

## ORIGINAL ARTICLE

## Naphthalene-based oligothiophene-stacked polymers

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We report the synthesis and properties of  $\pi$ -stacked polymers consisting of oligothiophene and naphthalene as the stacked  $\pi$ -system and the scaffold, respectively. The titled polymers were obtained by the Suzuki–Miyaura coupling reaction. Oligothiophene units were layered in proximity,  $\sim 3.0$  Å from each other. Contribution of the quinoidal structure of the oligothiophene units involving the naphthalene scaffolds in the excited state resulted in relatively high photoluminescence quantum efficiencies. The polymers have potential application to optoelectronic devices such as hole-transporting materials. *Polymer Journal* (2010) 42, 928–934; doi:10.1038/pj.2010.101; published online 27 October 2010

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## INTRODUCTION

Common conjugated polymers generally consist of sp- and/or sp<sup>2</sup>-carbon frameworks, and  $\pi$ -electrons are delocalized throughout the polymer backbone. Such conjugated polymers have attracted considerable attention because of their good processability and their readily tunable electronic and optical properties.<sup>1–3</sup> Recently, a new type of conjugated polymer that exhibits through-space interactions of  $\pi$ -electron systems has been developed. Poly(dibenzofulvene)s,<sup>4–11</sup> 7,7-diarylnorbornane-containing conjugated polymers,<sup>12,13</sup> cyclophane-containing polymers<sup>14–35</sup> and face-to-face ferrocene polymers<sup>36–38</sup> have been synthesized, and their optical and electrochemical properties have been studied in detail. Polymers with layered aromatic rings and  $\pi$ -electron systems have also been investigated;<sup>39–53</sup> for example, Chen *et al.*<sup>53</sup> recently reported the synthesis and formation of a two-dimensional assembly of polymeric ladder phanes containing face-to-face  $\pi$ -electron systems. These polymers have potential applications in optoelectronic devices and single-molecular devices such as single-molecular wires.

Cofacially aligned  $\pi$ -electron systems have an important role in biochemistry and material chemistry; DNA has face-to-face base pairs stacked in the double-stranded main chains,<sup>54</sup> and the performance of organic optoelectronic devices strongly depends on the arrangement of the  $\pi$ -electron systems.<sup>55</sup> We have recently reported the synthesis of aromatic-ring-layered polymers using xanthene compounds as scaffolds.<sup>40–47</sup> [2.2] Paracyclophane-layered polymers, which mimic multilayered cyclophanes,<sup>56–59</sup> exhibited fluorescence resonance energy transfer from the layered paracyclophanes to the end-capping groups. The use of xanthene as a scaffold enabled us to introduce various aromatic compounds, such as phenylenes,<sup>44</sup> carbazoles,<sup>45</sup> thiophenes<sup>46</sup> and anthracene,<sup>47</sup> into the polymers, with the distance between the layered aromatic units being  $\sim 4.5$  Å. Our next target is to construct layered and  $\pi$ -stacked aromatic systems in proximity, less than the sum of the van der Waals radius (3.40 Å) of an sp<sup>2</sup>-carbon, in the polymer backbone.

Nakayama and co-workers<sup>60–62</sup> and Iyoda and co-workers<sup>63,64</sup> have reported the synthesis of cofacially oriented naphthalene-based oligothiophenes, in which two or three bithiophenes were layered. In addition, Iyoda and co-workers have synthesized 2,2'-bithiophenophanes.<sup>63,64</sup> The layered bithiophenes in these compounds exhibit strong  $\pi$ - $\pi$  interactions. However, to the best of our knowledge, there has been no report on the synthesis of oligothiophene-stacked polymers. In this paper, we report the synthesis, characterization and properties of  $\pi$ -stacked polymers with oligothiophene as the  $\pi$ -stacked aromatic unit and naphthalene as the scaffold; these polymers were synthesized by the Suzuki–Miyaura coupling polymerization.

## EXPERIMENTAL PROCEDURE

## General experimental details

<sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-EX400 instrument (JEOL, Tokyo, Japan) at 400 and 100 MHz, respectively. The chemical shift values were expressed relative to Me<sub>4</sub>Si as an internal standard. High-resolution mass spectra were obtained on a JEOL JMS-SX102A spectrometer. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry measurement was performed on Voyager DE-STR (Applied Biosystems, Carlsbad, CA, USA) using all-*trans*-retinoic acid as a matrix. Gel permeation chromatography was carried out on a TOSOH 8020 (TSKgel G3000HXL column; Tosoh, Tokyo, Japan) instrument using CHCl<sub>3</sub> as an eluent after calibration with standard polystyrene samples. Recyclable preparative high-performance liquid chromatography was performed on a Japan Analytical Industry (Tokyo, Japan), Model 918R (JAIGEL-2.5H and 3H columns) using CHCl<sub>3</sub> as an eluent. UV–vis absorption spectra were obtained on a SHIMADZU UV3600 spectrophotometer (Shimadzu, Kyoto, Japan). Photoluminescence spectra were obtained on a Horiba FluoroMax-4 luminescence spectrometer (Horiba, Kyoto, Japan). Cyclic voltammetry was carried out on a BAS CV-50W electrochemical analyzer (BAS, Tokyo, Japan) in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M of sample and 0.1 M of Bu<sub>4</sub>NClO<sub>4</sub> with a glassy carbon working electrode, a Pt counter electrode, a Ag/AgCl (Ag/Ag<sup>+</sup>) reference electrode and a ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) external reference. Analytical thin-layer chromatography was performed with silica gel 60 Merck F<sub>254</sub> plates. Column chromatography was performed with

Wakogel C-300 silica gel. Elemental analyses were performed at the Micro-analytical Center of Kyoto University.

