

ORIGINAL ARTICLE

Synthesis of silicon- or carbon-bridged polythiophenes and application to organic thin-film transistors

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Silicon- and carbon-bridged polythiophenes, dithienosilole (DTS) and cyclopentadithiophene (DTC) homopolymers with 2-ethylhexyl or *n*-octyl substituents on the bridging atom, were synthesized and their optical and electrochemical properties were investigated. The polymers were black solids and their ultraviolet–visible (UV–vis) spectra showed broad absorption bands in the visible region. The absorption bands were shifted to the low energy region when the spectra were measured as films, indicating the interchain interaction of the polymers in the films. The DTS homopolymer with *n*-octyl groups (pDTS2) showed the most red-shifted absorption maxima among the present polymers, likely because of its high molecular weight ($M_n = 70\,000$). The HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) levels of the present polymers were estimated experimentally on the basis of anodic onset potentials derived from cyclic voltammometric studies and optical band gaps, and these agreed with those obtained by density functional theory calculations of the polymer models. Organic field-effect transistor (OFET) devices containing the present polymer films as the active layers were fabricated to investigate their carrier transport properties. The device based on pDTS2 showed the highest carrier mobility of $1.8 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, nearly the same as that of the previously reported germanium analog, poly(dithienogermole), that had the same substituents on the germanium atom.

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INTRODUCTION

Polythiophenes have been studied as functional materials in electronic devices, including organic field-effect transistors (OFETs), organic light-emitting diodes and organic photovoltaics.^{1–4} Of the known polythiophenes, regio-regular poly(3-hexylthiophene-2,5-diyl) (P3HT in Scheme 1) is of particular importance. The high planarity of its polymer backbone leads to the extended π -conjugation and enhances the interchain interaction in the solid state. In addition, the high solubility of P3HT provides excellent processability, making it suitable for use in organic electronic devices.^{1,3}

On the other hand, heteroatom-bridged 2,2'-bithiophene derivatives, such as dithienophosphole,⁵ -borole⁶ and -pyrrole,⁷ have been extensively studied as building units of conjugated oligomers and polymers. In these systems, the bithiophene unit is fixed to be highly planar by the bridge to enhance the conjugation. In addition, the bridging element often exhibits interesting electronic effects on the bithiophene electronic state. Previously, we introduced silicon- and germanium-bridged bithiophenes (dithienosilole (DTS) and dithienogermole (DTG) in Scheme 1),^{8,9} in which the bonding interaction between Si or Ge σ^* and bithiophene π^* -orbital ($\sigma^*-\pi^*$ conjugation) stabilizes LUMO (lowest unoccupied molecular orbital), whereas

HOMO (highest occupied molecular orbital) is also lowered, although only slightly. As a result, DTS and DTG show smaller HOMO–LUMO energy gaps than their carbon analog (cyclopentadithiophene (DTC) in Scheme 1). Based on these electronic characteristics, DTS and DTG have been used as building units of functional π -conjugated polymers. In particular, the use of donor–acceptor polymers with DTS and DTG as the donor, as the active layer of bulk heterojunction polymer solar cells and OFETs, has been explored.^{9–12} DTS homopolymers were also studied independently by our group¹³ and Marks and colleagues¹⁴ (Scheme 1), and were found to have a more expanded conjugation ($\lambda_{\text{max}} = 533 \text{ nm}$ for pDTS3 in Scheme 1) than P3HT ($\lambda_{\text{max}} = 458 \text{ nm}$).¹⁴ Recently, we prepared DTG homopolymers for the first time and applied them to bulk heterojunction polymer solar cells and OFETs (pDTG1 and pDTG2, Scheme 1).¹⁵ OFET devices made of the DTG homopolymers showed clear p-type transistor response. This contrasted the previous finding that pDTS3 ($R = n$ -hexyl) exhibited no transistor response in spite of its extended conjugation.¹⁴ It seemed that the nature of the bridging elements affected the semiconducting properties of the films, although it was also likely due to the lower molecular weight of pDTS3 ($M_n = 9000$) than that of pDTG2 ($M_n = 79\,000$) and the shorter side chains of the bridging silicon.

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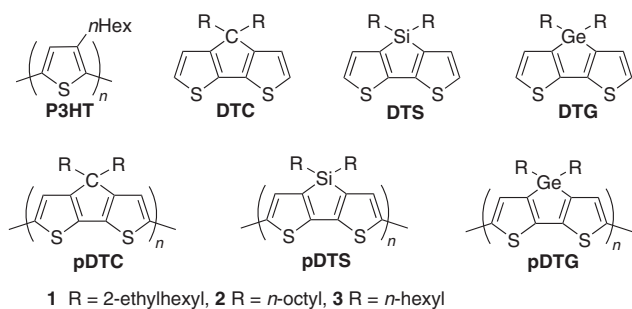
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Scheme 1 Structures of polythiophene derivatives (P3HT, pDTC, pDTS and pDTG) and heteroatom-bridged 2,2'-bithiophene derivatives (cyclopentadithiophene (DTC), dithienosilole (DTS) and dithienogermole (DTG)).

In the present study, we prepared new DTS homopolymers with the same alkyl chains (**pDTS1** and **pDTS2** in Scheme 1) as and similar molecular weights to those of DTG homopolymers to enable direct comparison of DTS and DTG polymers. We also prepared a DTC homopolymer with *n*-octyl groups for comparison (**pDTC2** in Scheme 1).

