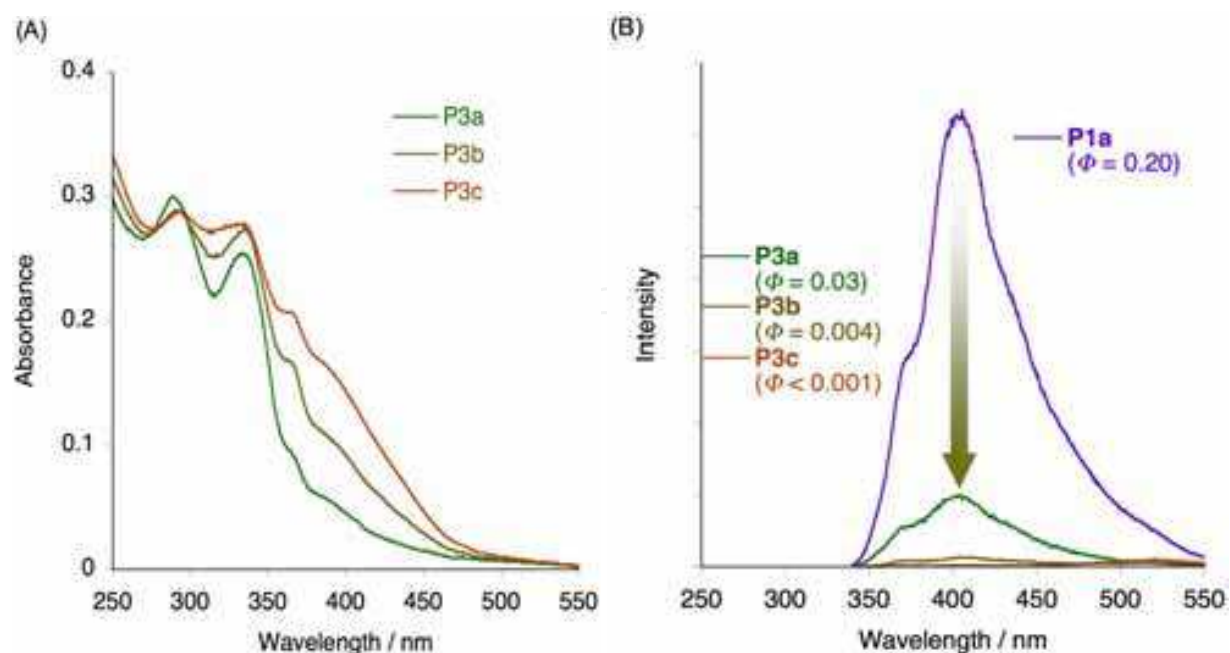
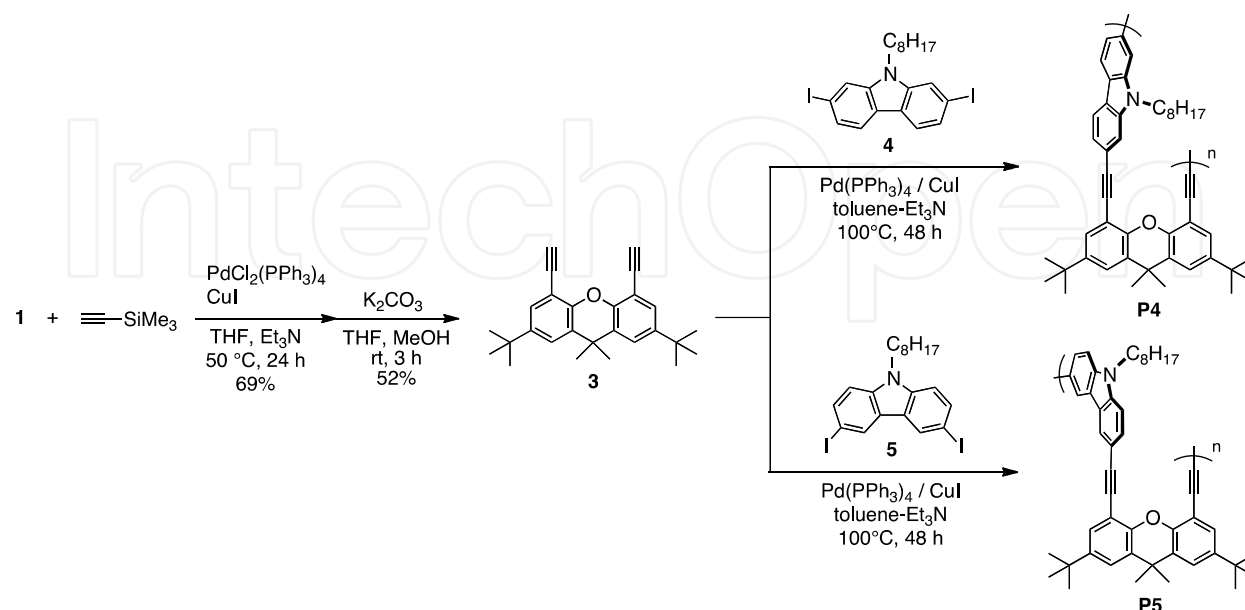


Fig. 4. (A) UV spectra in CHCl₃ (1.0 × 10⁻⁵ M) and photoluminescence (PL) spectra in CHCl₃ (5.0 × 10⁻⁷ M) of polymers **P3a-c**. (B) UV spectra in CHCl₃ (1.0 × 10⁻⁵ M) and PL spectra in CHCl₃ (5.0 × 10⁻⁷ M) of polymers **P1a** and **P3a-c**.

This synthetic approach using xanthene as the scaffold makes it possible to incorporate various aromatic compounds as the layered ring units in a single polymer chain. Scheme 3 shows the synthesis of 4,5-diethynylxanthene **3** as well as its polymerization with diiodocarbazoles **4** and **5**. The results of polymerization are summarized in Table 2. Polymers **P4** (Fernandes et al., 2010) and **P5** (Morisaki et al., 2009e) comprise 2,7-substituted and 3,6-substituted carbazoles, and their M_n values were calculated to be 2500 and 2300 (Table 2), respectively.



Scheme 3. Synthesis of monomer **3** and polymers **P4** and **P5**.

entry	Polymer	Yield (%)	M_n	M_w/M_n
1	P4	63	2500	1.3
2	P5	62	2300	1.1

Table 2. Synthesis of polymers **P4** and **P5**

M_n and M_w/M_n were calculated by MALDI-TOF mass spectra and GPC (CHCl₃, polystyrene standards), respectively.

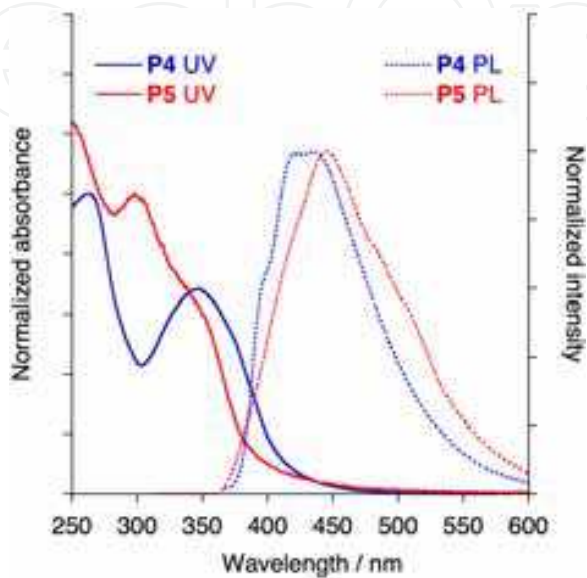


Fig. 5. UV spectra in CHCl₃ (1.0×10^{-5} M) and PL spectra in CHCl₃ (1.0×10^{-7} M) of polymers **P4** and **P5**.

The UV-vis absorption and photoluminescence spectra of **P4** and **P5** in diluted CHCl₃ solution are shown in Figure 5. The conjugation length of **P4**, which consists of 2,7-linked carbazole units, was longer than that of **P5**, which has 3,6-linked carbazole units. π -Conjugation of the 3,6-linked carbazole unit is not effective because the 3,6-linked carbazole unit on xanthene is twisted due to steric hindrance, which results in the shorter wavelength of the absorption peak in **P5** as compared to that of **P4**. In Figure 5, **P4** and **P5** are shown to exhibit emission peak maxima at 431 and 425 nm, respectively. The Stokes shift of **P5** was greater than that of **P4** suggesting that the conformation change from the ground state to the excited state of the 3,6-linked carbazole is larger than that of 2,7-linked carbazole due to the boomerang shape of the 3,6-linked carbazole unit (Morin et al., 2005; Grazulevicius et al., 2003).

The fluorescence emission spectrum of *N*-(*p*-tolyl)carbazole-layered polymer **P6** with nitrophenyl groups at the polymer chain ends was investigated to show its potential as a single molecular wire in comparison with **P7**. Figure 6A shows the photoluminescence spectra of polymers **P6** and **P7** in CHCl₃. The peak intensity of **P6** clearly decreased and the photoluminescence quantum yield (Φ_{PL}) of **P6** was estimated to be 1% indicating that the terminal nitrophenyl moieties in **P6** quenched the emission from the layered carbazole units. To compare, 1, 10, and 100 equivalents of nitrobenzene molecules per carbazole unit were added as a fluorescence quencher to a solution of **P7**, as shown in Figure 6B. However, ineffective quenching of the emission from the layered carbazole in **P7** was observed. The carbazole-layered polymer can also act as a molecular wire that transfers energy and/or electrons to the polymer termini in the same manner as the cyclophane-layered polymers discussed above.

