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# Synthesis and optical properties of poly(tetramethylsilarylenesiloxane) derivative bearing diphenylcyclopentadithiophene moiety

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#### ABSTRACT

The thermal and optical properties of a novel diphenylcyclopentadithiophene-based poly(tetramethylsilarylenesiloxane) derivative (**P1**), which was prepared via polycondensation of a novel disilanol monomer, i.e., 2,6-bis(dimethylhydroxysilyl)-4,4-diphenylcyclopentadithiophene (**M1**), were investigated. **P1** exhibited good solubility in common organic solvents, such as benzene, toluene, chloroform, dichloromethane and THF at ambient temperature. The glass transition temperature ( $T_g$ ) of **P1** was determined by differential scanning calorimetry to be 109 °C. No melting temperature ( $T_m$ ) of **P1** was observed, indicating the obtained **P1** was an amorphous polymer. The temperature at 5% weight loss ( $T_{d5}$ ) of **P1** was 454 °C, indicating the rather good thermostability of **P1**. Bathochromic and hyperchromic effects were observed in the absorption and fluorescence spectra by introducing dimethylsilyl substituents onto 4,4-diphenylcyclopentadithiophene skeleton. The fluorescence quantum yields ( $\Phi_{FS}$ ) of **M1** and **P1** in chloroform were determined to be 0.36 and 0.39, respectively. It was revealed that **M1** and **P1** exhibited the higher fluorescence intensity than diphenylcyclopentadithiophene as well as dimethylsilyl moieties onto 2- and 6-position of cyclopentadithiophene skeleton.

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## 1. Introduction

Polydimethylsiloxane (PDMS) has been well-known to be one of the typical polymers which exhibit good thermostability based on the high energy of siloxane bonding; however, PDMS has the low glass transition temperature ( $T_g$ : -123 °C) because of the flexible siloxane bonding [1]. On the other hand, poly(tetramethylsilarylenesiloxane) derivatives where aromatic moieties are introduced into the main chain of PDMS have been reported to exhibit the excellent thermostability as well as the high  $T_g$ . For example, the  $T_g$ s of a series of polv(tetramethylsilarylenesiloxane) derivatives have been reported to be in the range from -52 °C to 191 °C depending on the arylene moiety introduced [2–9]. Furthermore, poly(tetramethylsilarylenesiloxane) derivatives have been also reported to show bathochromic and hyperchromic effects in the absorption spectra by the alkylsilyl groups introduced onto aromatic moieties owing to the  $\sigma^* - \pi^*$  interaction between alkylsilyl and aromatic moieties [7–12]. In addition, it has been reported that incorporation of silyl substituents into the

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http://dx.doi.org/10.1016/j.polymer.2014.10.048 0032-3861/© 2014 Elsevier Ltd. All rights reserved. aromatic species results in high fluorescence quantum yield [7–15]. From these points of view, we have reported the synthesis of diphenylfluorene-based poly(tetramethylsilarylenesiloxane) derivative which exhibited the high  $T_g$  as well as the good thermostability and fluorescence property [8]. For example, poly(tetramethyl-9,9-diphenyl-2,7-silfluorenylenesiloxane) (**Pa** as shown in Fig. 1) exhibited the rather high  $T_g$  of 125 °C. In addition, the fluorescence quantum yield of **Pa** in chloroform solution was determined to be 0.19, which was five-fold value of 9,9-diphenylfluorene, indicating the introduction of dimethylsilyl moieties onto 9,9-diphenylfluorene was effective to improve the fluorescence quantum yield.