EXPERIMENTAL PROCEDURE

General

All reactions were carried out in dry argon. Chlorobenzene (purity 99.5%), toluene (99.0%) and ether (99%) that were used as the reaction solvents were purchased from Kanto Chemical Co. Inc. (Tokyo, Japan) and Wako Pure Chemical Industries, Ltd (Osaka, Japan), respectively. They were distilled from calcium hydride and stored over activated molecular sieves until use. Starting compounds 2,6-dibromo-4,4-bis(2-ethylhexyl)dithienosilole (**DTS1Br2**),¹⁰ 2,6-dibromo-4,4-dioctyldithienosilole (**DTS2Br2**),¹⁶ 4,4-dioctyl-2,6-bis(trimethylstannyl)dithienosilole (**DTS2Sn2**),¹⁷ and 2,6-dibromo-4,4-dioctyl-4*H*-cyclopenta[1,2-*b*:5,4-*b'*]dithiophene (**DTCBr2**)^{18,19} were prepared as reported in the literature. To remove palladium species, the filtered reaction mixtures were heated with a solution of sodium *N,N*-diethylthiocarbamate trihydride (3.1 g, Kanto Chemical Co. Inc., purity 92%) in 30 ml of water at 80 °C with stirring for 2 h. Then, the organic layer was separated and washed in the following order: with water, 3% acetic acid aqueous solution and water again. The organic layer was dried over anhydrous magnesium sulfate and the solvent was removed under vacuum. Nuclear magnetic resonance (NMR) spectra were recorded on Varian 400-MR and System-500 spectrometers (Agilent Inc., Santa Clara, CA, USA). Atmospheric pressure chemical ionization (APCI) mass spectra were measured on a Thermo Fisher Scientific LTQ (Waltham, MA, USA) Orbitrap XL spectrometer at the Natural Science Center for Basic Research and Development (N-BARD) Hiroshima University (Higashi-Hiroshima, Japan), and electron ionization mass spectra were recorded on a Shimadzu QP-2020 A spectrometer (Shimadzu Co., Kyoto, Japan). Ultraviolet–visible (UV–vis) absorption and photoluminescence (PL) spectra were measured on Hitachi U-3210 and Hitachi F-4500 spectrophotometers, (Hitachi, Ltd., Tokyo, Japan) respectively. Polymer molecular weights were determined by gel permeation chromatography (GPC) using serially connected Shodex (Showa Denko K.K., Tokyo, Japan) KF2001 and KF2002 columns and tetrahydrofuran (THF) as the eluent. OFET devices using the present polymers were fabricated as reported in the literature.²⁰

Preparation of 6-bromo-4,4-bis(2-ethylhexyl)-2-(trimethylstannyl)dithienosilole (DTS1BrSn). To a solution of **DTS1Br2** (1.788 g, 3.101 mmol) in 35 ml of ether was added *n*-butyllithium solution (1.9 ml, 1.64 M in hexane, Kanto Chemical Co. Inc.) slowly at –80 °C. After stirring the mixture at this temperature for 30 min, trimethyltin chloride (0.718 g, 3.601 mmol, Tokyo Chemical Industry Co., Ltd (Tokyo, Japan), purity >98%) was added and the mixture was allowed to warm to room temperature. The mixture was poured into ice water, and the organic layer was separated and dried over anhydrous magnesium sulfate. After the solvent was evaporated, the residue was purified by preparative GPC with toluene as eluent to give 1.346 g of a diastereomeric

mixture of **DTS1BrSn** as a yellow viscous oil (66% yield); ¹H NMR (δ in CDCl₃, 500 MHz) 0.37 (s, 9H), 0.77 (t, *J* = 7.0 Hz, 6H), 0.79–0.86 (m, 6H), 0.86–0.97 (m, 4H), 1.08–1.30 (m, 16H), 1.36–1.42 (m, 2H), 6.97 (s, 1H), 7.07 (s, 1H); ¹³C NMR (δ in CDCl₃, 125 MHz) –8.18, 10.80, 14.15, 17.50, 17.54, 17.62, 17.65, 22.94, 22.99, 28.76, 28.85, 28.87, 28.89, 35.52, 35.57, 35.77, 35.85, 110.37, 110.39, 110.41, 132.37, 132.39, 132.40, 137.65, 137.68, 137.70, 138.37, 138.39, 138.40, 142.43, 142.57, 142.73, 143.05, 143.09, 143.14, 149.45, 149.50, 153.93, 153.94 (coupling with Sn is included); high-resolution mass spectrometry (APCI) Calcd: [M⁺] 660.09318. Found: 660.09192.