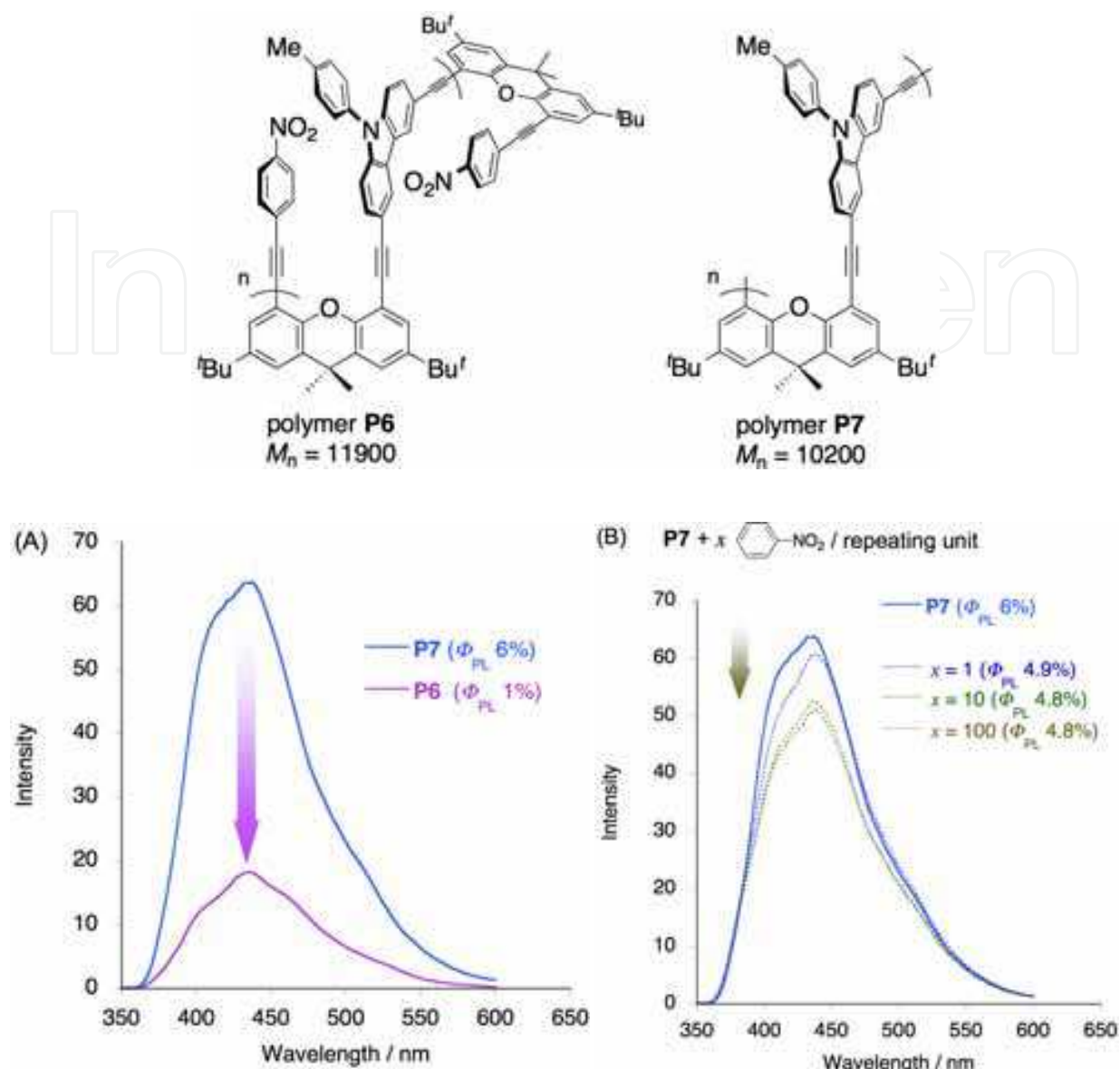
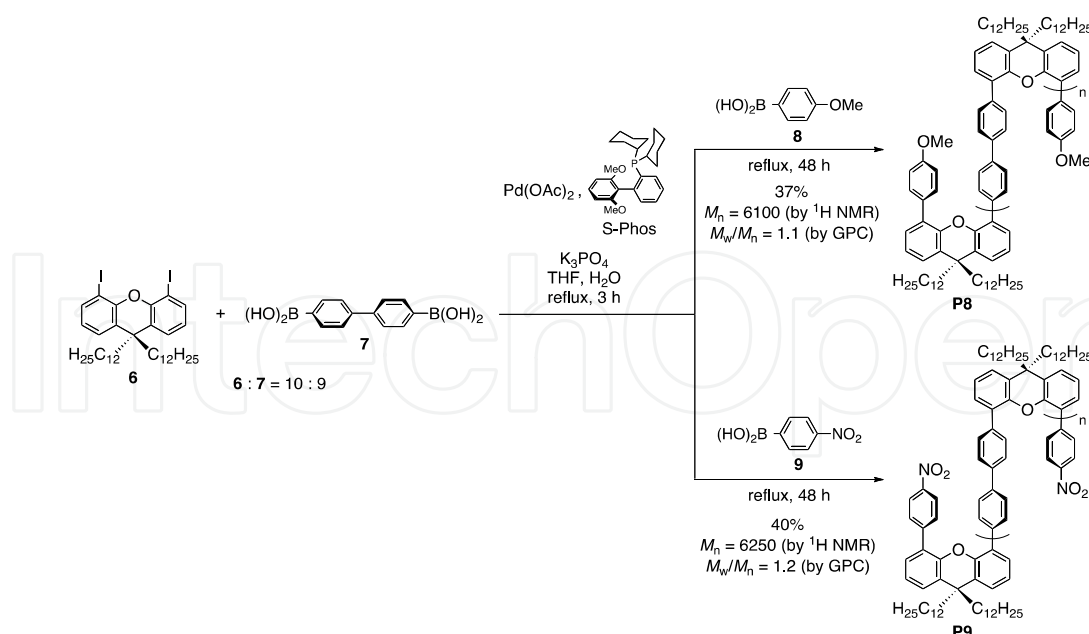


Fig. 6. (A) UV spectra of polymers **P6** and **P7** in $CHCl_3$ (1.0×10^{-5} M). (B) PL spectra of polymer **P7** with nitrobenzene in $CHCl_3$ (1.0×10^{-7} M).

By using xanthene as the scaffold, not only aromatic compounds but also π -conjugated oligomers can be one-dimensionally layered in a single polymer chain. Scheme 4 outlines the synthetic procedure of the oligo(*p*-phenylene)-layered polymers (Morisaki et al., 2009c) by modified Suzuki-Miyaura coupling (Miyaura et al., 1979; Miyaura & Suzuki, 1995). In this case, *tert*-butyl groups were not introduced into the xanthene skeleton because of their steric bulk and dodecyl groups were substituted at the 9-position of xanthene in order to improve the solubility of the polymers. The reaction of monomers **6** and **7** (10:9) was carried out in the presence of $Pd(OAc)_2$ with 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (S-Phos) as the ligand (Scheme 4) (Barder et al., 2005), and the successive addition of *p*-methoxyphenyl boronic acid **8** and *p*-nitrophenyl boronic acid **9** afforded the corresponding polymers **P8** and **P9** in 37% and 40% isolated yields with M_n values of 6100 and 6250, respectively.



Scheme 4. Synthesis of polymers **P8** and **P9**.

Figure 7A shows the photoluminescence spectra of **P8** and **P9** in diluted CHCl_3 solutions; the spectra are almost identical and feature peak maxima at around 410 nm. As can be expected, the peak intensity of **P9** ($\phi_{\text{PL}} = 55\%$) was lower than that of **P8** ($\phi_{\text{PL}} = 25\%$), indicating that the end-capping nitrobenzene units of **P9** quench the emission from the layered biphenylenes. The photoluminescence spectra of **P8**, which possesses *p*-methoxyphenyl chain ends, with an excess amount of nitrobenzene are shown in Figure 7B. However, the quenching effect of the additional nitrobenzene was quite low despite the addition of 100 equivalents of nitrobenzene per biphenylene unit. According to the Stern-Volmer plots, the Stern-Volmer coefficient (K_{sv}) of **P9** was 10^4 times larger than that of **P8** upon the addition of nitrobenzene. The two end-capping nitrophenyl moieties in **P9** effectively quenched the photoluminescence from the layered biphenylenes via through-space interactions of the single polymer chain.