In the meantime, conjugated polymers [16,17] obtained by polymerization of fused ring derivatives have emerged as attractive materials for flexible, low cost and low power electro-optic devices. Thiophene-based polymers and oligomers, such as dithienothiophene [18] derivatives, exhibit efficient charge transport in organic field-effect transistors (OFETs) [19,20], while polyfluorene is one of representative conjugated polymers suitable for use in optoelectronic and electronic devices such as organic light emitting diode (OLEDs) [21–23]. On the other hand, cyclopenta[2,1-b:3,4-b'] dithiophene (CPDT) [24,25] is regarded as an analogous compound of fluorene where the benzene rings are replaced by thiophene

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rings and composed of a fused bithiophene ring. There have been few reports on the fluorescent properties of CPDT derivatives or conjugated polymers based on CPDT [26,27], while CPDT derivatives have been rigid precursors of polymeric semiconducting materials for the development of organic photovoltaic devices [28-32]. The effect of the introduction of dimethylsilyl moieties onto 2- and 6-position of 4,4-dimethylCPDT skeleton on the optical properties was investigated in our previous report [27], where the introduction of dimethylsilvl moieties onto 2- and 6-position of 4.4-dimethylCPDT skeleton was not so effective to improve the fluorescence quantum yield. Thus, we have kept the effect of the introduction of dimethylsilyl moieties onto 9,9-diphenylfluorene as mentioned above in mind and been interested in the substituent effect on spiro carbon (4-position) of CPDT skeleton. Namely, we expected the introduction of bulky substituent such as phenyl moiety onto the spiro carbon of CPDT would inhibit the interaction of CPDT moieties to result in the inhibition of non-radiative transition and the improvement of the fluorescence quantum yield.

In this work, we studied the synthesis of novel poly(-tetramethylsilarylenesiloxane) derivative having 4,4-diphenylCPDT moiety (**P1**), as shown in Scheme 1. The effects of the introduction of 4,4-diphenylCPDT moiety (**P1**) into poly(tetramethylsilaryl enesiloxane) derivative on the thermal property will be discussed. In addition, the cooperative effects of the introduction of diphenyl groups onto spiro carbon of CPDT as well as dimethylsilyl moieties onto 2- and 6-position of CPDT skeleton will be revealed to improve the fluorescence quantum yield.

#### 2. Experimental procedure

#### 2.1. Materials

2,2'-Bithiophene (**1**) was prepared by the method reported in the literature [**33**]. *N*-Bromosuccinimide (NBS), acetic acid, zinc, hydrochloric acid, tin(IV) chloride anhydrous (SnCl<sub>4</sub>), 1.6 mol/L *n*-butyllithium in hexane, 2.6 mol/L *n*-butyllithium in hexane (KANTO KAGAKU), benzophenone (nacalai tesque, inc.), chlorodimethylsilane (Tokyo Kasei Kogyo Co., Inc.) and 5% palladium on charcoal (Wako Pure Chemical Industries, Ltd.) were commercially available and used as received. Tetrahydrofuran (THF, KANTO KAGAKU), diethyl ether (KANTO KAGAKU) and cyclopentyl methyl ether (ZEON corporation) were used after distillation over sodium. *N*,*N*,*N*,'*N*-Tetramethylethylenediamine (TMEDA, Tokyo Kasei Kogyo Co., Inc.) and chloroform (KANTO KAGAKU) were used after distillation over calcium hydride. 1,1,3,3-Tetramethylguanidinium 2-ethylhexanoate was obtained from the equimolar mixture of 1,1,3,3-tetramethylguanidine and 2-ethylhexanoic acid (Tokyo Kasei Kogyo Co., Inc.) [3–9].

