Synthesis of New Thiophene-Based π-Conjugated Organic Compounds and Polymer

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p-Dibromobenzenes and *p*-phenylenediboronate with π-conjugated bithiophene and terthiophene arms were synthesized. They showed UV–vis absorption peaks in the range of 376–417 nm. *p*-Phenylenediboronate with bithiophene arms were used for synthesis of a new π-conjugated polymer consisting of isothianaphthene and the *p*-phenylene units with π-conjugated bithiophene side chains.

Thiophene-based π-conjugated organic compounds and polymers are the subject of many papers.[1] They show interesting electronic and optical functionalities. In this paper we report preparation of new thiophene-based π-conjugated organic compounds such as that shown in Chart 1.

The new compounds have central bifunctional *p*-phenylene units with bromines or boronic groups and are thought to serve as starting compounds for various π-conjugated molecules. Synthesis of a π-conjugated polymer starting from organic compounds is also reported. Professor Hotta and his co-workers reported interesting optical properties of co-oligomers of thiophene and *p*-phenylene such as H–Ph$_2$–Th–Ph$_2$–H and H–Ph–Th–Ph–Th–Ph–H (Ph: *p*-phenylene; Th: thiophene-2,5-diyl).[2] H–Th$_n$–Ph–Th$_n$–H compounds[3] and R–Th$_2$–C≡C–Ph–C≡C–Th$_2$–R (R: H or hexyl) compounds[4] have also been attracting interest and their chemical properties and functionalities have been studied.

Reactions of 1,4-dibromo-2,5-diiodobenzene[5] (**1**) with the following boronic derivatives of alkylbithiophene and alkylterthiophene in the presence of [Pd(PPh$_3$)$_4$] (PPh$_3$: triphenylphosphine) catalyst gave the corresponding *p*-dibromobenzene with alkylbithiophene (TDec–Th–Th–: TDec: tetradecyl) and alkylterthiophene (Hex–Th–Th–Th–: Hex: hexyl) arms at the 2,5-positions in moderate yields. Synthetic details of **4** are described in Experimental and those of **1** and **5** are described in Supporting Information.

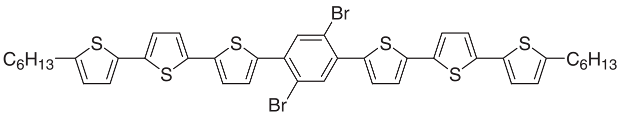
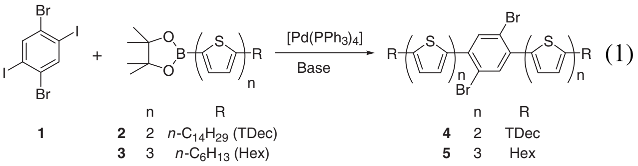
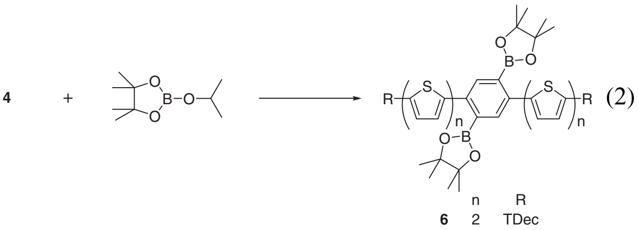


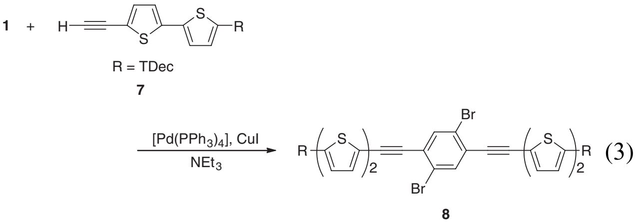
Chart 1.