## Materials

Tetrahydrofuran (THF) and Et<sub>2</sub>O were purchased and purified by passage through purification column under Ar pressure.<sup>65</sup> Dehydrated grade CHCl<sub>3</sub> was purchased and used without further purification. *N,N,N',N'*-tetramethylethylenediamine (TMEDA) was purchased commercially, and purified by distillation with KOH. 3-Hexylthiophene (**1**), *n*-butyllithium (*n*-BuLi) (1.6 M in hexane), *s*-BuLi (1.0 M in cyclohexane and *n*-hexane), ZnBr<sub>2</sub>, I<sub>2</sub>, Pd(PPh<sub>3</sub>)<sub>4</sub>, Pd(OAc)<sub>2</sub>, 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (S-Phos), K<sub>3</sub>PO<sub>4</sub>, FeCl<sub>3</sub>, bis(pinacolato)diboron (**M1**), 2,5-thiophenediboronic acid (**M2**) and 2,2-bithiophene-5,5'-diboronic acid bis(pinacol) ester (**M4**) were obtained commercially, and used without further purification. 1,8-Diiodonaphthalene (**2**)<sup>66</sup> and 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-thieno[3,2-*b*]thiophene (**M3**)<sup>67</sup> were synthesized according to the literature's procedure. All reactions were performed under Ar atmosphere.

### 1,8-Bis(4-hexylthien-2-yl)naphthalene (**3**)

**1** (3.6 mL, 20.0 mmol) in THF (2.5 mL) was slowly added drop wise to *n*-BuLi (1.6 M in hexane, 6.3 mL, 10.0 mmol) and TMEDA (2.2 mL, 15.0 mmol) in THF (5.0 mL) at -78 °C. After the solution was stirred at room temperature for 24 h, ZnBr<sub>2</sub> (9.0 g, 40.0 mmol) in THF (20.0 mL) was transferred to this solution via a cannula at 0 °C. The reaction mixture was stirred at room temperature for 24 h. This solution was transferred via a cannula into a flask with **2** (0.76 g, 2.0 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.20 g, 0.17 mmol). After the reaction mixture was stirred at reflux temperature (oil bath temperature at 70 °C) for 24 h, H<sub>2</sub>O (30 mL) and EtOH (15 mL) were added to quench the reaction. The aqueous layer was washed with CHCl<sub>3</sub> (25 mL) three times, and the organic layer was dried over MgSO<sub>4</sub>. After removal of MgSO<sub>4</sub>, the solvent was evaporated. The residue was subjected to column chromatography on SiO<sub>2</sub> with hexane as an eluent to obtain **3** (0.51 g, 1.1 mmol, 57%) as a pale yellow oil.

*R*<sub>f</sub> 0.21 (hexane). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ=0.98 (t, *J*=6.4 Hz, -CH<sub>3</sub>, 6H), 1.38 (m, -CH<sub>2</sub>-, 12H), 1.54 (m, -CH<sub>2</sub>-, 4H), 2.40 (t, *J*=7.6 Hz, -CH<sub>2</sub>-, 4H), 6.36 (s, thiophene H, 2H), 6.65 (s, thiophene H, 2H), 7.54 (t, *J*=7.6 Hz, naphthalene H, 2H), 7.66 (d, *J*=7.6 Hz, naphthalene H, 2H), 7.92 (d, *J*=8.4 Hz, naphthalene H, 2H) p.p.m. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ=14.1, 22.6, 29.2, 29.9, 30.3, 31.7, 118.0, 125.0, 128.9, 129.0, 130.3, 132.0, 132.8, 135.4, 142.7, 143.4 p.p.m. High-resolution mass spectra (FAB): *m/z* calcd. for C<sub>30</sub>H<sub>36</sub>S<sub>2</sub> (M<sup>+</sup>): 460.2258, found: 460.2254. Anal. calcd. for C<sub>30</sub>H<sub>36</sub>S<sub>2</sub>: C 78.21; H 7.88; S 13.92, found: C 78.33; H 8.09; S 14.11.

### 1,8-Bis(4-hexyl-5-iodothiophen-2-yl)naphthalene (**4**)

**3** (0.64 g, 1.4 mmol) in Et<sub>2</sub>O (15.0 mL) was slowly added drop wise to *s*-BuLi (1.0 M in cyclohexane and *n*-hexane, 10.0 mL, 10.0 mmol) and TMEDA (3.3 mL, 22.0 mmol) at -78 °C. After the solution was stirred at room temperature for 24 h, I<sub>2</sub> (2.8 g, 11.0 mmol) in Et<sub>2</sub>O (15.0 mL) was transferred to this solution via a cannula at -78 °C. The reaction mixture was stirred at room temperature for 24 h. Saturated Na<sub>2</sub>SO<sub>3</sub> aqueous (30 mL) was added to quench the reaction. The aqueous layer was washed with CHCl<sub>3</sub> three times, and the organic layer was dried over MgSO<sub>4</sub>. After removal of MgSO<sub>4</sub>, the solvent was evaporated. The residue was subjected to column chromatography on SiO<sub>2</sub> with hexane as an eluent to obtain **4** (0.60 g, 0.80 mmol, 58%) as a pale yellow solid.