## 2.2. Measurements

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AVANCE 400F spectrometer in deuterated chloroform (CDCl<sub>3</sub>) or dimethylsulfoxide [(CD<sub>3</sub>)<sub>2</sub>SO] at ambient temperature. IR spectra were measured on a Perkin-Elmer Spectrum One FT-IR spectrometer. Glass transition temperature  $(T_g)$  and melting temperature  $(T_m)$ were determined by differential scanning calorimetry (DSC) on a RIGAKU ThermoPlus DSC 8230 at a heating rate of 10 °C/min under a nitrogen flow rate of 10 mL/min. Thermogravimetry analysis (TGA) was performed on a RIGAKU ThermoPlus TG8110 at a heating rate of 10 °C/min under a nitrogen atmosphere. Number-average  $(M_n)$  and weight-average  $(M_w)$  molecular weights were estimated by size-exclusion chromatography (SEC) on an SHOWA DENKO Shodex GPC-101 system with polystyrene gel columns (a pair of Shodex GPC LF-804), eluted with THF using a calibration curve of polystyrene standards. Gas chromatography mass spectroscopy (GC/MS) was carried out using an Agilent 6890/5973 instrument. Absorption spectra were measured on a Shimadzu UV-2450 spectrophotometer. Emission spectra were measured on a Shimadzu RF-5300PC spectrophotometer by use of the solution degassed by argon bubbling for 30 min. Fluorescence quantum yields ( $\Phi_F$ s) were determined by use of pyrene ( $\Phi_F$ : 0.19) [8] as a standard. The optimized geometrical structures and the energies for the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) were estimated by the density functional theory (DFT) calculations at B3LYP/6-31G(d) level of theory using Spartan '08 for Windows (Wavefunction, Inc., Irvine, CA, USA) [34].

## 2.3. Synthesis of 3,5,5'-tribromo-2,2'-bithiophene (2)

2,2'-Bithiophene (1) (7.07 g, 0.0425 mol) and N-bromosuccinimide (22.7 g, 0.128 mol) were dissolved in chloroform/acetic acid (160 mL, 3:2, v/v). The reaction mixture was refluxed for 6 h under a dry argon atmosphere. Then, the reaction mixture was poured into the stirred mixture of chloroform (100 mL) and water (100 mL). The organic layer was separated and dried over anhydrous magnesium sulfate and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography eluted with hexane. The fraction with an  $R_f$  value of 0.70 was collected and concentrated under reduced pressure. The residue was recrystallized from the mixed solvent of chloroform and methanol to afford 2 as pale yellow plates with the yield of 89% (15.3 g, 0.0380 mol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  7.05 (d, J = 3.9 Hz, 1H, thienyl proton), 7.01 (d, J = 3.9 Hz, 1H, thienyl proton), 6.89 (s, 1H, thienyl proton).<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  133.7 (thienyl carbon), 132.7 (thienyl carbon), 132.1 (thienyl carbon), 129.0 (thienyl carbon), 126.0 (thienyl carbon), 112.7 (thienyl carbon), 110.5 (thienyl carbon), 106.3 (thienyl carbon). Mass (EI, *m/z*): 404 (M<sup>+</sup>). *T<sub>m</sub>*: 80–82 °C.



Scheme 1. Polycondensation of CPDT derivative having dimethylhydroxysilyl substituents.

#### 2.4. Synthesis of 3-bromo-2,2'-bithiophene (3)

Zn powder (10.8 g, 0.164 mol) was added in portions to a vigorously stirred refluxing mixture of 2 (22.1 g, 0.0548 mol) in 140 mL of ethanol containing 13 mL of water, 34 mL of acetic acid, and 3 mL of 3 mol/L HCl under a dry argon atmosphere. After refluxing for 11 h. the mixture was extracted with hexane and the combined organic laver was washed with saturated sodium hydrogen carbonate aqueous solution. The organic layer was dried over anhydrous magnesium sulfate and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography eluted with hexane. The fraction with an R<sub>f</sub> value of 0.50 was collected and concentrated under reduced pressure to afford **3** as pale yellow liquid with the yield of 94% (12.6 g, 0.0515 mol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ 7.35 (m, 2H, thienyl protons), 7.19 (d, J = 5.4 Hz, 1H, thienyl proton), 7.08 (m, 1H, thienyl proton), 7.02 (d, J = 5.4 Hz, 1H, thienyl proton). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  134.3 (thienyl carbon), 131.8 (thienyl carbon), 127.2 (thienyl carbon), 126.7 (thienyl carbon), 126.1 (thienyl carbon), 124.4 (thienyl carbon), 124.3 (thienyl carbon), 107.9 (thienyl carbon). Mass (EI, *m*/*z*): 246 (M<sup>+</sup>).