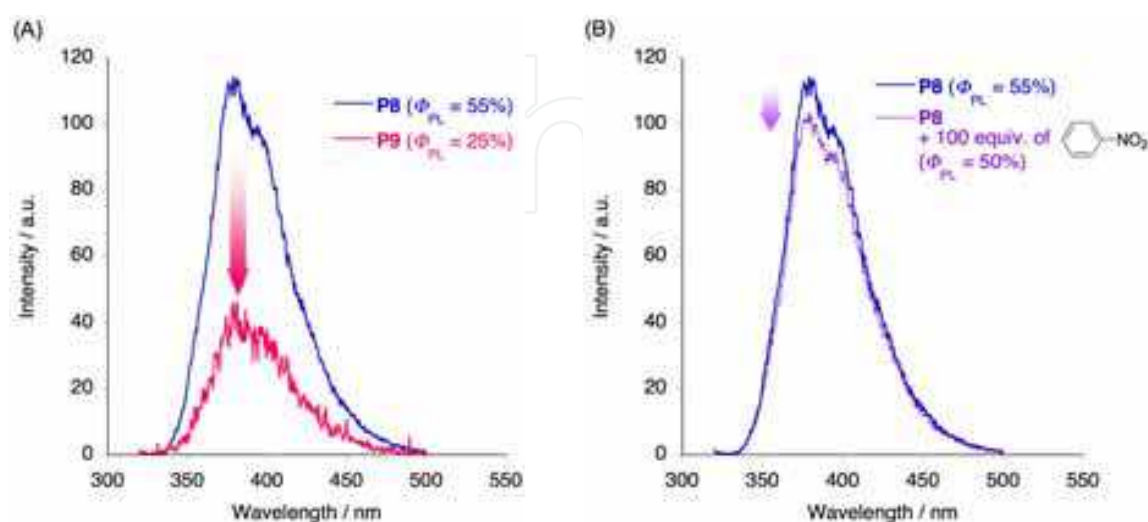
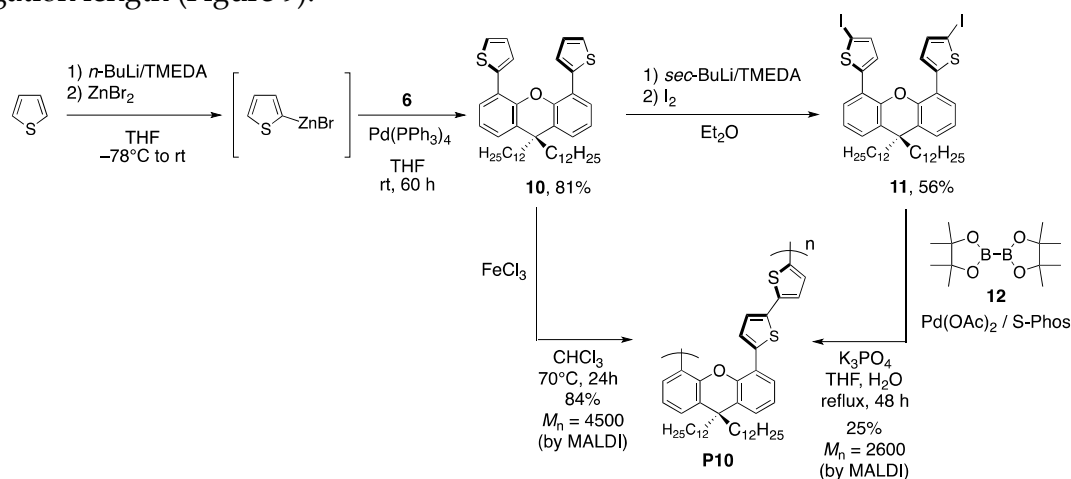


Fig. 7. (A) UV spectra of polymers **P8** and **P9** in CHCl_3 (1.0×10^{-5} M). (B) PL spectra of polymer **P8** with 100 equiv of nitrobenzene in CHCl_3 (1.0×10^{-7} M).

Oligothiophenes were also layered on xanthenes (Morisaki et al., 2009f; Morisaki et al., 2010b); the synthetic routes for the bithiophene-layered polymer **P10** by iron-mediated oxidative coupling and modified Suzuki-Miyaura coupling are shown in Scheme 5. Bis(thienyl)xanthene monomer **10** was prepared in 81% yield by Negishi coupling (Negishi et al., 1977; Negishi, 1982) of 2-thienylzinc bromide and **6** and then treated with FeCl_3 to obtain the corresponding polymer **P10** in 84% isolated yield with an M_n of 4500. However, **P10** was contaminated with a small amount of iron species. Therefore, an alternate synthesis was pursued; compound **10** was readily iodinated to afford monomer **11** in 56% yield, which was reacted with bis(pinacolato)diboron **12** in the presence of a catalytic amount of $\text{Pd}(\text{OAc})_2/\text{S-Phos}$ to give **P10** in 25% isolated yield with an M_n of 2600. The UV-vis absorption spectra of **P10** and model compound **13** in CHCl_3 solutions are shown in Figure 8. The absorption maximum of **P10** was observed at around 360 nm, while that of **13** appeared at 379 nm due to the contribution of the coplanarity of the bithiophene and the methoxyphenyl groups of **11** in the ground state (Figure 9). This was supported by the ^1H NMR spectrum of **13**. The bithiophene units in **P10** rotate freely to avoid steric hindrance, while the bithiophene units in **13** adopt a relatively planar structure to extend its conjugation length (Figure 9).



Scheme 5. Synthesis of polymer **P10**.

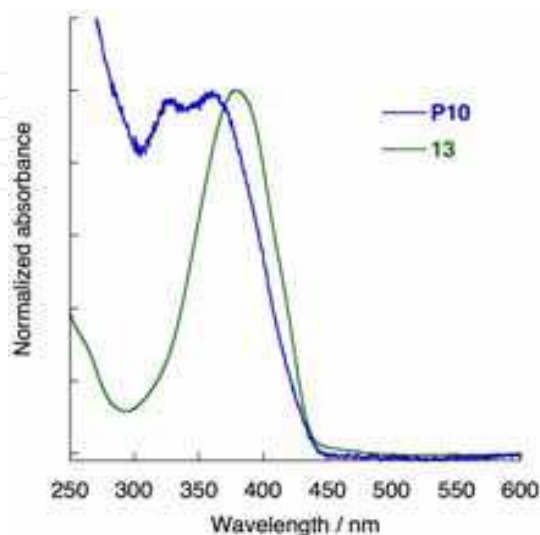


Fig. 8. UV spectra of polymer **P10** and compound **13** in CHCl_3 (1.0×10^{-5} M).

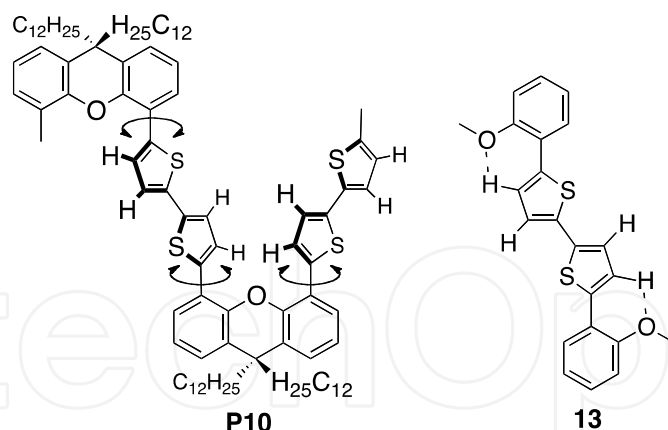
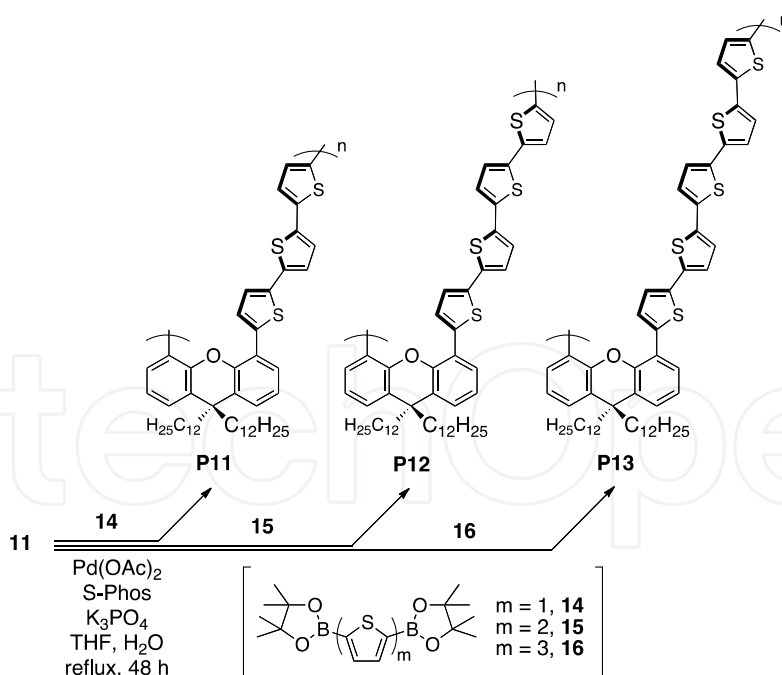


Fig. 9. Structures of polymer **P10** and compound **13**.

Terthiophene-, quarterthiophene- and quinquethiophene-layered polymers were synthesized by the coupling reaction of **11** with monomers **14–16**, as shown in Scheme 6; the polymerization results are listed in Table 3. The isolated yields of **P10–13** were relatively low (19%–40%) due to repeated reprecipitation and purification using recyclable liquid chromatography. The polymers obtained were soluble in common organic solvents such as THF, CH_2Cl_2 , CHCl_3 , and toluene. The polymer thin films were readily formed by spin-coating from their toluene solution. The thermal stabilities of the polymers were examined by thermogravimetric analysis (TGA) and all polymers were sufficiently stable with a 10% weight loss at temperatures around 400 °C under N_2 (Figure 10).



Scheme 6. Synthesis of polymers **P11–P13**.

The UV-vis absorption spectra and PL spectra of **P10–P13** in CHCl_3 are shown in Figure 11; the data are listed in Table 3. In Figure 11A, absorption bands assigned to the $\pi\text{--}\pi^*$ transition of oligothiophenes were observed, and the absorption maxima bathochromically shifted as the number of thiophene rings increased.

entry	Polymer	Yield (%)	M_n	M_w/M_n	$\lambda_{\text{abs,max}}$ (nm)	$\lambda_{\text{PL,max}}$ (nm)	Φ_{PL}
1	P10	25	2600	1.1	360	440, 470	0.12
2	P11	40	3200	1.0	358, 380(sh)	480, 504	0.20
3	P12	30	2800	1.1	412	520(sh), 541	0.29
4	P13	19	3800	1.1	420	534, 562	0.27

Table 3. Polymerization results and optical properties

M_n and M_w/M_n were calculated by MALDI-TOF mass spectra and GPC (CHCl₃, polystyrene standards), respectively. $\lambda_{\text{abs,max}}$ was measured in CHCl₃ (1.0 × 10⁻⁵ M). $\lambda_{\text{PL,max}}$ was measured in CHCl₃ (1.0 × 10⁻⁷ M) excited at each absorption maximum. Φ_{PL} was absolute quantum efficiency in solution.