*R*<sub>f</sub> 0.45 (hexane). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ=0.89 (t, *J*=6.4 Hz, -CH<sub>3</sub>, 6H), 1.32 (m, -CH<sub>2</sub>-, 12H), 1.46 (m, -CH<sub>2</sub>-, 4H), 2.32 (t, *J*=7.6 Hz, -CH<sub>2</sub>-, 4H), 6.12 (s, thiophene H, 2H), 7.54 (m, naphthalene H, 4H), 7.94 (m, naphthalene H, 2H) p.p.m. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ=14.3, 23.1, 29.6, 30.1, 32.0, 32.8, 72.4, 125.4, 128.9, 129.9, 131.9, 132.5, 147.6, 148.5 p.p.m. High-resolution mass spectra (FAB): *m/z* calcd. for C<sub>30</sub>H<sub>34</sub>I<sub>2</sub>S<sub>2</sub> (M<sup>+</sup>): 712.0191, found: 712.0197. Anal. calcd. for C<sub>30</sub>H<sub>34</sub>I<sub>2</sub>S<sub>2</sub>: C 50.57; H 4.81; S 9.00, found: C 50.75; H 4.72; S 8.98.

### 1,8-Bis(2-thienyl)naphthalene (**5**)

This compound was synthesized according to the procedure<sup>63,64</sup> with some modifications. ZnBr<sub>2</sub> was used instead of ZnCl<sub>2</sub>. The spectral data were matched with the literature's values.<sup>63,64</sup>

Yield 60%. *R*<sub>f</sub> 0.35 (hexane). High-resolution mass spectra (EI (electron impact)): *m/z* calcd. for C<sub>18</sub>H<sub>12</sub>S<sub>2</sub> (M<sup>+</sup>): 292.0381, found: 292.0380. Anal. calcd. for C<sub>18</sub>H<sub>12</sub>S<sub>2</sub>: C 73.93; H 4.14; S 21.93, found: C 73.66; H 4.09; S 21.93.

## Palladium-catalyzed coupling polymerization

A typical procedure<sup>68–70</sup> is as follows. Monomers **4** (187.0 mg, 0.20 mmol), **M2** (50.9 mg, 0.20 mmol), Pd(OAc)<sub>2</sub> (4.5 mg, 0.02 mmol), S-Phos (8.2 mg, 0.02 mmol) and K<sub>3</sub>PO<sub>4</sub> (169.8 mg, 0.30 mmol) in THF (4.0 mL) and H<sub>2</sub>O (1.0 mL) were refluxed for 48 h. After filtration by Celite, the solution was diluted in CHCl<sub>3</sub> (20 mL) and washed twice with aqueous NH<sub>4</sub>OH (25 mL), brine (25 mL), and H<sub>2</sub>O (25 mL). The organic layer was dried over MgSO<sub>4</sub>. After filtration, the solvent was evaporated. The crude product was dissolved in a small amount of CHCl<sub>3</sub> and precipitated from MeOH/acetone three times. And then precipitation was repeated twice with CHCl<sub>3</sub> and acetone to obtain polymer **P2** (52.3 mg, 0.09 mmol, 35%).

Polymer **P1**. Yield: 10%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz): δ=0.9 (br), 1.3 (br m), 2.3 (br), 6.3–6.8 (br m), 7.6 (br), 7.9 (br) p.p.m. <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz) δ=14.3, 23.1, 29–31 (m), 125 (m), 129–132 (m), 139.4, 141.8 p.p.m.

Polymer **P2**. Yield: 35%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ=0.8 (br), 1.2 (br), 1.5 (br), 2.4 (br m), 6.4 (br), 7.0 (br), 7.6 (br m), 7.9 (br) p.p.m. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ=14.1, 22.6, 29–32 (m), 34.9, 130–132 (m), 136, 140, 142 p.p.m.

Polymer **P3**. Yield: 71%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz): δ=0.8 (br m), 1.2 (br m), 1.5 (br m), 2.5 (br), 6.4 (br m), 7.2 (br m), 7.4–8.0 (br m) p.p.m. <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz): δ=14.3, 23.1, 29–32 (m), 118, 126, 129–133 (m), 136–144 (m) p.p.m.

Polymer **P4**. Yield: 35%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ=0.8 (br), 1.2 (br), 1.5 (br), 2.5 (br), 6.4 (br m), 6.9 (br), 7.1 (br), 7.6 (br m), 7.9 (br) p.p.m. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ=14.1, 22.7, 29–32 (m), 124 (m), 125 (m), 129–132 (m), 136 (m), 142, 143 p.p.m.

## Oxidative coupling polymerization

Monomer **3** (0.46 g, 1.0 mmol) was added to a mixture of FeCl<sub>3</sub> (0.65 g, 4.0 mmol) in CHCl<sub>3</sub> (15 mL). The reaction mixture was stirred at reflux temperature (oil bath temperature at 70 °C) for 24 h and poured into a large amount of MeOH to obtain dark greenish-brown precipitates. The precipitates were washed with MeOH with a Soxhlet extractor for 48 h to yield a brown solid. The polymer was extracted from the precipitates with CHCl<sub>3</sub> with the Soxhlet extractor for several hours to obtain a brown CHCl<sub>3</sub> solution. The CHCl<sub>3</sub> solution was washed with saturated aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and aqueous NH<sub>3</sub>. And then, the CHCl<sub>3</sub> solution was stirred with aqueous H<sub>2</sub>NNH<sub>2</sub> for 6 h. The CHCl<sub>3</sub> solution was separated and dried over MgSO<sub>4</sub>. After removal of MgSO<sub>4</sub>, the solvent was evaporated to obtain a brown solid, which was dried *in vacuo*. The solid was dissolved in a small amount of CHCl<sub>3</sub> and reprecipitated from a large amount of MeOH three times to obtain polymer **P1** in the form of the brown powder (73.3 mg, 0.16 mmol, 16%).