#### 2.5. Synthesis of 2,2'-(bithiophenyl-3-yl)-diphenylmethanol (4)

Under a dry argon atmosphere, 1.6 mol/L n-butyllithium in hexane (17 mL, 0.0272 mol) was added dropwise to 3 (6.67 g, 0.0272 mol) in dry diethyl ether (220 mL) at -78 °C. The mixture was stirred for 2 h, then, benzophenone (3.72 g, 0.0204 mol) in dry diethyl ether (80 mL) was added to this solution at -78 °C, and warmed to ambient temperature. The reaction mixture was stirred for 9 h at ambient temperature and poured into 150 mL of ammonium chloride aqueous solution with stirring. The crude product was extracted with ethyl acetate. The combined organic layer was washed with water several times, dried over anhydrous sodium sulfate and filtered. The filtrate was concentrated under reduced pressure and purified by silica gel column chromatography using the mixed solvent of hexane and ethyl acetate (8/1 v/v) as eluant. The collected fraction with an  $R_f$  value of 0.33 was concentrated under reduced pressure and the residue was recrystallized from a mixed solvent of hexane/ethyl acetate to afford 4 as black solid with the yield of 78% (5.55 g, 0.0159 mol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  7.52–7.23 (m, 11H, thienyl protons and phenyl protons), 7.12 (d, *J* = 5.4 Hz, 1H, thienyl proton), 6.86 (m, 1H, thienyl proton), 6.65 (m, 1H, thienyl proton), 6.37 (d, I = 5.4 Hz, 1H, thienyl proton), 3.40 (s, 1H, C-OH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  147.4 (phenyl carbon), 145.4 (thienyl carbon), 135.0 (thienyl carbon), 131.5 (thienyl carbon), 131.4(phenyl carbon), 128.7 (phenyl carbon), 128.0 (thienyl carbon), 127.6 (phenyl carbon), 127.5 (thienyl carbon), 127.4 (thienyl carbon), 127.3 (thienyl carbon), 123.6 (thienyl carbon), 80.6 (C–OH). IR (KBr, cm<sup>-1</sup>): 3300 (–OH). Mass (EI, *m/z*): 348 (M<sup>+</sup>). *T<sub>m</sub>*: 121–123 °C.

#### 2.6. Synthesis of 4,4-diphenylcyclopentadithiophene (5)

SnCl<sub>4</sub> (0.493 g, 1.89 mmol) and **4** (0.599 g, 1.72 mmol) in 60 mL of chloroform was stirred at ambient temperature for 30 min under a dry argon atmosphere. The reaction mixture was poured into 30 mL of saturated sodium hydrogen carbonate aqueous solution, and the crude product was extracted with chloroform. The combined organic layer was washed with saturated sodium hydrogen carbonate aqueous solution several times, dried over anhydrous so-dium sulfate and filtered. The filtrate was concentrated under reduced pressure and purified by silica gel column chromatography with hexane eluant. The collected fraction with an  $R_f$  value of 0.20 was concentrated under reduced pressure and the residue was

recrystallized from methanol to afford **5** as colorless crystals with the yield of 73% (0.413 g, 1.25 mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  7.24–7.04 (m, 12H, thienyl protons and phenyl protons), 7.04 (d, *J* = 1.8 Hz, 2H, thienyl protons). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  157.1 (thienyl carbon), 144.6 (thienyl carbon), 137.2 (phenyl carbon), 129.0 (phenyl carbon), 128.3 (thienyl carbon), 127.5 (phenyl carbon), 126.2 (phenyl carbon), 124.1 (thienyl carbon), 62.7 (>C(Ph)<sub>2</sub>). Mass (EI, *m/z*): 330 (M<sup>+</sup>). *T<sub>m</sub>*: 158–160 °C.