Preparation of 6-bromo-4,4-dioctyl-2-trimethylstannyl-4*H*-cyclopenta[1,2-*b*:5,4-*b'*]dithiophene (DTC2BrSn). To a solution of **DTC2Br2** (0.561 g, 1.001 mmol) in 12 ml of ether was added *n*-butyllithium solution (0.65 ml, 1.55 M in hexane) slowly at –80 °C. After stirring the mixture at this temperature for 30 min, trimethyltin chloride (0.219 g, 1.100 mmol) was added and the mixture was allowed to warm to room temperature. The mixture was poured into ice water, and the organic layer was separated and dried over anhydrous magnesium sulfate. After the solvent was evaporated, the residue was purified by preparative GPC using toluene as eluent to give 0.387 g of **DTC2BrSn** as a yellow viscous oil (60% yield); ¹H NMR (δ in CDCl₃, 400 MHz) 0.38 (s, 9H), 0.85 (t, *J* = 7.2 Hz, 6H), 0.93–1.00 (m, 4H), 1.15–1.26 (m, 20H), 1.76 (t, *J* = 8.2 Hz, 4H) 6.92 (s, 1H), 6.93 (s, 1H); ¹³C NMR (δ in CDCl₃, 100 MHz) –8.02, 14.12, 22.66, 24.52, 29.27, 29.31, 29.98, 31.82, 37.52, 53.53, 109.98, 124.85, 129.06, 137.07, 138.28, 141.73, 156.64, 159.59 (coupling with Sn is included); high-resolution mass spectrometry (APCI) Calcd: [M⁺] 644.11625. Found: 644.11523.

Preparation of pDTC2. A mixture of **DTC2BrSn** (0.202 g, 0.313 mmol), tris-(dizenyldieneacetone)dipalladium(0) (Pd₂(dba)₃, 14.3 mg, 0.016 mmol, Tokyo Chemical Industry Co., Ltd, purity >75%), tri(*o*-tolyl)phosphine (P(*o*-tol)₃, 19.1 mg, 0.063 mmol, Wako Pure Chemical Industries, Ltd, >96%) and 10 ml of chlorobenzene was vacuum degassed and heated to reflux for 4 days. The mixture was cooled to room temperature and the resulting precipitates were filtered. After removal of the palladium species as described above, reprecipitation of the residue from chlorobenzene/methanol, chlorobenzene/ethanol and then chlorobenzene/acetone provided 45.1 mg (36.1% yield) of **pDTC2** as black solids: m.p. >300 °C; ¹H NMR (δ in C₆D₅Cl, 400 MHz) 0.86 (t, *J* = 7.2 Hz, 6H, octyl), 1.09–1.21 (br m, 24H, octyl), 1.94 (br s, 4H, octyl), 7.25 (br s, 2H, thiophene); ¹³C NMR (δ in C₆D₅Cl, 100 MHz) 14.34, 23.01, 24.99, 29.73, 30.46, 32.16, 54.52 (sp² carbons could not be observed because of low solubility); GPC *M*_n = 12 000, *M*_w = 28 000, *M*_w/*M*_n = 2.3; UV–vis abs λ_{max} = 592 nm (in C₆H₅Cl).

Preparation of pDTS1. A mixture of **DTS1BrSn** (0.658 g, 0.996 mmol), Pd₂(dba)₃ (18.2 mg, 0.020 mmol), P(*o*-tol)₃ (30.2 mg, 0.099 mmol), CuO (79.2 mg, 0.997 mmol, Wako Pure Chemical Industries, Ltd, purity 99.9%) and 20 ml of chlorobenzene was vacuum degassed and heated to reflux for 5 days. The mixture was cooled to room temperature and the resulting precipitates were filtered. After removal of the palladium species as described above, reprecipitation of the residue from chlorobenzene/methanol gave polymeric substances that were then placed in a Soxhlet apparatus and washed with hot methanol, ethyl acetate and hexane. Finally, the residue that remained insoluble in those hot solvents was extracted with hot benzene. The benzene solution was poured into ethyl acetate and the resulting precipitates were collected to give **pDTS1** (0.337 g, 81%) as black solids: m.p. >300 °C; ¹H NMR (δ in CDCl₃, 500 MHz) 0.78–0.89 (m, 12H, 2-ethylhexyl), 0.94–1.05 (br m, 4H, 2-ethylhexyl), 1.13–1.35 (m, 16H, 2-ethylhexyl), 1.43–1.51 (br m, 2H, 2-ethylhexyl), 7.10 (br s, 2H, thiophene); ¹³C NMR (δ in CDCl₃, 125 MHz) 10.82, 14.19, 17.61, 23.02, 28.88, 28.92, 35.63, 35.92 (sp² carbon signals could not be observed because of low polymer solubility); GPC *M*_n = 42 000, *M*_w = 76 000, *M*_w/*M*_n = 1.8; UV–vis abs λ_{max} = 569, 597 nm (in C₆H₅Cl).

Preparation of pDTS2. A mixture of **DTS2Sn2** (0.651 g, 0.875 mmol), **DTS2Br2** (0.504 g, 0.874 mmol), Pd₂(dba)₃ (16.0 mg, 0.017 mmol), P(*o*-tol)₃ (26.0 mg, 0.085 mmol), CuO (69.6 mg, 0.875 mmol) and 20 ml of chlorobenzene was vacuum degassed and heated to reflux for 5 days. The mixture was cooled to room temperature and the resulting precipitates were filtered. After removal of the palladium species as described above, reprecipitation of the