## RESULTS AND DISCUSSION

Scheme 1 outlines the synthetic route to the naphthalene-based monomer **4**. The treatment of **1** with *n*-BuLi and TMEDA afforded 2-(4-hexylthienyl)lithium as an intermediate. The addition of ZnBr<sub>2</sub> afforded a 2-(4-hexylthienyl)zinc bromide intermediate, and the successive Negishi coupling reaction<sup>71</sup> with **2** in the presence of a catalytic amount of Pd(PPh<sub>3</sub>)<sub>4</sub> yielded **3** in 57% isolated yield. Monomer **4** was obtained in 58% isolated yield by lithiation of **3** with *s*-BuLi/TMEDA, followed by iodination.

Target polymers **P1–P4** were synthesized by polymerization of **4** and comonomers **M1–M4** by the modified Suzuki–Miyaura coupling reaction<sup>68–70</sup> in the presence of a catalytic amount of Pd(OAc)<sub>2</sub> and a bulky phosphine ligand, 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (S-Phos), with K<sub>3</sub>PO<sub>4</sub> in THF/H<sub>2</sub>O at reflux temperature for 48 h, as shown in Scheme 2. Cyclic oligomers<sup>63,64</sup> were not detected under this reaction condition because of the steric hindrance of pinacolborane moieties. The polymerization results are listed in

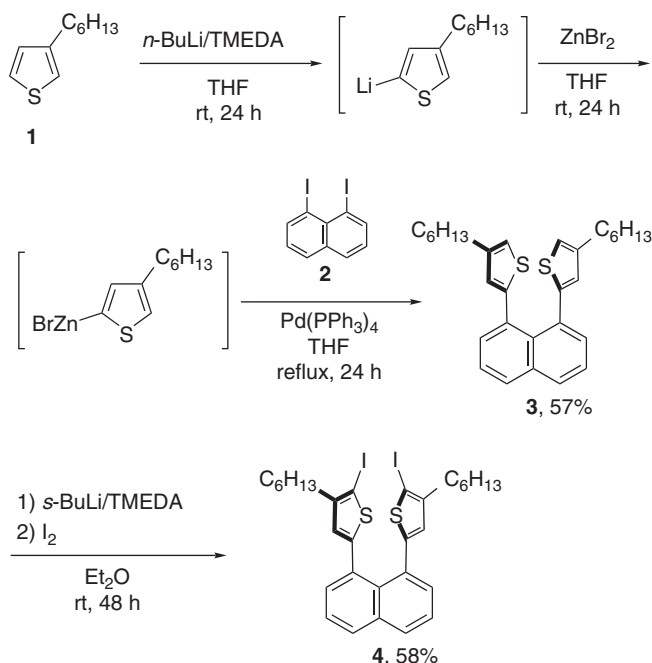
Scheme 1 Synthesis of compounds **3** and **4**.

Table 1. Polymer **P1** with the head-to-head structure<sup>72</sup> was also obtained by the oxidative coupling reaction of compound **3** with  $\text{FeCl}_3$  in  $\text{CHCl}_3$  (Scheme 3). The reaction of **3** with  $\text{FeCl}_3$  in  $\text{CHCl}_3$  afforded crude polymer **P1** as a dark greenish-brown solid. This solid was purified with MeOH using a Soxhlet extractor; it was then treated with saturated aqueous  $\text{Na}_2\text{S}_2\text{O}_3$ , aqueous  $\text{NH}_3$ , and aqueous  $\text{H}_2\text{NNH}_2$  to remove iron species. The polymer solution was dried over  $\text{MgSO}_4$ , and repeated reprecipitation was carried out to yield polymer **P1** in 16% isolated yield as a brown solid. However, we found a small amount of contamination by iron species ( $\sim 1.3$  wt%) in the polymer prepared by  $\text{FeCl}_3$ -mediated oxidative coupling reaction (Supplementary Figure S13).