#### 2.7. Synthesis of 2,6-dibromo-4,4-diphenylcyclopentadithiophene (6)

N-Bromosuccinimide (0.634 g, 3.57 mmol) and 5 (0.589 g, 1.78 mmol) and in 30 mL of chloroform was stirred at -30 °C for 3 h under a dry argon atmosphere. The reaction mixture was poured into 30 mL of saturated sodium thiosulfate aqueous solution, and the crude product was extracted with chloroform. The combined organic layer was washed with saturated sodium chloride aqueous solution several times, dried over anhydrous sodium sulfate and filtered. The filtrate was concentrated under reduced pressure and the residue was recrystallized from methanol to afford **6** as yellow crystals with the yield of 84% (0.730 g, 1.50 mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ 7.28–7.24 (m, 6H, phenyl protons), 7.16 (m, 4H, phenyl protons), 7.03 (s, 2H, thienyl protons). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  155.1 (thienyl carbon), 142.5 (thienyl carbon), 136.1 (phenyl carbon), 128.5 (phenyl carbon), 127.3 (thienyl carbon), 127.1 (phenyl carbon), 126.0 (phenyl carbon), 112.1 (thienyl carbon), 63.3 (>C(Ph)<sub>2</sub>). Mass (EI, *m/z*): 488 (M<sup>+</sup>). *T<sub>m</sub>*: 289–291 °C.

# *2.8. Synthesis of 2,6-bis(dimethylsilyl)-4,4- diphenylcyclopentadithiophene* (**7**)

Under a dry argon atmosphere, 2.6 mol/L n-butyllithium in hexane (1.6 mL, 4.29 mmol) with TMEDA (0.498 g, 4.29 mmol) was added dropwise to 6 (0.523 g, 1.07 mmol) in dry THF (44 mL) at -78 °C. After the mixture was stirred for 1 h, chlorodimethylsilane (0.405 g, 4.29 mmol) was added to this solution at -78 °C, and warmed to ambient temperature. The reaction mixture was stirred for 24 h and poured into 50 mL of water with stirring. The crude product was extracted with ethyl acetate. The combined organic layer was washed with water several times, dried over anhydrous sodium sulfate and filtered. The filtrate was concentrated under reduced pressure and purified by silica gel column chromatography using hexane as eluant. The collected fraction with an  $R_f$  value of 0.40 was concentrated under reduced pressure and the residue was recrystallized from methanol to afford 7 as colorless crystals with the yield of 67% (0.318 g, 0.651 mmol). <sup>1</sup>H NMR (400 MHz, (CD<sub>3</sub>)<sub>2</sub>SO, ppm): δ 7.45 (s, 2H, thienyl protons), 7.29–7.18 (m, 10H, phenyl protons), 4.50 (m, 2H,  $-Si(CH_3)_2-H$ ), 0.39 (s, 12H,  $-Si(CH_3)_2-$ ). <sup>13</sup>C NMR (100 MHz,  $(CD_3)_2$ SO, ppm):  $\delta$  160.3 (thienyl carbon), 144.0 (thienyl carbon), 141.8 (phenyl carbon), 138.2 (phenyl carbon), 132.8 (thienyl carbon), 129.0 (phenyl carbon), 127.9 (phenyl carbon), 127.3 (thienyl carbon), 61.7 (>C(Ph)<sub>2</sub>), -2.5 (-Si(CH<sub>3</sub>)<sub>2</sub>-). IR (KBr, cm<sup>-1</sup>): 2100 (-Si-H). Mass (EI, *m/z*): 446 (M<sup>+</sup>). *T<sub>m</sub>*: 128–130 °C.

#### 2.9. Synthesis of 2,6-bis(dimethylhydroxysilyl)-4,4diphenylcyclopenthadithiophene (**M1**)

To 5%-Pd on C (3.0 mg) with  $H_2O$  (30 mg, 1.68 mmol) in THF (3.0 mL), was added dropwise **7** (0.25 g, 0.560 mmol) in dry THF (5.0 mL) at room temperature under a dry argon atmosphere. The reaction mixture was stirred for 19 h and filtered. The filtrate was concentrated under reduced pressure and the residue was recrystallized from a mixed solvent of benzene/hexane to afford **M1** as colorless crystals with the yield of 86% (0.230 g, 0.480 mmol). <sup>1</sup>H