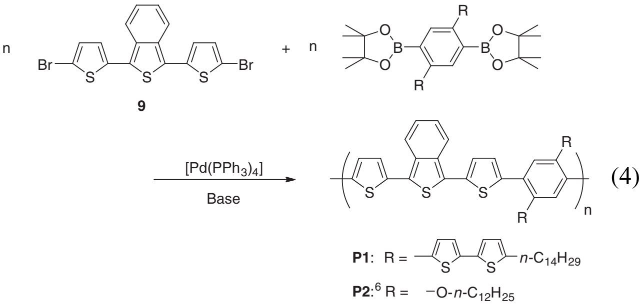
One of the *p*-dibromo compounds, **4**, was further converted into a *p*-diboronate, **6**.



On the other hand, reaction of **1** with an ethynyl-2,2′-bithiophene derivative **7** (cf. Supporting Information) afforded the following new π-conjugated organic compound, **8**.



These compounds, **4**, **5**, **6**, and **8**, are expected to be starting materials of π-conjugated polymers, and the following π-conjugated polymer **P1** was synthesized using **6** and isothianaphthene-containing dibromo compound **9** as monomers for Suzuki-type organometallic polycondensation. We previously reported an analogous polymer **P2** with non-π-conjugated –O–*n*-C$_{12}$H$_{25}$ side chains, instead of the –Th–Th–TDec side chains.[6]



P1 was insoluble in organic solvents at room temperature, similar to **P2**. At elevated temperature (e.g., 130 °C) **P1** (as well as **P2**[6]) was soluble in *o*-dichlorobenzene, and preparation of thin cast films of **P1** was possible; however solubility of **P1** was lower than that of **P2**. Once **P1** was dissolved in *o*-dichlorobenzene at elevated temperatures, cooling the solution to room temperature did not cause apparent precipitation of **P1**, and UV–vis spectra of **P1** in *o*-dichlorobenzene at room temperature was observed. Gel permeation chromatography (GPC) of **P1** using *o*-dichlorobenzene at 135 °C was not possible, presumably due to partial aggregation of the polymer even at that temperature. π-Conjugated polymers with π-conjugated side chains such as *p*-phenylene side chains and

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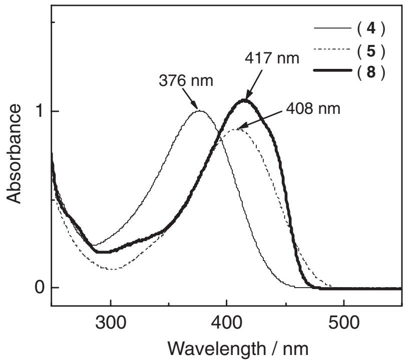

Figure 1. UV–vis spectra of (a) **4**, (b) **5**, and (c) **8** in chloroform.

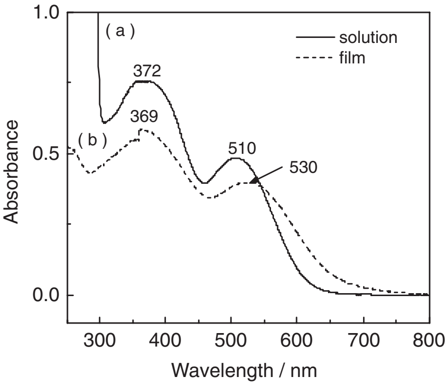

Figure 2. UV–vis spectra of **P1** in (a) *o*-dichlorobenzene (solid line) and (b) cast film (dashed line).

acetylenic side chains have attracted interest of polymer chemists, and papers have been published about such polymers.[7]