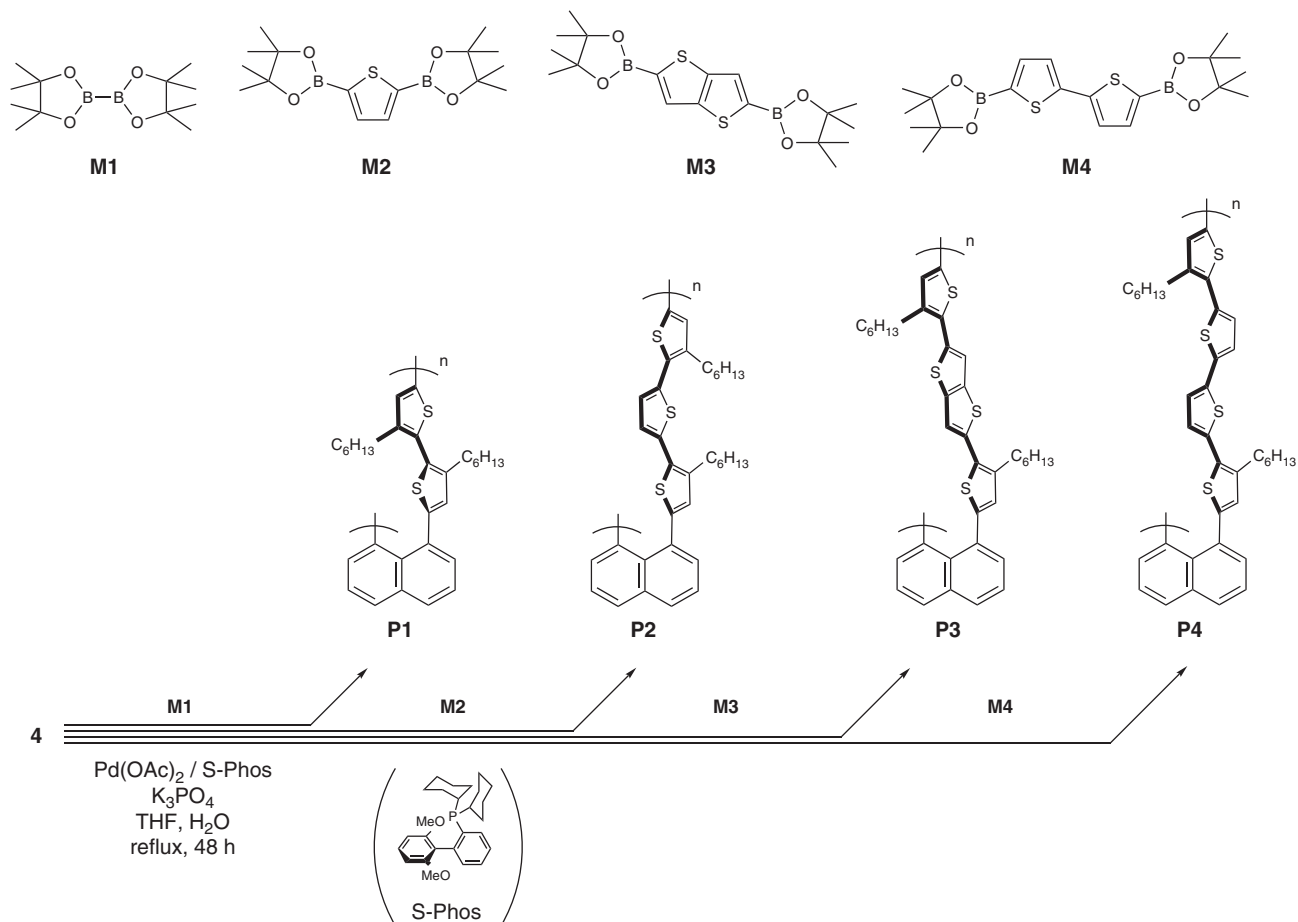
All polymers **P1–P4** had good solubility in common organic solvents, such as cyclohexane, toluene,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$  and THF.

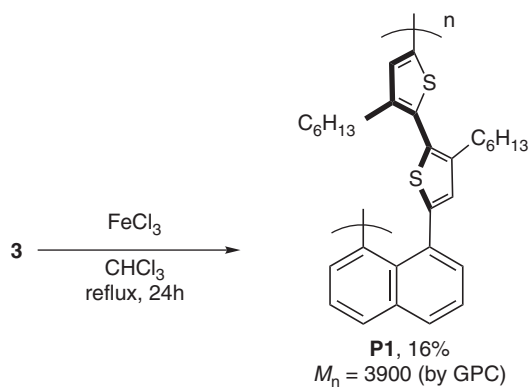
Table 1 Results of polymerization

Entry	Polymer	Yield (%) <sup>a</sup>	$M_n^b$	$M_w/M_n^b$
1	<b>P1</b>	10	1300	1.1
2	<b>P2</b>	35	2800	1.5
3	<b>P3</b>	71	3300	1.5
4	<b>P4</b>	35	3600	1.4

<sup>a</sup>Isolated yield.

<sup>b</sup>Estimated by gel permeation chromatography ( $\text{CHCl}_3$ ) using polystyrene as standards.