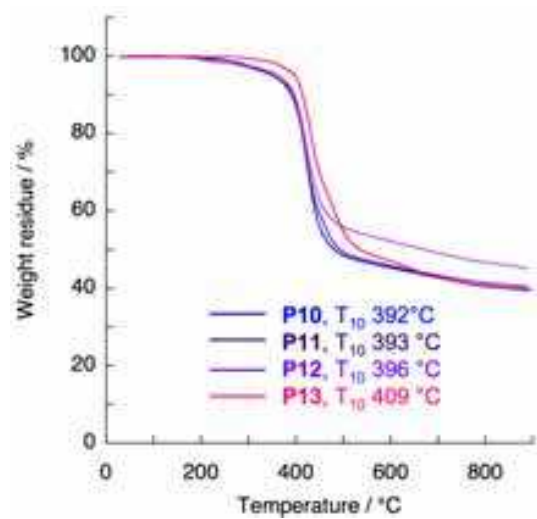


Fig. 10. TGA thermograms of polymers **P10-13**.

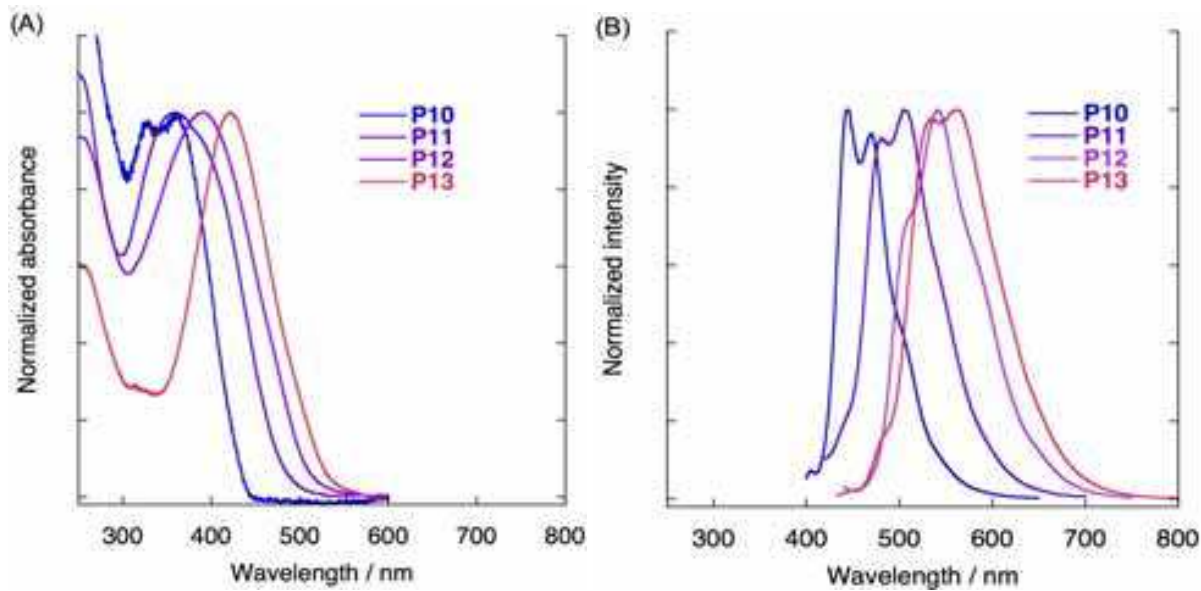


Fig. 11. (A) UV spectra of polymers **P10-13** in CHCl₃ (1.0 × 10⁻⁵ M). (B) PL spectra of polymers **P10-13** in CHCl₃ (1.0 × 10⁻⁷ M).

Figure 11B exhibits the photoluminescence spectra of **P10–P13** by excitation at each absorption maximum. The red-shift of the spectra was observed with an increase in the number of the thiophene rings in the same manner as in common conjugated systems. The photoluminescence absolute quantum efficiencies (Φ_{PL}) in CHCl_3 solutions were estimated to be 0.12–0.29, as listed in Table 3. Generally, the Φ_{PL} values of the π -stacked bithiophenes were low (0.001–0.054) because of the intermolecular aggregation of bithiophenes due to strong π - π interactions. The layered oligothiophenes are considered to be isolated in a single polymer chain due to the relatively long distance between the 4- and 5-positions of the xanthene skeleton despite the layered structure of **P10–P13**.

Cyclic voltammetric (CV) analyses of **P10–P13** were carried out in CH_2Cl_2 , and the resultant cyclic voltammograms are shown in Figure 12. Broad oxidation peaks were observed ranging from 0.4 to 0.5 V with a ferrocene/ferrocenium (Fc/Fc^+) external reference, as shown in Figure 12. The onset potentials of **P10–P13** were found to be approximately 0.15 V (vs. Fc/Fc^+); they decreased slightly as the number of thiophene rings increased. The HOMO energy levels of the polymers were calculated to be approximately -5.0 eV, suggesting that the oligothiophene-layered polymers have potential for applications in optoelectronic devices as hole-transporting materials.

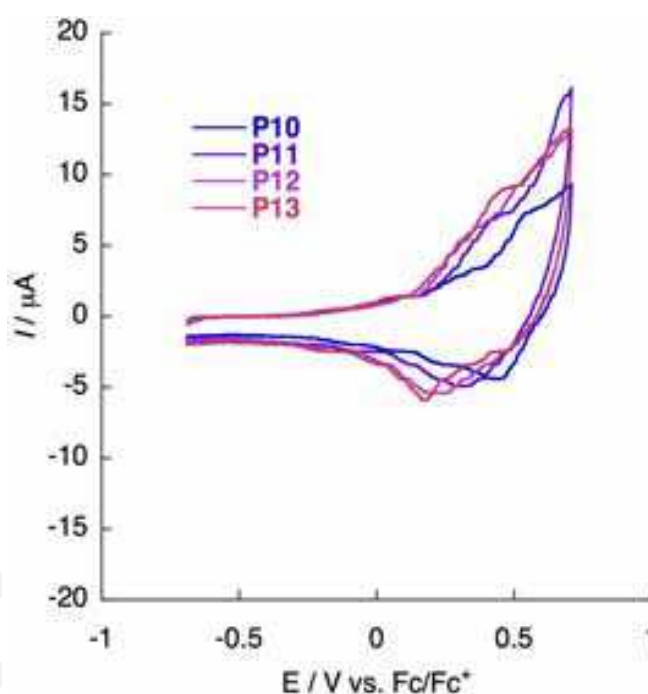
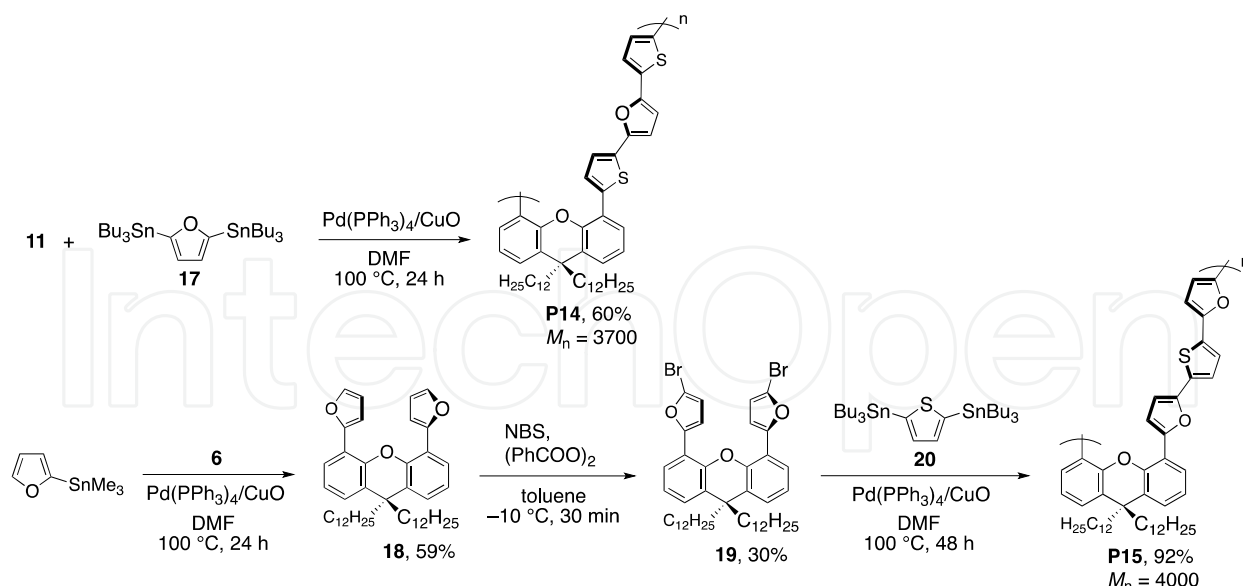
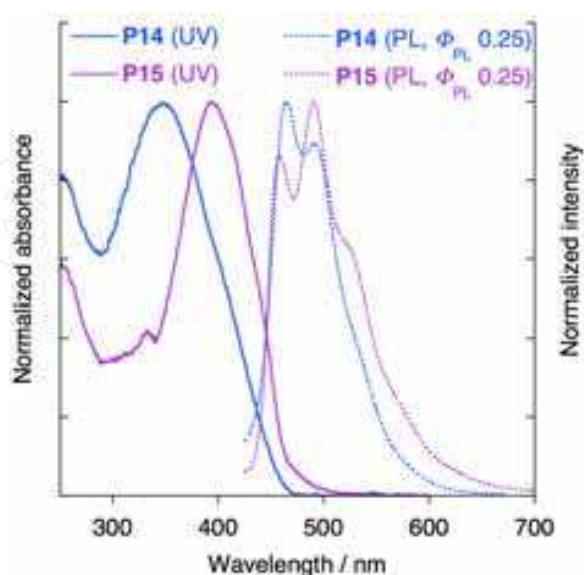


Fig. 12. Cyclic voltammograms of polymers **P10–13** in CH_2Cl_2 (vs. ferrocene/ferrocenium).