Figure 1 shows UV–vis spectra of **4**, **5**, and **8**. **5** reasonably shows the UV–vis peak ($\lambda_{\mathrm{max}} = 408\,\mathrm{nm}$) at a longer wavelength than **4** ($\lambda_{\mathrm{max}} = 376\,\mathrm{nm}$). The UV–vis peak of **4** appears at a shorter wavelength, compared with that of the corresponding H–Th$_2$–Ph–Th$_2$–H ($\lambda_{\mathrm{max}} =$ ca. $440\,\mathrm{nm}^{3a}$), presumably because of twisting of the main chain due to the presence of steric repulsion between Br at the *p*-phenylene ring and H of the thiophene ring. **5** in $CHCl_3$ shows a photoluminescence (PL) peak (λ_{EM}) at 506 nm with a shoulder peak at 535 nm and a quantum yield of 27% when irradiated with 412 nm light. On the other hand, **8** shows the UV–vis peak ($\lambda_{\mathrm{max}} = 417\,\mathrm{nm}$) at a somewhat longer wavelength than the corresponding diethynyl compound R–Th$_2$–C≡C–Ph–C≡C–Th$_2$–R (R: H ($\lambda_{\mathrm{max}} =$ ca. 390 nm) or hexyl ($\lambda_{\mathrm{max}} =$ ca. 400 nm)).[4] In the case of **8**, there seems to be no steric repulsion caused by the Br substituents, and the bathochromic shift of the UV–vis peak of **8** from that of R–Th$_2$–C≡C–Ph–C≡C–Th$_2$–R suggests some contribution of Br to π-electronic states of R–Th$_2$–C≡C–Ph–C≡C–Th$_2$–R. **8** in $CHCl_3$ shows a PL peak at $\lambda_{\mathrm{EM}} = 469\,\mathrm{nm}$ with a shoulder peak at 493 nm and a quantum yield of 30%.

Figure 2 shows UV–vis spectra of **P1** in *o*-dichlorobenzene and cast film (vide ante). The UV–vis peak of **P1** in *o*-dichlorobenzene at 510 nm shows a shift to a longer wavelength from that of **4** (376 nm; cf. Figure 1) because of the expansion of the π-conjugation length along the polymer main chain, however, it appears at a shorter wavelength than that of **P2** ($\lambda_{\mathrm{max}} =$ ca. 580 nm) presumably due to twisting of the polymer main chain caused by the bulkier side chains. In a cast film, the UV–vis peak of **P1** shifts to a longer wavelength. Such a shift to a longer wavelength by changing from solution to solid is often observed for π-conjugated polymers when they assemble in the solid phase;[8] electronic interaction between π-conjugated polymers is thought to bring about such a shift to a longer wavelength and X-ray diffraction data of **P1** (Figure S1 in Supporting Information) suggest an ordered structure of **P1** in the solid state. **P1** in $CHCl_3$ shows a PL peak at $\lambda_{\mathrm{EM}} = 643\,\mathrm{nm}$ with a quantum yield of 7.4%. λ_{EM} essentially agrees with the onset position of the UV–vis absorption band of **P1**.

As described above new π-conjugated oligomers with bifunctional central *p*-phenylene and oligothiophene or ethynyl-2,2′-bithiophene arms have been prepared. These compounds are considered to serve as starting materials for functional compounds including π-conjugated polymers.

Experimental

Materials and Measurements. The dibromo monomer **9** (cf., eq 4) was prepared according to the literature.[9] ^{1}H NMR and UV–vis spectra were recorded on a JEOL JNM-EX300 and Shimadzu UV-3100PC spectrometers, respectively.

Synthesis of *p*-Dibromobenzene with Bithiophene Arms 4. To a dry THF (90 mL) solution of 2,2′-bithiophene (50 g, 30 mmol), BuLi (2.6 M, 12 mL) was added at −78 °C. After stirring for 1 h, the reaction mixture was warmed to 0 °C and stirred for 30 min. The reaction mixture was cooled to −78 °C, and 1-bromotetradecence (8.59 g, 31 mmol) was added. After the mixture was stirred for 15 h at room temperature (r.t.), it was poured into an excess amount of water, and the product was extracted with diethyl ether (Et_2O) and dried over $MgSO_4$. After removal of Et_2O by evaporation, the product was dissolved in THF and reprecipitated in methanol to obtain 6.3 g (58% yield) of 5-tetradecyl-2,2′-bithiophene (TDec–Th–Th–H). The product was confirmed by ^{1}H NMR spectroscopy and used for the next reaction. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.16 (d, $J = 4.2$ Hz, 1H), 7.09 (d, $J = 3.5$ Hz, 1H), 6.98 (m, 2H), 6.68 (d, $J = 3.5$ Hz, 1H), 2.79 (t, $J = 7.5$ Hz, 2H), 1.64 (m, 2H), 1.25 (m, 22H), 0.88 (t, $J = 6.9$ Hz, 3H).