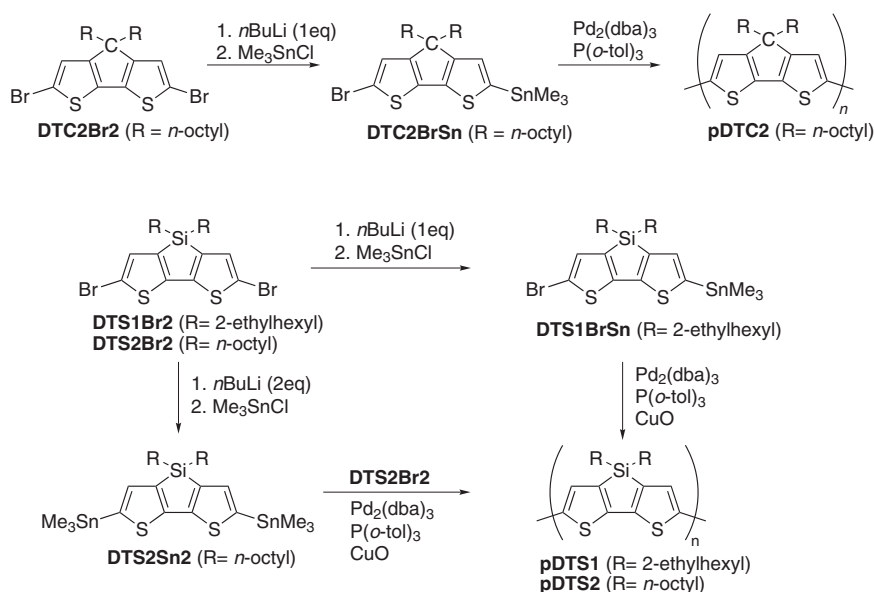
residue from chlorobenzene/methanol gave polymeric substances that were then placed in a Soxhlet apparatus and washed with hot methanol, ethyl acetate and hexane. Finally, the residue that remained insoluble in those hot solvents was extracted with hot benzene. The benzene solution was poured into hexane/benzene (3:2) and the resulting precipitates were collected to give **pDTS2** (0.483 g, 66%) as black solids: m.p. > 300 °C; ¹H NMR (δ in C₆D₄Cl₂, 500 MHz) 0.86 (t, *J* = 5.0 Hz, 6H), 1.09–1.25 (br m, 24H), 1.52 (br s, 4H), 7.35 (br s, 2H); ¹³C NMR (δ in C₆D₄Cl₂, 125 MHz) 14.35, 23.02, 24.56, 29.50, 29.66, 32.17 (sp² carbon signals could not be observed because of low polymer solubility); GPC *M_n* = 70 000, *M_w* = 175 000, *M_w*/*M_n* = 2.5; UV-vis abs λ_{max} = 603 nm (in C₆H₄Cl₂).

RESULTS AND DISCUSSION

Polymer synthesis

Poly(dithienosilole-2,6-diyl)s **pDTS1** and **pDTS2**, which have branched and linear solubilizing alkyl groups on the silicon atoms,

respectively, were prepared, as shown in Scheme 2, similarly to what was previously reported for **pDTG1** and **pDTG2**. The progress of polymerization was monitored by GPC and the reaction was quenched when the molecular weights no longer increased. All the polymers were obtained as black solids. Stille homocoupling of **DTS1BrSn** that was prepared by monolithiation of dibromide **DTS1Br2** followed by stannylation of the resulting bromolithiodithienosilole with trimethyltin chloride in refluxing chlorobenzene using Pd₂(dba)₃/P(*o*-tol)₃/CuO as the catalyst (Scheme 2) gave **pDTS1**. On the contrary, selective monolithiation of **DTS2Br2** failed, similar to the DTG analog. Attempted monolithiation of **DTS2Br2**/**DTG2Br2** always proceeded nonselectively to give mixtures of mono- and dilithiated compounds and the starting **DTS2Br2**/**DTG2Br2**. Therefore, **pDTS2** was obtained by the cross-coupling reaction of **DTS2Sn2** and **DTS2Br2**. For **pDTG1** and **pDTG2**, fractional extraction using a Soxhlet apparatus provided



Scheme 2 Synthesis of dithienosilole (DTS) and cyclopentadithiophene (DTC) polymers.

Table 1 Properties of present and reported polymers

Polymer	Yield/%	<i>M_n</i> (<i>M_w</i> / <i>M_n</i>) ^a	<i>UV-vis abs. λ_{max}/nm</i>		<i>λ_{em}</i> /nm ^b	<i>T_d</i> ^{5c} /°C	HOMO ^d /eV	LUMO ^e /eV
			Solution	Film				
pDTC2	36	12 000 (2.3)	592 ^f	597	663 ^f	400	−4.9	−3.1
pDTS1	81	42 000 (1.8)	569, 597 ^f	597	649 ^f	414	−5.0	−3.0
pDTS2	66	70 000 (2.5)	603 ^g	613	646 ^g	358	−4.9	−3.2
pDTS2L	48 ^h	47 000 (1.4)	598 ^g	602	644 ^g		−4.9	−3.1
pDTG1Hⁱ	55	46 000 (1.6)	568	605	640	390	−5.0	−3.0
pDTG1Lⁱ	41	10 000 (2.5)	563	598	637	391	−5.0	−3.0
pDTG2Hⁱ	39	79 000 (2.7)	610	614, 658	641	386	−4.8	−2.9
pDTG2Lⁱ	24	33 000 (2.9)	609	616, 657	643	400	−4.8	−2.9
pDTS3^j	66	9000 (2.9)	533	535	601	250	−5.6	−3.8

Abbreviations: abs., absorption; HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital; UV-vis, ultraviolet-visible.