Furan can also be incorporated as the layered-aromatic unit into the oligothiophene-layered polymers (Fernandes et al., 2011). As shown in Scheme 7, the treatment of **11** with 2,5-bis(tributylstannyl)furan **17** in the presence of $\text{Pd}(\text{PPh}_3)_4/\text{CuO}$ afforded the corresponding polymer **P14**, which contains a thiophene/furan/thiophene oligomer as the layered unit. Migita-Kosugi-Stille coupling (Kosugi et al., 1977; Milstein & Stille, 1978) of 4,5-bis(bromofuryl)xanthene **19** and 2,5-bis(tributylstannyl)thiophene **20** yielded polymer **P15**, which contains a furan/thiophene/furan oligomer as the layered unit (Scheme 7). The M_n values of **P14** and **P15** were 3700 and 4000, respectively.


 Scheme 7. Synthesis of polymers **P14** and **P15**.

In the UV-vis absorption spectra (1.0×10^{-5} M in THF) of **P14** and **P15** (Figure 13), the absorption maximum of **P14**, which was ascribed to the π - π^* transition band of the thiophene/furan/thiophene moieties, was observed at 344 nm, while the absorption maximum of **P15**, consisting of furan/thiophene/furan units, appeared at 396 nm. It is reported that the absorption spectra were almost identical regardless of the thiophene/furan sequence. In addition, in the case of furan- and thiophene-substituted porphyrin systems, a longer π -conjugation length between the porphyrin ring and *meso*-substituted-furan was observed than between the porphyrin ring and *meso*-substituted-thiophene due to steric repulsion. Therefore, it is implied that the thiophene/furan/thiophene moiety in **P14** is more twisted against the xanthene scaffold than the furan/thiophene/furan moiety in **P15** in the ground state.


 Fig. 13. UV spectra in CHCl_3 (1.0×10^{-5} M) and PL spectra in CHCl_3 (1.0×10^{-7} M) of polymers **P14** and **P15**.

The photoluminescence spectra of **P14** and **P15** (1.0×10^{-7} M in THF) are shown in Figure 13. Both polymers exhibited similar photoluminescence spectra with the peak around 480 nm and photoluminescence quantum efficiencies of 0.25. The conformational change of **P14** from the twisted structure to the coplanar structure by photo-excitation resulted in a larger Stokes shift for **P14** than for **P15**. It is possible that the interactions among the layered π -electron systems in a single polymer chain are weak because of the relatively long distance between the 4- and 5-positions of the xanthene skeleton as well as because of the coplanarity of the layered π -electron system with xanthene in the excited state.

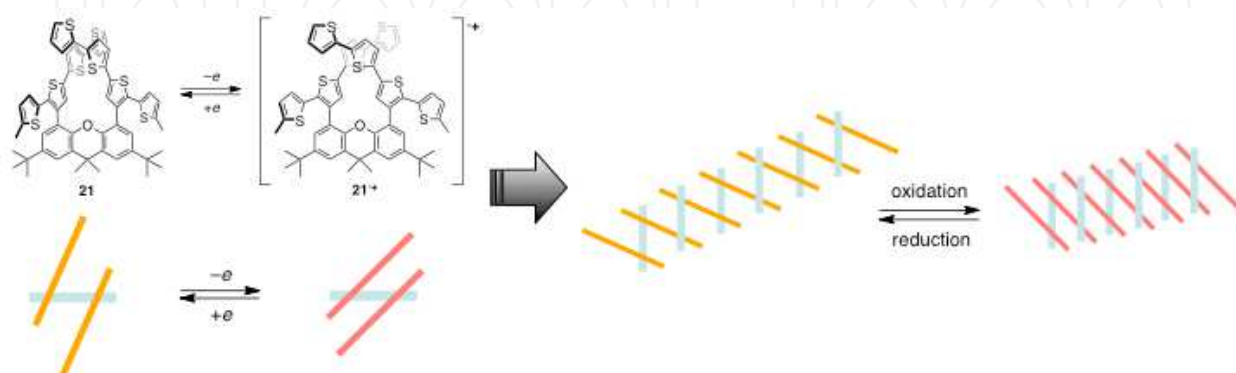


Fig. 14. Redox behavior of compound **21**.

Although it is not a polymer, xanthene-based compound **21**, which consists of layered quaterthiophenes, was synthesized (Takita et al., 2008), as shown in Figure 14. By chemical oxidation with $\text{Et}_3\text{O SbCl}_6$ or electrical oxidation, one quaterthiophene was oxidized to form a π -dimer (mixed-valence compound). This class of polymer can potentially be applied to molecular actuation responding to the redox of quaterthiophenes (Figure 14). Oligothiophene-layered polymers based on calix[4]arene also exhibit similar redox behaviors (Yu et al., 2003; Yu et al., 2004; Casanovas et al., 2006; Alemán et al., 2006; Scherlis & Marzari, 2005; Song & Swager, 2008), suggesting that they are candidates for sensing and actuating materials as well.

3. Xanthene-based oligomers

Perilenediimide and its derivatives have been focused on as the active materials for light-harvesting system photovoltaics and charge/electron transfer processes. In order to obtain insight into the nature of the photophysical properties of perilenediimide aggregates, they were layered onto the xanthene scaffold. As shown in Figure 15, reference compound **22** as well as oligomers **23a-b**, and **24**, which contain two and three cofacial perilenediimides, respectively, were prepared (Giaimo et al., 2008; Yoo et al., 2010). Their photophysical data are listed in Table 4. The absorption maxima of **23a-b** and **24** were shifted hypsochromically in comparison with that of **22** due to the formation of *H*-like aggregates. The photoluminescence spectrum of **22** exhibited a sharp spectrum with an emission maximum at 534 nm and vibronic structures at 576 nm and 624 nm. In contrast, the photoluminescence spectra of **23a-b** and **24** were broad and featureless; the spectrum of **23a** was highly broad with a peak at around 700 nm, and that of **23b** had a shoulder peak at around 550 nm and a broad peak at 650 nm. Time-resolved absorption and photoluminescence spectroscopy indicated that **23b** having 12-tricosanyl substituents exhibited slower formation of the

excimer-like excited state and had a higher energy than **23a**, which has n-octyl substituents, because of its more bulky substituents. These results imply that perilenediimide chromophores in **23a** adopt nearly optimal π -stacking. Their photophysical properties in the polymer matrix were also studied (Yoo et al, 2010). It was observed that the photoluminescence intensity and lifetime depended on the molecular conformations in the polymer matrix. Intramolecular overlap of the π -electron systems in perilenediimides would favor the use of n-type semiconductors.

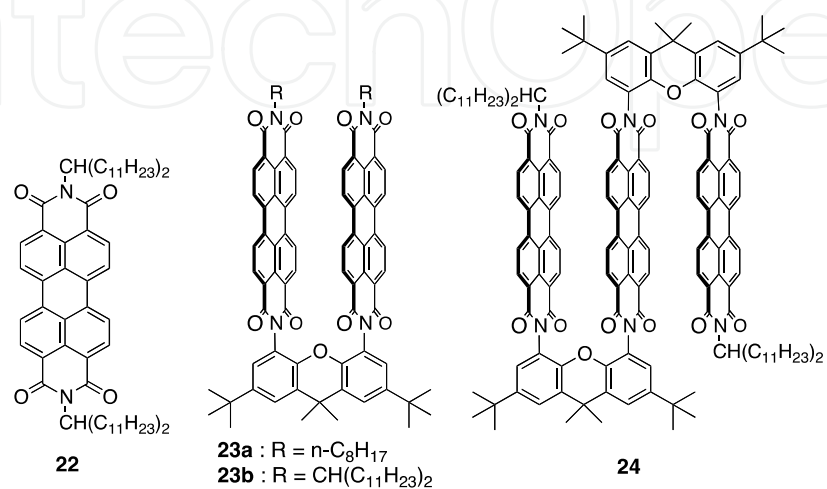


Fig. 15. Structures of compounds **22-24**.

entry	Compound	$\lambda_{\text{abs,max}} / \text{nm}$	$\lambda_{\text{em,max}} / \text{nm}$	Φ_{PL}	$\tau_{\text{PL}} / \text{ns} (\lambda_{\text{em}})$
1	22	527	533	0.98	3.8±0.1 (550)
2	23a	490	735	0.02	9.2±0.1 (700)
3	23b	491	647	0.19	0.05±0.01 (550) 28.6±0.1 (700)
4	24	488	647	0.13	0.05±0.01 (550) 22.5±0.1 (700)

Table 4. Photophysical Data of Compounds 22-24

Photoluminescence spectra, quantum efficiencies (Φ_{PL}), and lifetimes (τ_{PL}) were determined with an excitation wavelength of 400 nm.

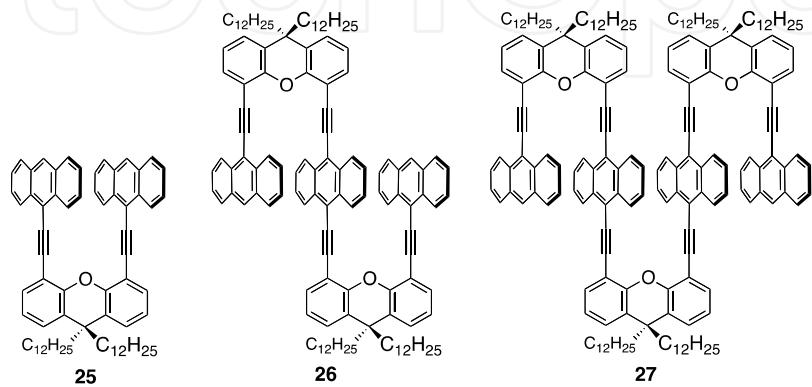
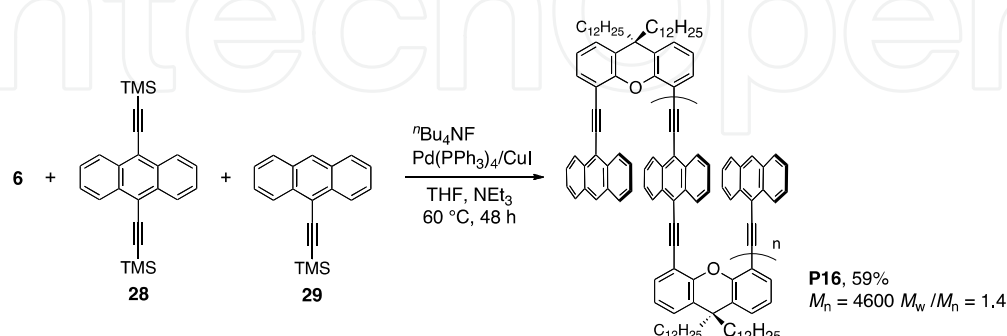


Fig. 16. Structures of oligomers **25-27**.