NMR (400 MHz, (CD<sub>3</sub>)<sub>2</sub>SO, ppm):  $\delta$  7.33 (s, 2H, thienyl protons), 7.25–7.16 (m, 10H, phenyl protons), 6.16 (s, 2H,  $-Si(CH_3)_2-OH$ ), 0.29 (s, 12H,  $-Si(CH_3)_2-$ ). <sup>13</sup>C NMR (100 MHz, (CD<sub>3</sub>)<sub>2</sub>SO, ppm):  $\delta$  160.0 (thienyl carbon), 144.2 (thienyl carbon), 142.8 (phenyl carbon), 141.4 (phenyl carbon), 130.8 (thienyl carbon), 129.1 (phenyl carbon), 127.9 (phenyl carbon), 127.3 (thienyl carbon), 61.6 (>*C*(Ph)<sub>2</sub>), 2.0 ( $-Si(CH_3)_2-$ ). IR (KBr, cm<sup>-1</sup>): 3300 (-OH). Mass (EI, *m/z*): 478 (M<sup>+</sup>). *T<sub>m</sub>*: 171–173 °C.

#### 2.10. Synthesis of polymer (P1)

To **M1** (0.250 g, 0.522 mmol) dissolved in cyclopentyl methyl ether (1.7 mL), was added 1,1,3,3-tetramethylguanidinium 2-ethylhexanoate (0.20 g). After the reaction mixture was refluxed for 12 h, it was filtered and poured into 100 mL of methanol to isolate the corresponding polymer (**P1**) as white precipitates with the yield of 62% (0.158 g). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  7.21–7.18 (m, 10H, phenyl protons), 7.13 (s, 2H, thienyl protons), 0.32 (s, 12H, -Si(CH<sub>3</sub>)<sub>2</sub>–). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  160.1 (thienyl carbon), 144.1 (thienyl carbon), 142.3 (phenyl carbon), 147.8 (phenyl carbon), 126.8 (thienyl carbon), 61.5 (>C(Ph)<sub>2</sub>), 1.7 (-Si(CH<sub>3</sub>)<sub>2</sub>–). IR (KBr, cm<sup>-1</sup>): 1100 (Si–O–Si).

## 3. Results and discussion

#### 3.1. Synthesis of monomer and polymer

Scheme 2 shows the synthetic pathways for disilanol monomer (M1). In the first step, 2,2'-bithiophene (1) was brominated using

*N*-bromosuccinimide to generate 3,5,5'-tribromo-2,2'-bithiophene (**2**) that was then selectively debrominated with Zn powder to give 3-dibromo-2,2'-bithiophene (**3**). Compound **3** was lithiated using *n*-butyllithium and then treated with benzophenone to afford (2,2'-bithiophenyl-3-yl)-diphenylmethanol (**4**), which was transformed using SnCl<sub>4</sub> to generate 4,4-diphenylcyclopentadithiophene (**5**). 2,6-Dibromo-4,4-diphenylcyclopentadithiophene (**6**) was synthesized by bromination reaction of **5** using *N*-bromosuccinimide. 2,6-Bis(dimethylsilyl)-4,4-diphenylcyclopentadithiophene (**7**) was synthesized by lithiation reaction of **6** using *n*-butyllithium at -78 °C and successive reaction with chlorodimethylsilane. **M1** was synthesized by the hydrolysis reaction of **7** using 5 %-Pd on C.

The obtained **M1** underwent polycondensation using 1,1,3,3tetramethylguanidinium 2-ethylhexanoate as a catalyst to afford the corresponding poly(tetramethylsilarylenesiloxane) derivative **P1** as shown in Scheme 1. As reported previously [3–9], any solvents forming azeotropic mixtures with water and dissolving both monomer and the resulting polymer, such as benzene and toluene, can be used for the present polycondensation; however, the use of cyclopentyl methyl ether as solvent resulted in high molecular weight of the obtained polymer probably because of the good solubility of both **M1** and **P1**. The result of the polycondensation of **M1** is summarized in Table 1.