^aDetermined by gel permeation chromatography (GPC) relative to polystyrene standards.

^bExcited at the absorption maximum.

^cBy thermogravimetric analysis (TGA) in nitrogen at 10 °C per min.

^dBased on cyclic voltammogram (CV) oxidation onset of the polymer cast film.

^eEstimated from HOMO energy level and optical band gap.

^fIn chlorobenzene.

^gIn *o*-dichlorobenzene.

^hSeparated from **pDTS2** as a fraction soluble in *o*-dichlorobenzene at 40 °C. Yield is based on the starting monomers.

ⁱSee Ohshita *et al.*¹⁵

^jSee Lu *et al.*¹⁴

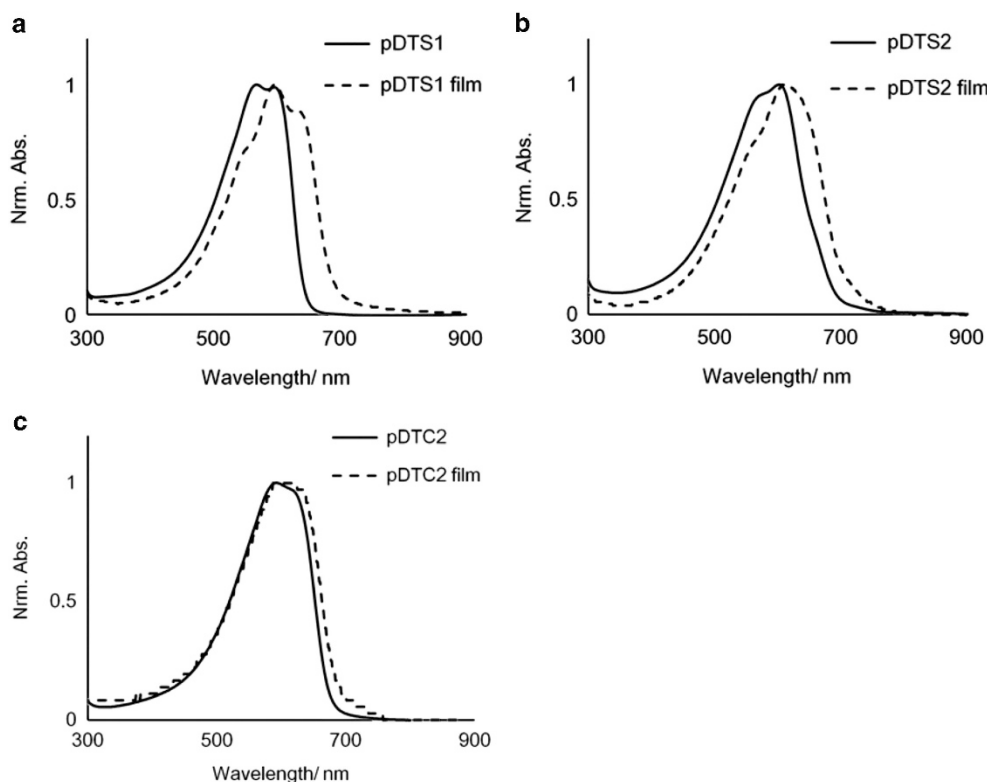


Figure 1 Ultraviolet-visible (UV-vis) absorption spectra of (a) **pDTS1** in chlorobenzene, (b) **pDTS2** in *o*-dichlorobenzene, and (c) **pDTC2** in chlorobenzene (solid line), and those as films (dashed line).

higher and lower molecular weight fractions, **pDTG1H** and **pDTG1L**, and **pDTS1** and **pDTS2**, respectively, as summarized in Table 1.¹⁵ However, similar Soxhlet extraction separated only small amounts of low molecular weight fractions of **pDTS1** and **pDTS2**. It was found that the introduction of branched 2-ethylhexyl substituents in place of *n*-octyl groups tended to decrease the molecular weights for both the DTS- and DTG-containing polymers. This is likely because the large 2-ethylhexyl substituents cover the reactive center of DTS and DTG to suppress the reactivity.

For **pDTC2**, monolithiation of **DTC2Br2** followed by treatment of the resulting monolithiated DTC with trimethyltin chloride gave bromo(trimethylstannyl)cyclopentadithiophene **DTC2BrSn** cleanly, and this was polymerized by a similar palladium-catalyzed Stille coupling reaction in chlorobenzene using $\text{Pd}_2(\text{dba})_3/\text{P}(o\text{-tol})_3$ as the catalyst (Scheme 2). The behavior of **DTC2Br2** was different from that of DTS and DTG derivatives with *n*-octyl groups (**DTS2Br2**, **DTG2Br2**) whose monolithiation did not proceed selectively as mentioned above.