π -Stacked oligomers **25–27** comprising anthracene as the layered unit and xanthene as the scaffold were synthesized (Morisaki et al., 2010a) by repeated Sonogashira-Hagihara couplings (Figure 16). An anthracene-stacked polymer, **P16**, was also prepared by the reaction of **6** with **28** and **29** in 59% yield with an M_n of 4600, as shown in Scheme 8. According to the ^1H NMR spectra of oligomers **25–27** and polymer **P16**, the chemical shifts of the anthracene protons moved to a higher magnetic field than those of the common anthracene derivatives. Their signals gradually shifted as the number of stacked anthracene moieties increased because of the effect of the ring current of the neighboring anthracene rings.



Scheme 8. Synthesis of polymer **P16**.

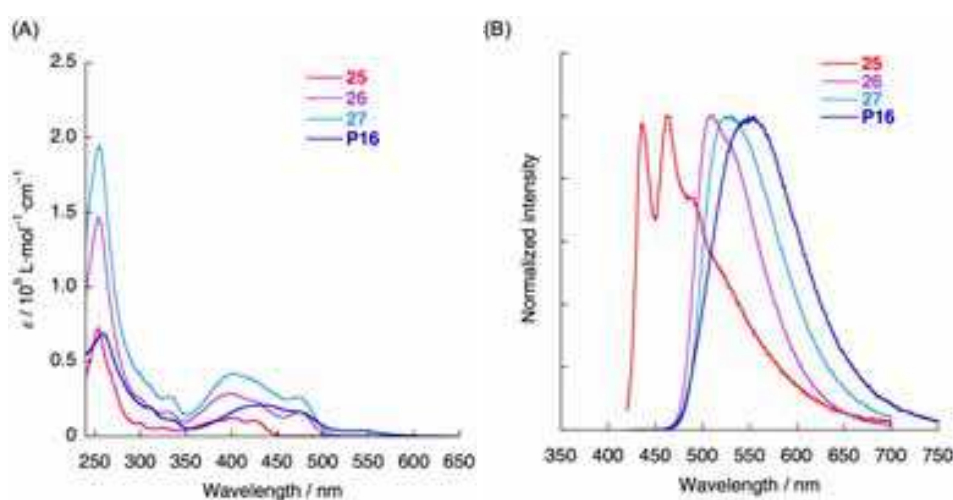
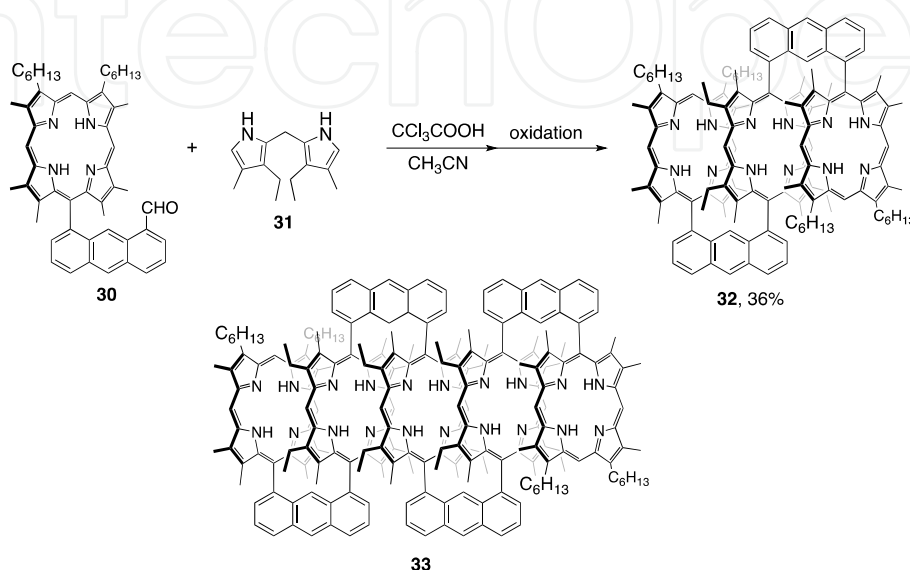


Fig. 17. (A) UV spectra of oligomers **25–27** and polymer **P16** in CHCl_3 (1.0×10^{-5} M). (B) PL spectra of oligomers **25–27** and polymer **P16** in CHCl_3 (1.0×10^{-7} M).

As shown in Figure 17A, the molar extinction coefficient (ϵ) of an absorption and a broad band at around 250 nm and 400 nm, respectively, increased in accordance with the number of anthracene rings. The photoluminescence spectrum of **25** in CHCl_3 revealed an emission peak at around 450 nm with a clear vibrational structure (Figure 17B); excimer-like emission did not appear despite the face-to-face orientation of the two anthracenes in **25**. In contrast, the photoluminescence spectra of **26**, **27**, and **P16** were broad without any vibrational structure. A fluorescence life time measurement of **P16** indicated emission from the excimer-like structures of the anthracene moieties, whereas oligomers **26**, **27**, and polymer **P16** exhibited emission mainly from aggregates because of the buttressing effect of the anthracene rings. These phenomena are attributed to the intramolecular π -stacked structure of the anthracene rings in both the excited and ground states.

4. Anthracene-based oligomers and polymers

Anthracene can be employed as the scaffold to layer aromatic rings one-dimensionally. Aromatic rings at the 1- and 8-positions of anthracene readily face each other due to the presence of hydrogen at the 9-position. Face-to-face porphyrin arrays, **32**, were constructed by condensation of formyl- and porphyrin-substituted anthracene, **30**, with dipyrromethane **31** followed by oxidation (Scheme 9) (Nagata et al., 1990). In addition, oligomer **33** comprising five-layered porphyrin was prepared from dimeric porphyrin (Scheme 9).



Scheme 9. Synthesis of oligomer **32** and structure of oligomer **33**.

According to the absorption spectra of **32–35** in 1,2-dichlorobenzene solutions, the Soret bands of the zinc complexes of **32** and **33** (face-to-face systems) were hypsochromically shifted, without being split, as the number of layered porphyrins increased. In contrast, those of **34** and **35** (linear systems, Figure 18) bathochromically shifted with a split that became larger with an increasing number of porphyrins. These results can be explained by the exciton coupling theory.

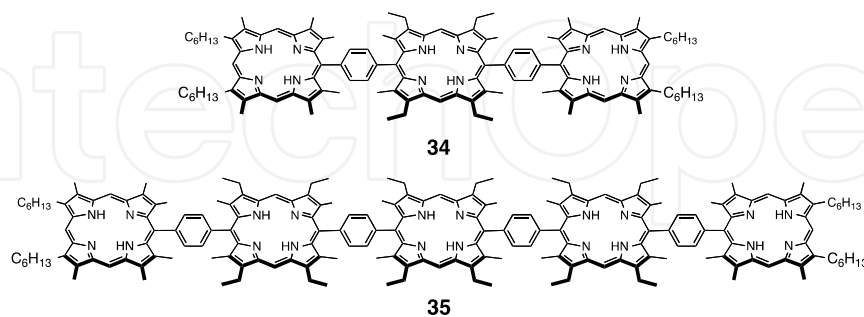


Fig. 18. Structures of linear oligomers **34** and **35**.

A 1,8-anthracene-linked Fe(III)-porphyrin trimer, **36**, (Figure 19) was synthesized (Naruta et al., 1994); the Fe(III) ions were connected by imidazoles. According to electron paramagnetic resonance (ESR) and magnetic susceptibility measurements, the anti-ferromagnetic exchange coupling ($-\mathcal{J}$) was calculated to be 15.3 cm^{-1} . Without the imidazole moieties, no magnetic interaction among the Fe(III) ions was observed. The appropriate

distance and the face-to-face arrangement of the Fe(III) ions resulted in a short distance of ~ 2.0 Å between the Fe(III) ion and nitrogen atom of imidazolate leading to the anti-ferromagnetic exchange coupling among the Fe(III) ions.

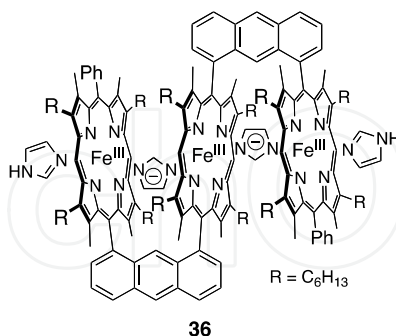
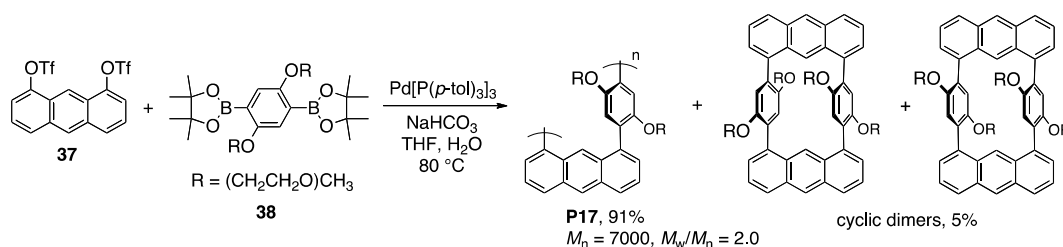


Fig. 19. Structure of oligomer **36**.