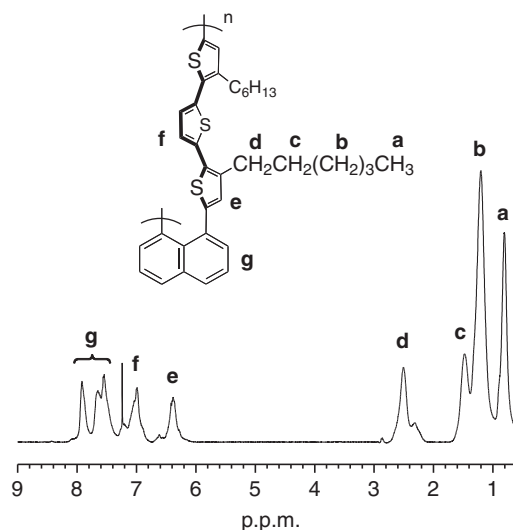
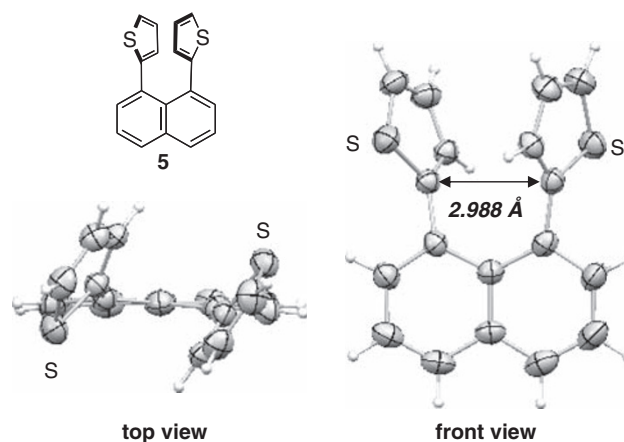
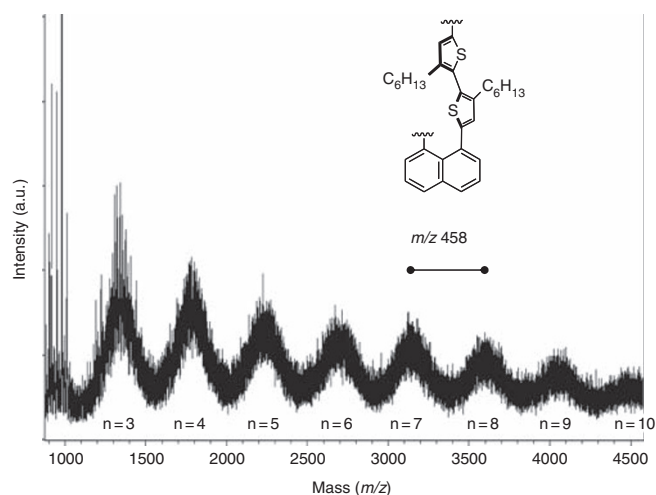
Scheme 2 Synthesis of polymers **P1–P4**.

**Scheme 3** Synthesis of polymer **P1** by the oxidative coupling reaction.

Polymer thin films were readily formed by spin coating or casting from toluene solutions. They were characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy, which are shown in Supporting Information. Figure 1 shows the  $^1\text{H}$  NMR spectrum of **P2** in  $\text{CDCl}_3$  as a representative example. The signals attributable to hexyl protons appeared at around 0.8, 1.2, 1.5 and 2.5 p.p.m. The signals for the terthiophene unit appeared at higher magnetic field at around 6.4–7.0 p.p.m, and those of the naphthalene unit were observed from 7.5 to 8.0 p.p.m. The layered terthiophenes are  $\pi$ -stacked with each other, which results in the upfield shift of thiophene protons to around 6.4 p.p.m, because of the ring current effect. Such an upfield shift was not observed in the xantheno-based oligothiophene-layered polymers.<sup>46</sup> The shortest distance between oligothiophene units in the polymers is expected to be  $\sim 3 \text{ \AA}$  based on the X-ray crystal structures of 1,8-bis(5,2'-bithiophen-2-yl)naphthalene<sup>61</sup> and bithiophenophane.<sup>64,73</sup> We also obtained the X-ray crystal structure of **5**, as shown in Figure 2 (the data are shown in Supporting Information). Thiophene rings adopted the face-to-face structure, and their shortest distance was estimated to be 2.988  $\text{\AA}$  in the solid state. This distance of  $\sim 3 \text{ \AA}$  is much shorter than the sum of the van der Waals radii of an  $\text{sp}^2$ -carbon (3.4  $\text{\AA}$ ); thus  $\pi$ - $\pi$  interactions between the layered oligothiophenes of the polymers in solution are expected.