The solubility of the present polymers was dependent on their molecular weights and alkyl chains. **pDTS2** bearing *n*-octyl groups with high molecular weight showed low solubility. It was slightly soluble in *o*-dichlorobenzene and nearly insoluble in chloroform, toluene, acetone, hexane, ethyl acetate and ethanol at room temperature, but soluble in hot *o*-dichlorobenzene. **pDTS1** with 2-ethylhexyl groups showed higher solubility than **pDTS2**, presumably because of its molecular weight being lower than that of **pDTS2** and the branched 2-ethylhexyl chains on the silicon atom. The branched 2-ethylhexyl groups hindered the interchain interaction of the polymers to improve the solubility. **pDTS1** was moderately soluble in *o*-dichlorobenzene, chlorobenzene, THF and toluene, but insoluble in acetone, hexane, ethyl acetate and ethanol. **pDTC2** showed even higher solubility; it was

soluble in ethyl acetate, hexane, THF, toluene, chlorobenzene and *o*-dichlorobenzene, but not in ethanol. This was also likely because of its molecular weight being lower than that of **pDTS2**.

These polymers were characterized mainly by NMR analysis (for the ¹H NMR spectra, see Supplementary Figures S1–S3 in Supplementary Information). The ¹H and ¹³C NMR spectra of the polymers were consistent with those based on the regular structures shown in Scheme 2, although sp² carbon signals could not be clearly observed for the present polymers because of their low solubility. The thermal stability of the present polymers was confirmed by thermogravimetric analysis; the polymers showed 5% weight loss at temperatures (T_d^5) higher than 350 °C in nitrogen, similar to **pDTG1** and **pDTG2** (Table 1).¹⁵ The T_d^5 values were much higher than that reported for **pDTS3**¹⁴ by more than 100 °C, likely reflecting the higher molecular weights.

Optical and electrochemical properties of the present polymers

The UV-vis absorption spectra of polymers **pDTS1**, **pDTS2** and **pDTC2** were measured in chlorobenzene or *o*-dichlorobenzene solution and as spin-coated films (Figure 1). The UV-vis spectra of the present polymers showed red-shifted absorption bands relative to those of regio-regular P3HT (Aldrich Sigma Inc., St Louis, MO, USA, head-to-tail content > 95%, $\lambda_{\text{max}} = 458 \text{ nm}$). This indicates that the introduction of the carbon and silicon bridging units enhances the conjugation of polythiophenes, similar to the previously reported **pDTS3**¹⁴ and DTG polymers.¹⁵ Two broad bands were observed at ~570 and 600 nm when **pDTS1** was measured in solution. The band at shorter wavelength was relatively suppressed and a new peak at ~650 nm appeared when the polymers were measured as films. The new absorption bands in the low energy region reflected the interchain interactions in the aggregated polymer chains in film. The absorption bands in the high energy region were because of the aggregation-free

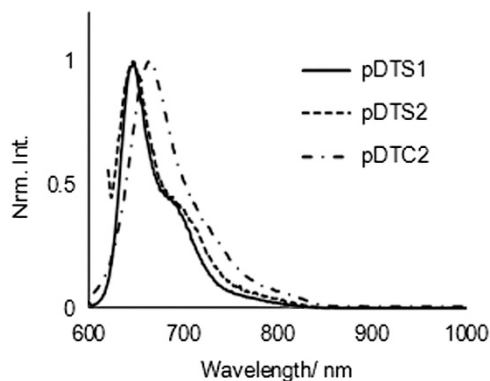


Figure 2 Photoluminescence (PL) spectra of dithienosilole (DTS) and cyclopentadithiophene (DTC) polymers in solution excited at the absorption maxima (**pDTS1** and **pDTC2** in chlorobenzene, and **pDTS2** in *o*-dichlorobenzene).

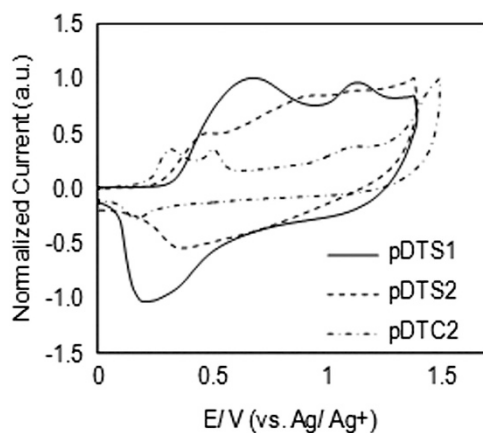


Figure 3 Cyclic voltammograms (CVs) of polymer cast films.