A benzene ring-layered polymer, **P17**, was synthesized via Suzuki-Miyaura polycondensation between 1,8-bis(trifluoromethyl)anthracene **37** and *p*-phenylene diboronate **38**, as shown in Scheme 10 (Sangvikar et al., 2009). Additionally, cyclic dimers were also isolated in 5% yield. The M_n of **P17** was relatively high ($M_n = 7000$, $M_w/M_n = 2.0$), which suggests the possibility of obtaining this class of polymers with a longer chain length.

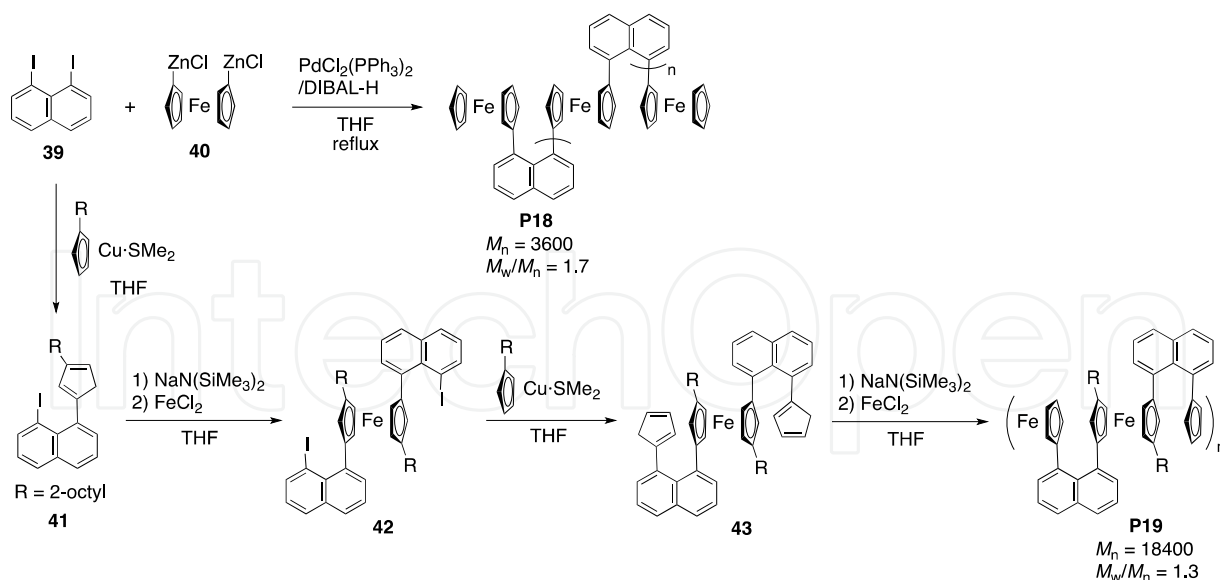
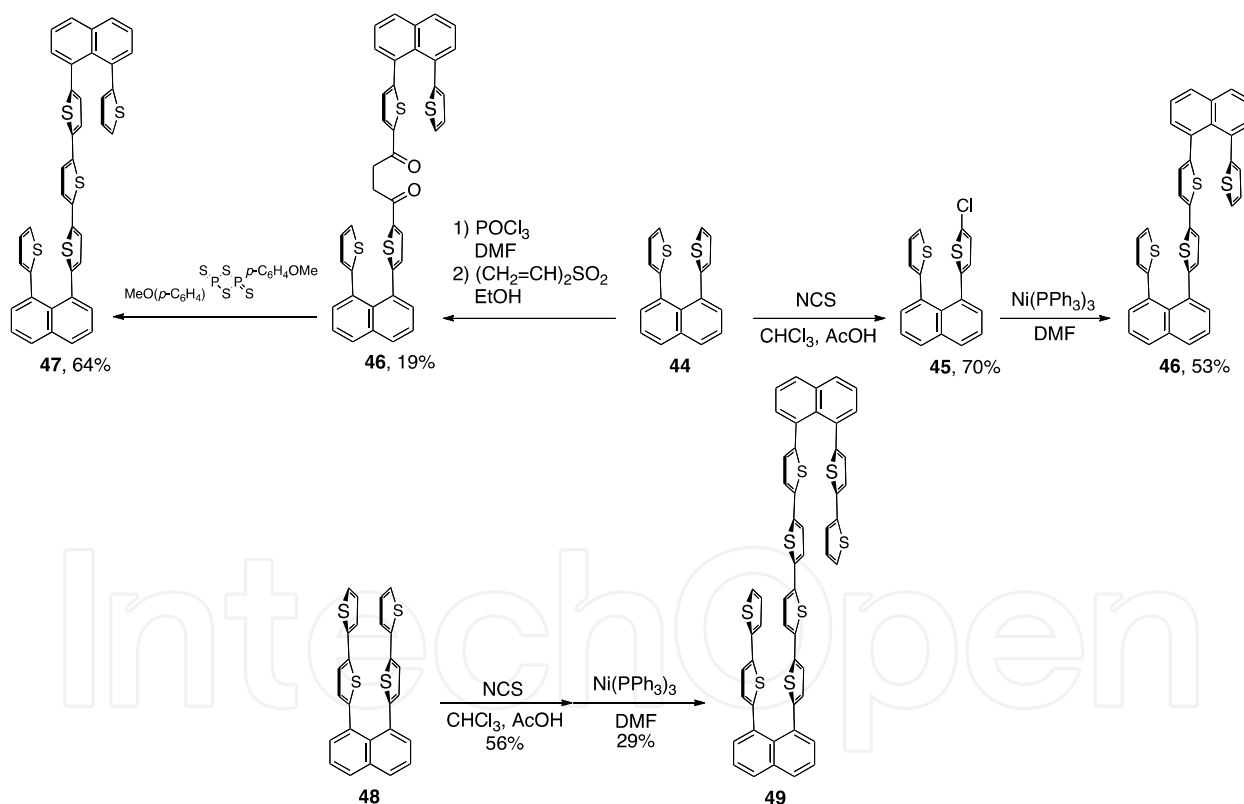


Scheme 10. Synthesis of polymer **P17**

5. Naphthalene-based oligomers and polymers

The distance between the 1- and 8-carbon atoms of naphthalene compounds is approximately 2.5–2.6 Å; therefore, aromatic groups substituted at the 1,8-positions of naphthalene derivatives are constrained in a face-to-face arrangement. Various 1,8-diarylnaphthalenes have been synthesized, and their π -stacked structures and π - π interactions have been studied. However, oligomers and polymers composed of multi-stacked aromatic rings have rarely been developed.

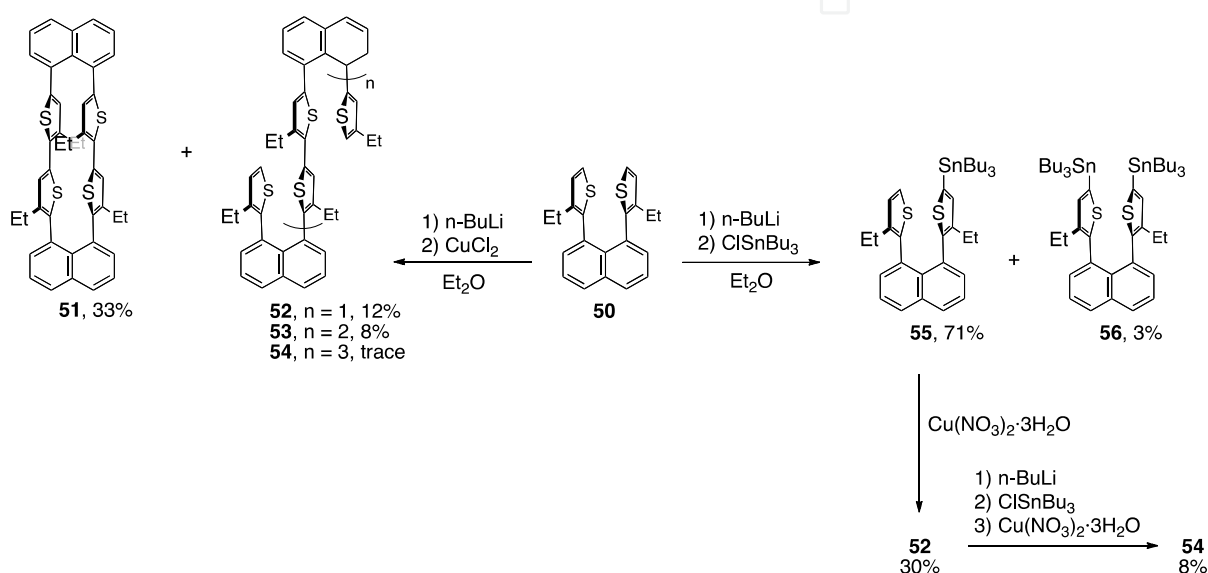
π -Stacked metallocene polymers were obtained, as shown in Scheme 11. The treatment of 1,8-diiodonaphthalene **39** with 1,1'-ferrocenyldizinc chloride **40** by Negishi coupling afforded polymer **P18** with a relatively low M_n of 3600 (Arnold et al., 1988). The synthetic procedure was modified as follows: the treatment of bis(2-octyl)ferrocene **43** with $\text{NaN}(\text{SiMe}_3)_2$ and FeCl_2 provided the ferrocene-stacked polymer **P19** with an M_n of 18400 (Nugent & Rosenblum, 1993; Rosenblum et al., 1995; Hudson et al., 1999). The addition of CoCl_2 and NiBr_2 instead of FeCl_2 yielded the corresponding ferrocene/cobaltocene-stacked and ferrocene/nickelocene-stacked polymers, respectively. The stacked ferrocenes in **P19** adopted a weakly interacting mixed-valence system by chemical doping with I_2 , after which the electrical conductivity increased from 10^{-12} to $6.7 \times 10^{-3} \text{ Scm}^{-1}$.