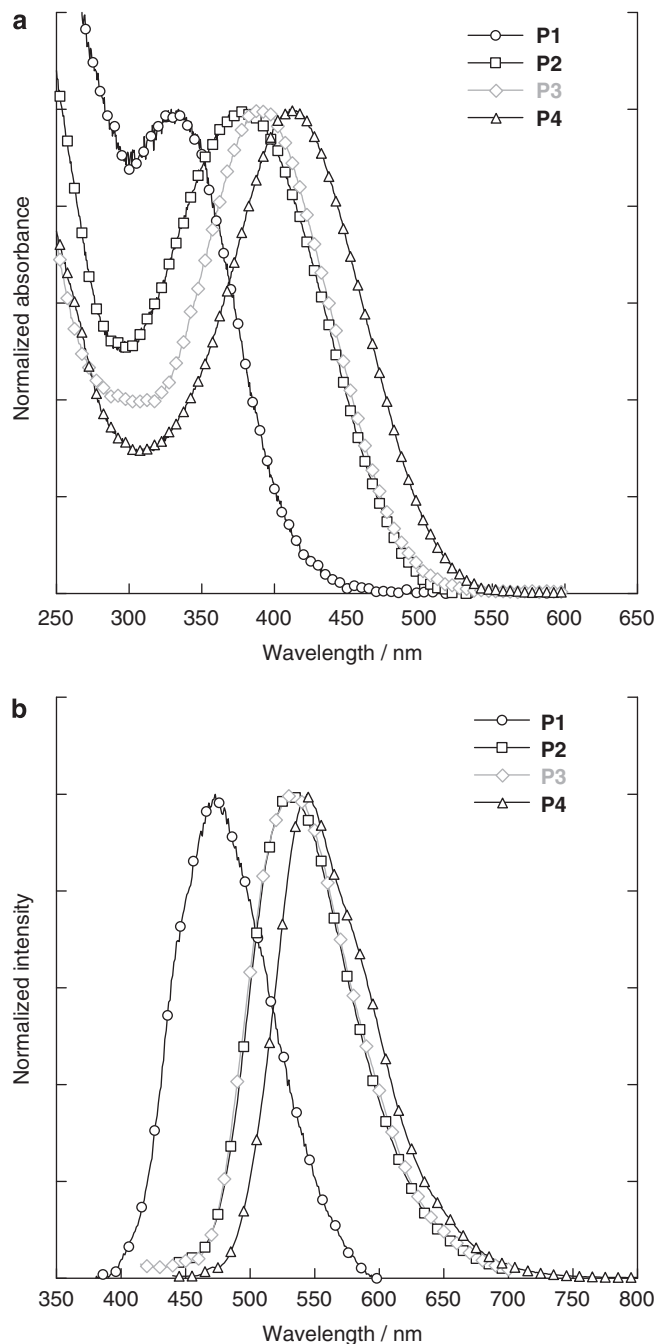
The number-average molecular weights ( $M_n$ ) of the polymers were estimated by gel permeation chromatography (polystyrene standards); they are summarized in Table 1. They were calculated to be  $M_n = 2200$ – $3400$ , from which the number-average degrees of polymerization were estimated to be 5–6. The matrix-assisted laser desorption/ionization time-of-flight mass spectrum of polymer **P1** was successfully obtained, as shown in Figure 3, although the spectrum was highly broadened. Polymer **P1** exhibited a major series of peaks that were regularly separated by the molar mass of a repeating unit ( $m/z$  458), which is in accordance with the proposed structure.

The optical properties of polymers **P1**–**P4** were examined,<sup>74–77</sup> and the data are summarized in Table 2. Figure 4a shows their UV–vis absorption spectra in  $\text{CHCl}_3$  ( $1.0 \times 10^{-5} \text{ M}$ ). An increase in the  $\lambda_{\text{abs,max}}$  value was observed with increasing thiophene ring number (Table 1 and Figure 4a). The absorption maximum ( $\lambda_{\text{abs,max}}$ ) of **P1** was observed at 331 nm (Entry 1 in Table 2 and Figure 4a); this value is almost identical to that of bithiophene-layered oligomers ( $\lambda_{\text{abs,max}} = 330 \text{ nm}$ ).<sup>64</sup> It is suggested that this absorption band is assigned to the  $S_0 \rightarrow S_1$  transition of the bithiophene-naphthalene moiety and the  $S_1$  state adopts a quinoidal-like structure of thiophene with naphthalene.<sup>75,76</sup> The bithiophenes in **P1** as well as oligothiophenes in **P2**–**P4** have difficulty in rotating freely because of the hexyl

**Figure 1**  $^1\text{H}$  nuclear magnetic resonance spectrum of polymer **P2** in  $\text{CDCl}_3$ .**Figure 2** Structure of compound **5** and its X-ray crystal structure. Thermal ellipsoids are drawn at the 30% probability level.**Figure 3** Matrix-assisted laser desorption/ionization time-of-flight mass spectrum of polymer **P1** using all-*trans*-retinoic acid as a matrix.

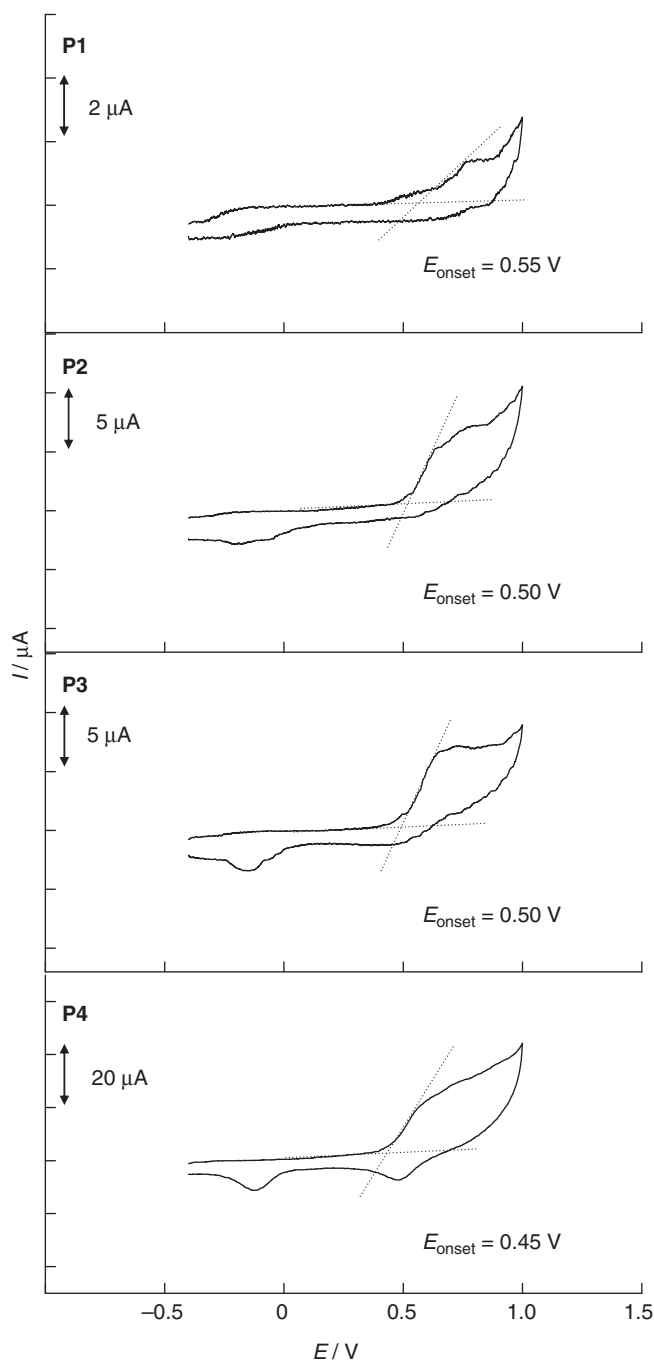
**Table 2** Optical properties of the polymers