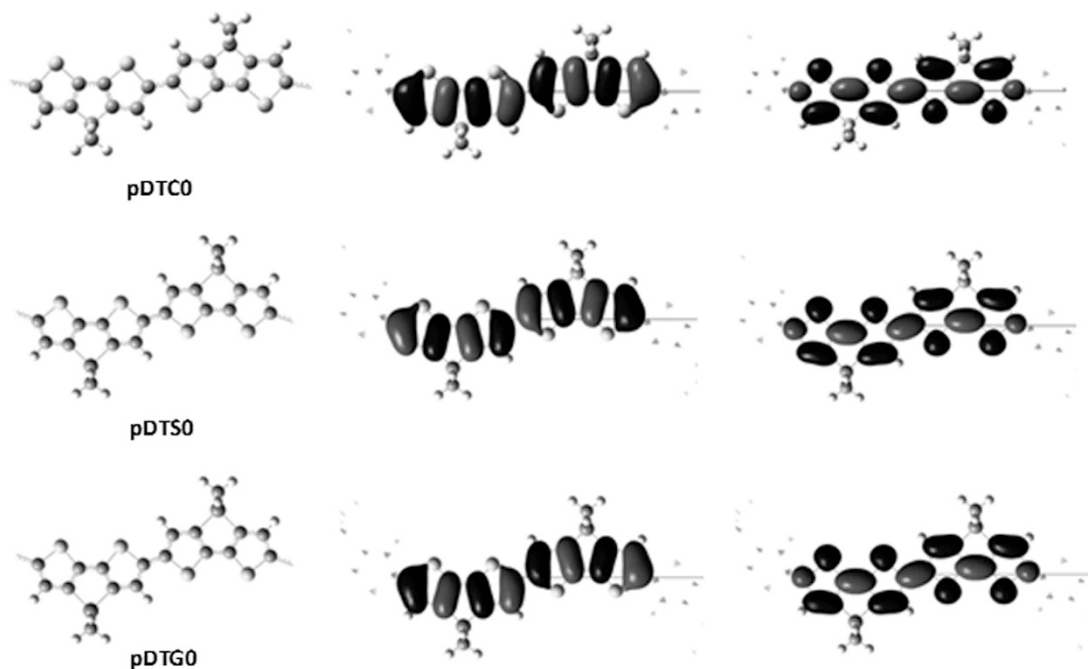


Figure 4 Optimized geometries (left) and HOCO (middle) and LUCO (right) profiles of **pDTC0**, **pDTS0** and **pDTG0**. HOCO, highest occupied crystal orbital; LUCO, lowest unoccupied crystal orbital.

polymer segments. In contrast, the absorption spectrum of **pDTS2** in solution showed a shoulder peak at ~ 670 nm arising from aggregation already in solution that was enhanced when measured as film, indicating that **pDTS2** exhibited stronger interchain interaction than **pDTS1**. The absorption spectra of **pDTC2** showed no significant changes regardless of the state (in solution or film), suggesting the low degree of aggregation in film compared with **pDTS2** and **pDTG2**. The UV absorption maxima of the polymers in solution were shifted to longer wavelengths in the order of **pDTG1L** < **pDTG1H** < **pDTC2** < **pDTS1** < **pDTS2** < **pDTG2L** < **pDTG2H**. Polymer **pDTS2** showed the most red-shifted absorption maximum among the present polymers. The high molecular weight of **pDTS2** compared with those of **pDTS1** and **pDTC2** may be a reason for the red-shift. However, the shifts are rather small as **pDTG1** and **pDTG2** exhibited only small shifts of the absorption maxima depending on the molecular weights.¹⁵ The PL spectra of the polymers are presented in Figure 2: the maxima are at nearly the same wavelengths regardless of substituent for **pDTS1** and **pDTS2**, although **pDTC2** appeared at slightly lower energy. The absolute PL quantum efficiencies were determined by using an integration sphere to be <2%.

Cyclic voltammograms of the polymer cast films containing 10 equiv of tetrabutylammonium perchlorate (TBAP) on platinum electrodes, which were measured in acetonitrile containing 100 mM TBAP as the supporting electrolyte, showed irreversible anodic peaks (Figure 3). The oxidation onset potentials of the present polymer films were similar to those of **pDTG**; however, **pDTG2** with *n*-octyl groups showed relatively higher HOMO and LUMO levels than the present polymers (Table 1).¹⁵ No obvious changes of cyclic voltammogram onset potential depending on the molecular weight were noted.

To know about the effects of molecular weight on the polymer properties, we separated **pDTS2L** from **pDTS2** as a fraction that was soluble in dichlorobenzene at 40 °C. As listed in Table 1, the UV absorption and PL maxima in solutions moved to higher energies by 5 and 2 nm, respectively, from those of **pDTS2** because of the less

Table 2 HOCO and LUCO energy levels and band gaps of model polymers, derived from DFT calculations at B3LYP/6–31G(d)

	HOCO/eV	LUCO/eV	E_g /eV
pDTCO	–4.16	–2.28	1.88
pDTSO	–4.22	–2.39	1.83
pDTGO	–4.20	–2.36	1.84

Abbreviations: DFT, density functional theory; HOCO, highest occupied crystal orbital; LUCO, lowest unoccupied crystal orbital.

extended conjugation. However, these shifts are rather small and effects of the molecular weights do not seem to be significant for pDTS2 and pDTS2L. The UV absorption maximum of the film was also blue-shifted, but to a larger extent (11 nm), indicating that the longer molecular weight led to the better interchain interaction.

When the UV absorption and PL spectra of pDTS1 and pDTS2L with similar molecular weights were compared, no clear tendency of positions of the maxima were seen, indicating that the nature of substituents (linear or branched) exerted no unambiguous influences on the polymer electronic states. However, UV absorption spectrum of pDTS2L in solution still showed a shoulder at ~ 670 nm ascribed to the polymer aggregation, similar to that of pDTS2. This indicates that the stronger interchain interaction of pDTS2 than pDTS1 is not only because of the larger molecular weight but also the liner substituents (*vide supra*). Lack of the evident substituent effects on the polymer conjugation for the present DTS polymers led to a conclusion that the blue-shifted absorption PL bands of pDTS3 from those of pDTS1 and pDTS2 were because of the low molecular weight.