 Scheme 11. Synthesis of polymers **P18** and **P19**.

 Scheme 12. Synthesis of oligomers **46**, **47**, and **49**.

Oligothiophenes were stacked by a step-wise reaction. Scheme 12 illustrates the construction of three oligothiophene-layered systems (Kuroda et al., 1994). The chlorination of the thiophene ring by *N*-chlorosuccinimide (NCS) and a successive Ni-catalyzed coupling reaction afforded compounds **46** and **49**. Compound **47** was synthesized by cyclization with Lawesson's reagent. X-ray crystallographic analysis of **46** revealed that the outer thiophene rings and the inner bithiophene moiety are almost parallel and that the dihedral angle

between the thiophene planes and naphthalenes is approximately 53° . The CV oxidation potentials of **46**, **47**, and **49** decreased with the increasing number of thiophenes and were lower than the CV oxidation potentials of the monomeric compounds due to the stabilization of radical cations among the three-layered oligothiophenes.

Stepwise coupling reactions of the naphthalene-based stannylthiophenes yielded the corresponding oligothiophene-stacked oligomers (Scheme 13) (Iyoda et al., 2001; Nakao et al., 2008). Cyclic dimer **51** was primarily obtained along with oligomers **52–54** by the oxidative coupling reaction of **50** with BuLi and CuCl₂. The treatment of **55** with Cu(NO₃)₂·3H₂O afforded the coupling product **52** in 30% yield. Compound **52** was reacted with BuLi and ClSnBu₃ followed by treatment with Cu(NO₃)₂·3H₂O to obtain the corresponding thiophene-layered oligomer **54** in 8% yield.



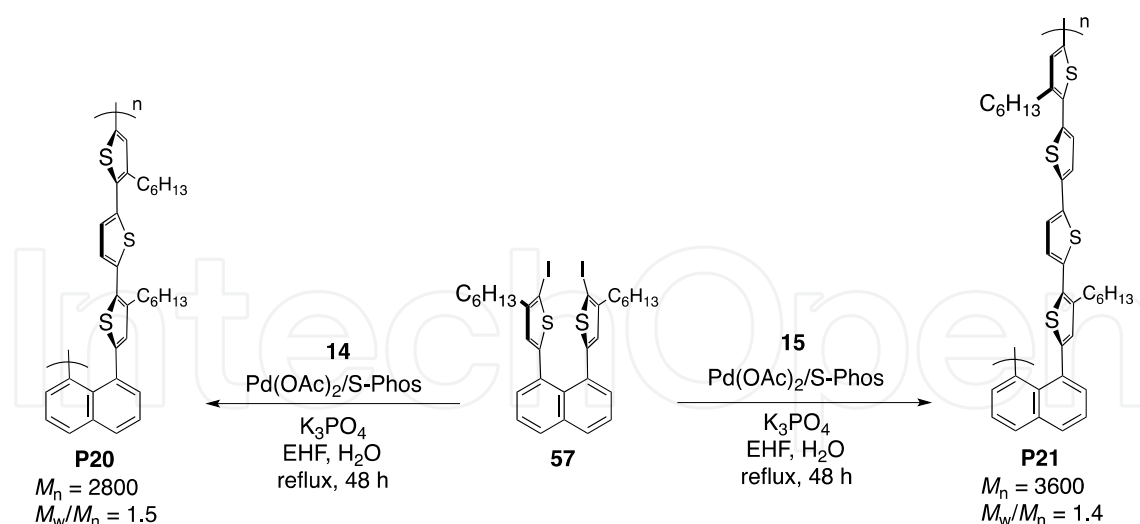
Scheme 13. Synthesis of oligomers **52–54**.

entry	Oligomer	$\lambda_{\text{abs,max}} / \text{nm}$	$\lambda_{\text{em,max}} / \text{nm}$	Φ_{PL}	$E_{\text{ox}}^1, E_{\text{ox}}^2 / \text{V}$
1	52	325	471	0.033	0.67
2	53	330	481	0.021	0.40, 0.60
3	54	333	485	0.007	0.40, 0.64

Table 5. Optical Data and Oxidation Potentials

Optical data were collected in their benzene solutions. Oxidation potentials were determined in *o*-dichlorobenzene using a ferrocene/ferrocenium external reference.

The optical and electrochemical behaviors of the compounds were studied and the results are summarized in Table 5. The absorption maxima of the oligomers were slightly red-shifted as the number of layered thiophenes increased. The long-wavelength absorption was assigned to the S_0 to S_1 transition of the bithiophene moieties. Their photoluminescence spectra were broad and featureless, and the photoluminescence quantum efficiencies, which were estimated to range from 0.007–0.033, were low. Oligomers **52–54** exhibited the redox properties of the π -donor. Oligomer **52** showed the one-electron oxidation wave ($E_{\text{ox}} = 0.67$ V) of a bithiophene unit, while two-step one-electron oxidation waves were observed for **53** and **54**.



Scheme 14. Synthesis of polymers **P20** and **P21**.

Scheme 14 shows the synthetic pathway for oligothiophene-stacked polymers. Polymers **P20** and **P21** were synthesized by the polymerization of **57** and co-monomers **14** and **15** via modified Suzuki-Miyaura coupling using a catalytic amount of $\text{Pd}(\text{OAc})_2$ and a bulky phosphine ligand (S-Phos) (Morisaki et al., 2010c). The M_n values of **P20** and **P21** were estimated to be 2800 and 3600, from which the number-average degrees of polymerization were estimated to be 5 and 6, respectively.

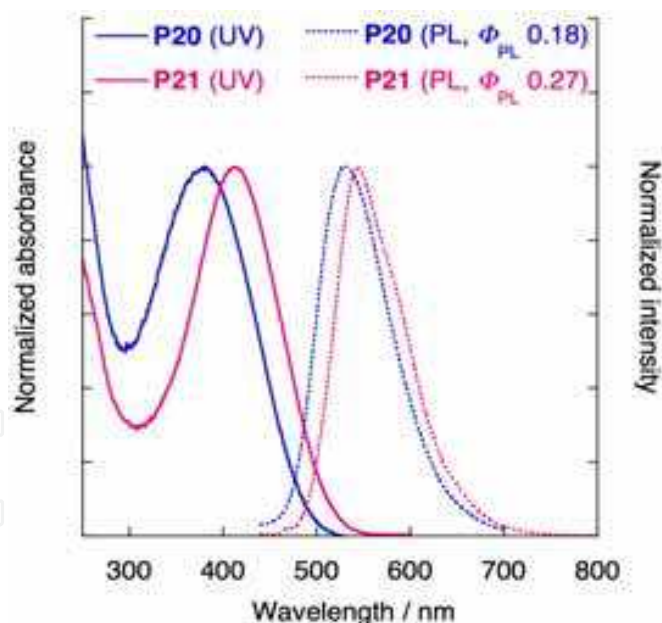


Fig. 20. UV spectra in CHCl_3 (1.0×10^{-5} M) and PL spectra in CHCl_3 (1.0×10^{-7} M) of polymers **P20** and **P21**.

The UV-vis absorption spectra in CHCl_3 (1.0×10^{-5} M) and photoluminescence spectra in CHCl_3 (1.0×10^{-7} M) of **P20** and **P21** are shown in Figure 20. An increase in the absorption maxima was observed with an increasing number of thiophene rings. The absorption maxima of **P20** and **P21** appeared at 379 and 410 nm, respectively. It is suggested that this absorption band should also be assigned to the $S_0 \rightarrow S_1$ transition of the bithiophene-

naphthalene moieties. It is expected that the S_1 state forms a quinoidal-like structure of thiophene with naphthalene (Seixas de Melo et al., 2001; Pina et al., 2009). Bathochromic shifts of the photoluminescence spectra and an increase in the absolute Φ_{PL} were observed with an increasing number of thiophene rings. The Φ_{PL} values of **P20** and **P21** were similar to the values found for naphthalene-based bithiophene and quaterthiophene oligomers, respectively. Concentration-quenching was not observed among the layered oligothiophenes indicating that the main quenching pathway is radiationless intersystem crossing from S_1 to T_1 . The HOMO energy levels of **P20** and **P21** were approximately -5.30 and -5.25 eV, respectively, as calculated from the E_{onset} values of their cyclic voltammograms. The oligothiophene-stacked polymers can potentially be applied in electronic devices such as hole-transporting materials.

6. Conclusion

In this chapter, the synthesis and properties of aromatic-ring- and π -electron-systems-layered polymers using xanthene, anthracene, and naphthalene as scaffolds were depicted. The oligomers introduced here were limited to three or more face-to-face aromatic systems, although dimeric compounds prevail. From a synthetic point of view, the method of using xanthene, anthracene, and naphthalene scaffolds is ideal for constructing face-to-face arrangements of a variety of aromatic rings and π -electron systems. The application of this class of polymers and oligomers to optoelectronic devices such as field emission transistors, photovoltaic devices, and charge-transporting materials has not yet been extensively investigated. It is worth noting that the presence of the π -stacked structure and the orientation of the π -electron systems play an important role in the effective charge transfer, energy transfer, and delocalization of excitons in the devices, leading to great potential of these systems in optoelectronic devices. The challenge for the near future is the development of controlled polymerization instead of stepwise oligomer synthesis to obtain aromatic-ring-layered polymers with narrow polydispersity, which would lead to high-performance next-generation organic optoelectronic devices.

7. References

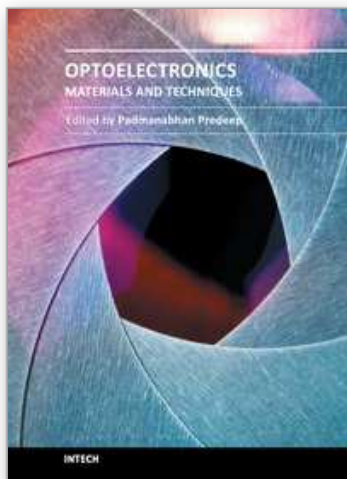
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