Entry	Polymer	$\lambda_{abs,max}$ (nm) <sup>a</sup>	$\lambda_{PL,max}$ (nm) <sup>b</sup>	$\Phi_{PL}$ <sup>c</sup>
1	<b>P1</b>	331	473	0.05
2	<b>P2</b>	379	529	0.18
3	<b>P3</b>	391	534	0.27
4	<b>P4</b>	410	544	0.27

<sup>a</sup>In CHCl<sub>3</sub>, 1.0 × 10<sup>-5</sup> M.<sup>b</sup>In CHCl<sub>3</sub>, 1.0 × 10<sup>-7</sup> M, excited at absorption maximum.<sup>c</sup>Absolute photoluminescence quantum efficiency.**Figure 4** (a) UV-vis absorption spectra in CHCl<sub>3</sub> (1.0 × 10<sup>-5</sup> M) and (b) normalized fluorescence spectra in CHCl<sub>3</sub> (1.0 × 10<sup>-7</sup> M, excited at absorption maxima) of polymers **P1–P4**.

substituent; however, they can twist and have a degree of  $\pi$ -conjugation with the naphthalenes.

Photoluminescence spectra of **P1–P4** in a diluted CHCl<sub>3</sub> solution (1.0 × 10<sup>-7</sup> M) were recorded by the excitation at each absorption maximum (Figure 4b). We found bathochromic shifts of the spectra (Figure 4b) and an increase in the absolute photoluminescence quantum efficiencies ( $\Phi_{PL}$ ) with increasing number of thiophene rings (Table 2).<sup>75–77</sup> For polymer **P3**, which has a rigid fused-ring

**Figure 5** Cyclic voltammograms of polymers **P1–P4** in CH<sub>2</sub>Cl<sub>2</sub> (0.1 M) containing Bu<sub>4</sub>NClO<sub>4</sub> (0.1 M) using a glassy carbon working electrode, a Pt counter electrode, a Ag/Ag<sup>+</sup> reference electrode, and ferrocene/ferrocenium as an external reference.

structure, the  $\Phi_{PL}$  value was 0.27, which was the same as that for **P4** consisting of quaterthiophenes (Entries 3 and 4 in Table 2). The  $\Phi_{PL}$  values of **P1**, **P2** and **P4** were similar to the values found for naphthalene-based bithiophene, terthiophene and quaterthiophene oligomers,<sup>75,76</sup> respectively. Concentration quenching was not observed among the layered oligothiophenes for **P1–P4**, suggesting that the main quenching pathway is radiationless intersystem crossing from  $S_1$  to  $T_1$ . The energy migration and conformational relaxation of the oligothiophene–naphthalene moieties within  $\sim 100$  picoseconds should be considered for further studies to clarify these points, will be in progress.<sup>75,76</sup>

The electrochemical behaviors of **P1–P4** were studied by cyclic voltammetry in  $\text{CH}_2\text{Cl}_2$  containing 0.1 M  $\text{Bu}_4\text{NClO}_4$  with a  $\text{Ag}/\text{AgCl}$  ( $\text{Ag}/\text{Ag}^+$ ) reference and a ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) external reference. Their cyclic voltammograms are shown in Figure 5. Irreversible and ambiguous peaks were observed, which impeded the determination of their half-wave potentials ( $E^{1/2}$ ). The onset potentials ( $E_{\text{onset}}$ ) of **P1–P4** ranged from  $\sim 0.55$  to  $0.45$  V (vs  $\text{Fc}/\text{Fc}^+$ ); the  $E_{\text{onset}}$  values decreased with increasing number of thiophene rings. The highest occupied molecular orbital (HOMO) energy levels of the polymers were estimated from the  $E_{\text{onset}}$  values and were found to be approximately  $-5.35$  to  $-5.25$  eV.<sup>78</sup> Thus, the oligothiophene-stacked polymers can be potentially applied in electronic devices such as hole-transporting materials.

In summary, we synthesized naphthalene-based oligothiophene-stacked polymers by the Suzuki–Miyaura coupling polymerization. The polymers consist of the stacked oligothiophenes in proximity of  $\sim 3.0$  Å from each other. The contribution of the quinoidal structure of the oligothiophene units involving the thiophene scaffolds in the excited state resulted in relatively high photoluminescence quantum efficiencies. The electrochemical behaviors of the polymers suggest that they can be potentially applied in electronic devices, such as hole-transporting materials and field-effect transistors. Further studies will focus on the control of their higher-ordered structure in the solid state and fabrication of such devices.

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