Quantum chemical calculations

To understand the differences in electronic properties among pDTC, pDTS, and pDTG, we carried out crystal orbital (CO) calculations of the polymer models simplified by using methyl groups as the substituents on the bridging atoms (pDTCO, pDTSO and pDTGO) at the level of B3LYP/6–31G(d) on the Gaussian 09 program (Gaussian, Inc., Wallingford, CT, USA). Optimized geometries of the unit cells, and HOCO and LUCO (highest occupied and lowest unoccupied CO) profiles of the polymers are depicted in Figure 4. The optimized geometries have high planarity and interplane angles $< 1^\circ$. The HOCO and LUCO energy levels and the band gaps derived from the calculations are summarized in Table 2. Both HOCO and LUCO of pDTSO and pDTGO were more stable than those of pDTCO. The theoretical band gap of pDTCO was slightly larger than those of pDTSO and pDTGO. These suggested the higher stability of pDTS and pDTG toward atmospheric oxidation than pDTC despite the more extended conjugation, although in real systems, the optical band gap of pDTG2 (1.9 eV) was slightly larger than those of pDTC2 (1.8 eV) and pDTS2 (1.7 eV).

Semiconducting properties

OFETs using pDTS and pDTC films as the active layer were fabricated to investigate polymer semiconducting properties. The devices showed clear p-type transistor response (Supplementary Figures S4–S6 in Supplementary Information) in contrast to pDTS3 that was reported to be transistor inactive.¹⁴ As shown in Table 3, pDTS2 had higher carrier mobility than pDTS1, likely because of the stronger interchain interaction of pDTS2 in the film than that of pDTS1 as indicated by the UV–vis absorption spectra. This was similar to pDTG1 and pDTG2 and it did not seem unusual that the linear substituents enhance the aggregate-forming property of the polymers, likely

Table 3 OFET parameters of DTC, DTS and DTG polymers

Polymer	μ cm ² V ^{–1} s ^{–1}	On/off
pDTC2	1.2×10^{-4}	10
pDTS1 ^a	5.3×10^{-4}	10 ⁵
pDTS2 ^a	1.8×10^{-3}	10 ⁵
pDTS2L ^b	9.8×10^{-4}	10 ⁴
pDTG1H ^c	3.7×10^{-4}	10 ³
pDTG1L ^c	3.1×10^{-5}	10 ²
pDTG2H ^{c,d}	1.9×10^{-3}	10 ⁴
pDTG2L ^{a,c}	1.6×10^{-3}	10 ²

Abbreviations: DTC, cyclopentadithiophene; DTG, dithienogermole; DTS, dithienosilole; OFET, organic field-effect transistor.

^aAnnealed at 140 °C.

^bAnnealed at 60 °C.

^cSee Ohshita *et al.*¹⁵

^dAnnealed at 100 °C.

because of easy interdigitation of the alkyl chains.¹⁵ pDTS2L showed slightly lower mobility than that of pDTS2, likely reflecting both the less enhanced conjugation and interchain interaction because of the lower molecular weight. However, the influence was not significant, as observed for pDTG1H/pDTG2H and pDTG1L/pDTG2L. For polymers with the same *n*-octyl groups, pDTG2 and pDTS2 exhibited higher carrier mobility than pDTC2. It seemed that the strong interchain interaction of pDTG2 and pDTS2 enhanced carrier transport in the polymer film, likely because of the higher flexibility of substituents on the bridging silicon and germanium, arising from longer Si–C and Ge–C bonds and the larger van der Waals interaction of these heavier elements. It was also noted that polymer pDTC2 showed a low on/off ratio compared with the other polymers.

CONCLUSIONS

In summary, we synthesized carbon- and silicon-bridged polythiophenes (pDTC2, pDTS1 and pDTS2). Polymers pDTS1 and pDTS2 had high molecular weights, similar to pDTG1 and pDTG2 reported previously, whereas pDTC2 had a low molecular weight. Attempted preparation of pDTC2 with a higher molecular weight by changing the reaction conditions was unsuccessful. The less flexible side chains of pDTC2, which were because of the shorter distance between the substituent carbon and the bridging element, than that of pDTS resulted in the lower solubility of pDTC2, thus suppressing the polymerization. Interestingly, the present polymers showed similar optical and electrochemical properties to pDTG1 and pDTG2. However, the UV–vis spectra indicated that pDTC2 exhibited less tendency to form polymer aggregates than the other polymers with DTS and DTG units.

All the polymers exhibited p-type transistor properties and pDTS2 had the highest carrier mobility, in contrast to pDTS3 that was previously reported to be nontransistor active.¹⁴ It was also noteworthy that pDTC2 had much lower activity in OFET than the other polymers. It is speculated that the suppressed aggregate-forming property of pDTC2 is responsible for the low carrier mobility. The bridging elements, substituents and the molecular weights affected the aggregate formation, thus being important factors to enhance the transistor activity of the polymers. Although the transistor activities of the DTS and DTG homopolymers are lower than those recently reported for other low-band gap donor–acceptor copolymers with DTG or DTS as the donor,^{21,22} the results from the present work on simple polymers seem to provide the information of how the nature of bridging group 14 elements affects the properties of bridged

polythiophenes, and this would be useful for the molecular design of new functional polythiophene-based materials.

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