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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 alkyl lithium 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.
Optoelectronics - Materials and Techniques

Scheme 1. Synthesis of monomer 1

Scheme 2. Synthesis of polymers P1-P3

<table>
<thead>
<tr>
<th>entry</th>
<th>Mono-ethylarene</th>
<th>Feed ratio x : y : z</th>
<th>Polymer</th>
<th>Yield (%)</th>
<th>$M_n$ (calcd.)</th>
<th>$M_n$ (found by $^1$H NMR)</th>
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<tr>
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<td></td>
<td>10 : 9 : 2</td>
<td>P1a</td>
<td>79</td>
<td>5956</td>
<td>4100</td>
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<tr>
<td>2</td>
<td></td>
<td>5 : 4 : 2</td>
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<td>65</td>
<td>3082</td>
<td>3100</td>
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<tr>
<td>3</td>
<td></td>
<td>3 : 2 : 1</td>
<td>P1c</td>
<td>50</td>
<td>1933</td>
<td>2100</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>10 : 9 : 2</td>
<td>P2a</td>
<td>70</td>
<td>5896</td>
<td>7500</td>
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<tr>
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<td></td>
<td>5 : 4 : 2</td>
<td>P2b</td>
<td>50</td>
<td>3022</td>
<td>4200</td>
</tr>
<tr>
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<td></td>
<td>3 : 2 : 1</td>
<td>P2c</td>
<td>65</td>
<td>1872</td>
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<td>10 : 9 : 2</td>
<td>P3a</td>
<td>76</td>
<td>5786</td>
<td>5750</td>
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<tr>
<td>8</td>
<td></td>
<td>5 : 4 : 2</td>
<td>P3b</td>
<td>59</td>
<td>2912</td>
<td>3000</td>
</tr>
<tr>
<td>9</td>
<td>NO$_2$</td>
<td>3 : 2 : 1</td>
<td>P3c</td>
<td>56</td>
<td>1762</td>
<td>1700</td>
</tr>
</tbody>
</table>

Table 1. Polymerization results

As shown in Scheme 2, the Sonogashira-Hagihara coupling (Tohda et al., 1975; Sonogashira, 2002) of diiodoxanthene 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 $^1$H NMR spectra.

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Fig. 1. UV-vis absorption (UV) spectra of polymers P1a-c in CHCl₃ (1.0 × 10⁻⁵ M).

Fig. 2. (A) UV-vis absorption spectra in CHCl₃ (1.0 × 10⁻⁵ M) and photoluminescence (PL) spectra in CHCl₃ (5.0 × 10⁻⁷ M) of P1a. (B) UV-vis absorption spectra in CHCl₃ (1.0 × 10⁻⁵ M) and PL spectra in CHCl₃ (5.0 × 10⁻⁷ M) of P2b.

As shown in the UV-vis absorption spectra (in CHCl₃ 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 (Mₙ = 4100) and P2b (Mₙ = 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 CHCl₃.

The UV-vis absorption spectra of the nitrobenzene-end-capped polymers P₃a–c (in CHCl₃, 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 × 10⁴ times more effectively than the addition of nitrobenzene to a P₁a solution.
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.

Table 2. Synthesis of polymers P4 and P5

<table>
<thead>
<tr>
<th>Mn</th>
<th>Mw/Mn</th>
<th>Entry</th>
<th>Polymer</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>P4</td>
<td>63</td>
<td>2500</td>
<td>1.3</td>
</tr>
<tr>
<td>2</td>
<td>P5</td>
<td>62</td>
<td>2300</td>
<td>1.1</td>
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Mn and Mw/Mn were calculated by MALDI-TOF mass spectra and GPC (CHCl₃, polystyrene standards), respectively.

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. 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 (ΦPL) 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.
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.

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).

Figure 7A shows the photoluminescence spectra of $P_8$ and $P_9$ 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 $P_9$ ($\Phi_{PL} = 55\%$) was lower than that of $P_8$ ($\Phi_{PL} = 25\%$), indicating that the end-capping nitrobenzene units of $P_9$ quench the emission from the layered biphenylenes. The photoluminescence spectra of $P_8$, 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 $P_9$ was $10^4$ times larger than that of $P_8$ upon the addition of nitrobenzene. The two end-capping nitrophenyl moieties in $P_9$ effectively quenched the photoluminescence from the layered biphenylenes via through-space interactions of the single polymer chain.

Fig. 7. (A) UV spectra of polymers $P_8$ and $P_9$ in CHCl$_3$ (1.0 × 10$^{-5}$ M). (B) PL spectra of polymer $P_8$ 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 FeCl₃ 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 Pd(OAc)$_2$/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 CHCl₃ 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 bisthiophene and the methoxyphenyl groups of 11 in the ground state (Figure 9). This was supported by the $^1$H 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).


Fig. 8. UV spectra of polymer P10 and compound 13 in CHCl₃ (1.0 × 10⁻⁵ M).
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–P13 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$_2$Cl$_2$, 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).