A dry THF (30 mL) solution of NBS (2.06 g, 11.6 mmol) was added to a dry THF (70 mL) solution of TDec–Th–Th–H (4.2 g, 11.6 mmol) at 0 °C, and the mixture was stirred for 1 h at that temperature and for 6 h at r.t. The mixture was poured to an excess amount of water and extracted with CH_2Cl_2. After drying over $MgSO_4$, CH_2Cl_2 was removed by evaporation, and the product was recrystallized from ethanol to obtain a light blue solid of 5-bromo-5′-tetradecyl-2,2′-bithiophene (TDec–Th–Th–Br). The product was confirmed by ^{1}H NMR spectroscopy and used for the next reaction. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.94 (d, $J = 3.6$ Hz, 1H), 6.91 (d, $J = 3.8$ Hz, 1H), 6.83 (d, $J = 3.8$ Hz, 1H), 6.66 (d, $J = 3.6$ Hz, 1H), 2.77 (t, $J = 7.5$ Hz, 2H), 1.68 (m, 2H), 1.25 (m, 22H), 0.88 (t, $J = 6.9$ Hz, 3H).

To a dry THF (100 mL) solution of TDec–Th–Th–Br, BuLi (2.6 M, 3.7 mL, 9.6 mmol) was added at −78 °C. After stirring for 1 h, the reaction mixture was warmed to 0 °C and stirred for

30 min. The reaction mixture was cooled to $-78\,°C$, and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.9 mL, 9.2 mmol) was added. After stirring for 12 h at r.t., the mixture was poured into an excess amount of water, and the product was extracted with Et_2O. After drying over $MgSO_4$, Et_2O was removed by evaporation, and the product was recrystallized from ethanol to obtain 3.8 g (84%) of 2-(5′-tetradecyl-2,2′-bithiophene-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2**, TDec–Th–Th–B(OR′)$_2$). The product was confirmed by ^{1}H NMR spectroscopy and used for the next reaction. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50 (d, $J = 3.6$ Hz, 1H), 7.15 (d, $J = 3.6$ Hz, 1H), 7.04 (d, $J = 3.6$ Hz, 1H), 6.68 (d, $J = 3.6$ Hz, 1H), 2.79 (t, $J = 7.5$ Hz, 2H), 1.68 (m, 2H), 1.45–1.20 (m, 34H), 0.88 (t, $J = 6.9$ Hz, 3H).

1,4-Dibromo-2,5-diiodobenzene (**1**, 0.48 g, 1.0 mmol) and **2** (1.07 g, 2.0 mmol) were dissolved in 50 mL of dimethoxyethane. After bubbling with N_2, [Pd(PPh$_3$)$_4$] (tetrakis(triphenylphosphine)palladium, 0.12 g, 0.10 mmol) and an aqueous solution of Na_2CO_3 (1 M, 5 mL) were added. After stirring for 2 days at 85 °C, the mixture was poured into an excess amount of water, and the precipitate was collected by filtration. After washing with methanol and ethanol twice, respectively, the product was recrystallized from a 1:2 mixture of $CHCl_3$ and hexane to obtain a yellow solid of **4** (0.39 g, 41%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85 (s, 2H), 7.32 (d, $J = 3.8$ Hz, 2H), 7.13 (d, $J = 3.8$ Hz, 2H), 7.07 (d, $J = 3.8$ Hz, 2H), 6.73 (d, $J = 3.8$ Hz, 2H), 2.81 (t, $J = 7.5$ Hz, 4H), 1.69 (m, 4H), 1.45–1.20 (m, 44H), 0.88 (t, $J = 6.9$ Hz, 6H). Anal. Calcd for $C_{50}H_{68}Br_2S_4$: C, 62.74; H, 7.16; Br, 16.70; S, 13.40%. Found: C, 63.06; H, 6.86; Br, 16.95; S, 13.57%.