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 π-π* transition of oligothiophenes were observed, and the absorption maxima bathochromically shifted as the number of thiophene rings increased.
Table 3. Polymerization results and optical properties

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

$M_n$ and $M_w/M_n$ were calculated by MALDI-TOF mass spectra and GPC (CHCl$_3$, polystyrene standards), respectively. $\lambda_{\text{abs,max}}$ was measured in CHCl$_3$ (1.0 x 10$^{-5}$ M). $\lambda_{\text{PL,max}}$ was measured in CHCl$_3$ (1.0 x 10$^{-7}$ M) excited at each absorption maximum. $\Phi_{\text{PL}}$ was absolute quantum efficiency in solution.
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 ($\Phi_{PL}$) in CHCl$_3$ solutions were estimated to be 0.12–0.29, as listed in Table 3. Generally, the $\Phi_{PL}$ values of the π-stacked bisthiophenes were low (0.001–0.054) because of the intermolecular aggregation of bisthiophenes 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$_2$Cl$_2$, 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$_2$Cl$_2$ (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 Pd(PPh$_3$)$_4$/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.

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 CHCl₃ (1.0 × 10⁻⁵ M) and PL spectra in CHCl₃ (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.](image)

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 Et₃O·SbCl₆ 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 \textbf{23a}, which has n-octyl substituents, because of its more bulky substituents. These results imply that perilenediimide chromophores in \textbf{23a} adopt nearly optimal \Pi -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 \Pi -electron systems in perilenediimides would favor the use of n-type semiconductors.

<table>
<thead>
<tr>
<th>entry</th>
<th>Compound</th>
<th>(\lambda_{abs,\text{max}}) / nm</th>
<th>(\lambda_{em,\text{max}}) / nm</th>
<th>(\Phi_{\text{PL}})</th>
<th>(\tau_{\text{PL}}) / ns ((\lambda_{em}))</th>
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<td>1</td>
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<td>527</td>
<td>533</td>
<td>0.98</td>
<td>3.8(\pm)0.1 (550)</td>
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<tr>
<td>2</td>
<td>\textbf{23a}</td>
<td>490</td>
<td>735</td>
<td>0.02</td>
<td>9.2(\pm)0.1 (700)</td>
</tr>
<tr>
<td>3</td>
<td>\textbf{23b}</td>
<td>491</td>
<td>647</td>
<td>0.19</td>
<td>0.05(\pm)0.01 (550) 28.6(\pm)0.1 (700)</td>
</tr>
<tr>
<td>4</td>
<td>\textbf{24}</td>
<td>488</td>
<td>647</td>
<td>0.13</td>
<td>0.05(\pm)0.1 (550) 22.5(\pm)0.1 (700)</td>
</tr>
</tbody>
</table>

Table 4. Photophysical Data of Compounds 22-24

Photoluminescence spectra, quantum efficiencies (\(\Phi_{\text{PL}}\)), and lifetimes (\(\tau_{\text{PL}}\)) were determined with an excitation wavelength of 400 nm.

Fig. 15. Structures of compounds \textbf{22-24}.

Fig. 16. Structures of oligomers \textbf{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 $^1$H 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.](image)

As shown in Figure 17A, the molar extinction coefficient ($\epsilon$) 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.

![Fig. 17.](image)
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 dipyrrromethane 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.](image)

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.](image)

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 imidazolates. According to electron paramagnetic resonance (ESR) and magnetic susceptibility measurements, the antiferromagnetic exchange coupling \( -J \) 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 \(~2.0\,\text{Å}\) between the Fe(III) ion and nitrogen atom of imidazolate leading to the antiferromagnetic 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 diborionate 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 \(\pi\)-stacked structures and \(\pi\)-\(\pi\) interactions have been studied. However, oligomers and polymers composed of multistacked aromatic rings have rarely been developed.

\(\pi\)-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 NaN(SiMe₃)₂ and FeCl₂ 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 CoCl₂ and NiBr₂ instead of FeCl₂ 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 I₂ after which the electrical conductivity increased from \(10^{-12}\) to \(6.7 \times 10^{-3}\) Scm⁻¹.
Scheme 11. Synthesis of polymers \( P_{18} \) and \( P_{19} \).

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.](image)

<table>
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<tr>
<th>entry</th>
<th>Oligomer</th>
<th>λₘₐₓ / nm</th>
<th>λₘₐₓ / nm</th>
<th>Φₜ</th>
<th>Eₒₓ₁, Eₒₓ₂ / V</th>
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</thead>
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<tr>
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<td>325</td>
<td>471</td>
<td>0.033</td>
<td>0.67</td>
</tr>
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<td>53</td>
<td>330</td>
<td>481</td>
<td>0.021</td>
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</tr>
<tr>
<td>3</td>
<td>54</td>
<td>333</td>
<td>485</td>
<td>0.007</td>
<td>0.40, 0.64</td>
</tr>
</tbody>
</table>

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 S₀ to S₁ 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 (Eₒₓ = 0.67 V) of a bithiophene unit, while two-step one-electron oxidation waves were observed for 53 and 54.

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 Pd(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$_0$→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 P_20 and P_21 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 P_20 and P_21 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-system-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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