Synthesis of 6. To a dry THF (10 mL) solution of **4** (100 mg, 0.10 mmol) BuLi (2.6 M, 0.10 mL, 0.26 mmol) was added at $-78\,°C$. After stirring for 1 h, the reaction mixture was warmed to 0 °C and stirred for 30 min. The reaction mixture was cooled to $-78\,°C$, and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.07 mL, 0.35 mmol) was added. After the mixture was warmed to 0 °C and stirred for 12 h, it was poured into an excess amount of water, and the product was extracted with $CHCl_3$. After drying over $MgSO_4$, $CHCl_3$ was removed by evaporation, and the product was recrystallized from hexane to yield 50 mg (48% yield) of yellow **6**. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.73 (s, 2H), 7.08 (d, $J = 3.6$ Hz, 2H), 7.04 (d, $J = 3.8$ Hz, 2H), 7.01 (d, $J = 3.8$ Hz, 2H), 6.72 (d, $J = 3.0$ Hz, 2H), 2.81 (t, $J = 7.5$ Hz, 4H), 1.69 (m, 4H), 1.45–1.20 (m, 68H), 0.88 (t, $J = 6.9$ Hz, 6H). Anal. Calcd for $C_{62}H_{92}B_2O_4S_4$: C, 70.83; H, 8.82; S, 12.20%. Found: C, 70.59; H, 9.00; S, 11.95%.

Synthesis of 8. A mixture of **1** (330 mg, 0.68 mmol), **7** (580 mg, 1.49 mmol), [Pd(PPh$_3$)$_4$] (80 mg, 0.07 mmol), and CuI (13 mg, 0.07 mmol) in dry THF (24 mL) and NEt_3 (12 mL) was stirred at 45 °C. After 15 h the reaction mixture was poured into an excess amount of water, and the solid was separated by filtration. The solid was dissolved in $CHCl_3$ and reprecipitated in ethanol. Recrystallization from a 1:2 mixture of hexane and $CHCl_3$ gave yellow **8** (0.47 g, 67% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.73 (s, 2H), 7.23 (d, $J = 3.6$ Hz, 2H), 7.02 (d, $J = 3.8$ Hz, 2H), 7.00 (d, $J = 3.8$ Hz, 2H), 6.70 (d, $J = 3.6$ Hz, 2H), 2.80 (t, $J = 7.5$ Hz, 4H), 1.67 (m, 4H), 1.25 (m, 44H), 0.88 (t, $J = 6.9$ Hz, 6H). Anal. Calcd for $C_{54}H_{68}Br_2S_4$: C, 64.52; H, 6.82; S, 12.76%. Found: C, 64.84; H, 6.47; S, 12.45%.

Synthesis of P1. Monomers **6** (43 mg, 0.04 mmol) and **9** (18 mg, 0.04 mmol) were dissolved in 5 mL of toluene, and N_2 was bubbled for 10 min. After addition of [Pd(PPh$_3$)$_4$] (8 mg, 7 µmol) and an aqueous solution of Ba(OH)$_2$ (0.3 M, 1 mL, 0.3 mmol), the mixture was stirred for 2 days at 95 °C. The reaction mixture was poured into 200 mL of methanol, and the suspension was stirred for 1 h at room temperature. The precipitate was separated by filtration, and washed with water and methanol. The polymer was dissolved in *o*-dichlorobenzene and reprecipitated in methanol. After drying under vacuum, **P1** was obtained as a black powder (40 mg, 89% yield). Anal. Calcd for $(C_{66}H_{76}S_7)_n$: C, 72.47; H, 7.00; S, 20.52%. Found: C, 69.23; H, 6.45; S, 20.11%. The discrepancy between the calculated and found values may partly be due to high thermal stability of the polymer.

Supporting Information

Synthetic data of **1**, **5**, and **7** and powder XRD pattern of **P1**. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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