**P1** was soluble in common organic solvents such as THF, chloroform, dichloromethane, toluene, and so on. The formation of **P1** was confirmed by SEC measurement and NMR spectroscopy. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **M1** and **P1** are shown in Figs. 2 and 3, respectively. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **P1** were almost similar to those of **M1**; however, the progress of polycondensation of **M1** to afford **P1** was confirmed by the disappearance of a signal at



Scheme 2. Synthetic pathways for CPDT derivative having dimethylhydroxysilyl substituents.

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## Table 1

Results	of	polyconder	nsation	and	thermal	properties	of <b>P1</b> .
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Polymer	Yield (%) <sup>a</sup>	$M_n^{b}$	$M_w/M_n^{\rm b}$	$T_g (^{\circ}C)^{c}$	$T_m (^{\circ}C)^{\mathbf{d}}$	$T_{d5} (^{\circ}C)^{e}$
P1	62	18000	1.41	109	_f	454

<sup>a</sup> Insoluble part in methanol.

<sup>b</sup> Estimated from SEC eluted with THF based on polystyrene standards.

 $^{\rm c}\,$  Glass transition temperature determined by DSC on a second heating scan at a rate of 10 °C/min in N\_2.

 $^{\rm d}\,$  Melting temperature determined by DSC at a heating rate of 10  $^\circ C/min$  under a nitrogen atmosphere.

 $^{e}\,$  Temperature at 5% weight loss determined by TG in N\_2.

<sup>f</sup> Not detected from -50 °C to 400 °C.

6.16 p.p.m. based on –OH groups as observed in the <sup>1</sup>H NMR spectrum of **M1**. The structure of **P1** as described in Fig. 3 was also confirmed by the consistent integrated ratio of each <sup>1</sup>H NMR signal. The SEC profile of **P1** indicated that the obtained polymer was

unimodal and that the low-molecular weight species such as a cyclic dimer or trimer were almost completely removed by reprecipitation in methanol as depicted in Fig. S1. It would be speculated that the ratio of the cyclic oligomers in the reaction mixture was below 38% because the yield of linear polymer was 62%. These results would support that no side-reactions occurred during the polycondensation.

## 3.2. Thermal characterization of polymer

Fig. 4 shows the DSC trace of **P1** on a second heating scan under a nitrogen atmosphere at a heating rate of 10 °C/min. The glass transition temperature ( $T_g$ ) of **P1** was determined by DSC to be 109 °C as summarized in Table 1. No melting temperature ( $T_m$ ) was observed in the DSC thermogram of **P1**. This result would indicate that **P1** was a noncrystalline polymer as observed in the other poly(tetramethylsilarylenesiloxane) derivatives [3,4,6,8]. 9,9-



Fig. 2. (a) <sup>1</sup>H NMR (solvent: DMSO-d<sub>6</sub>, 400 MHz) and (b) <sup>13</sup>C NMR spectra (solvent: DMSO-d<sub>6</sub>, 100 MHz) of M1 at ambient temperature.





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Fig. 4. DSC thermogram of P1 on a second heating scans under a  $N_2$  flow rate of 10 mL/ min and a cooling or heating rate of 10  $^\circ\text{C}/\text{min}.$ 

Diphenylfluorene-based poly(tetramethylsilarylenesiloxane) has the structural correlation with **P1**, and it bears the same substituents on the spiro-carbon moiety such as 9-position of fluorene and 4-position of CPDT. The  $T_g$  of 9,9-diphenylfluorene-based poly(tetramethylsilarylenesiloxane) (**Pa** as shown in Fig. 1) has been reported to be 125 °C [8] and somewhat higher than that of **P1** (109 °C). In addition, **Pa** has been reported to exhibit the crystallizing temperature ( $T_c$ ) and  $T_m$  at 194 °C and 276 °C during a heating scan, respectively; however, CPDT-based **P1** showed neither  $T_c$  nor  $T_m$  during a heating scan, indicating the introduction of CPDT moieties instead of fluorenylene ones in the main chain decreased the crystallization tendency of polymer chain. The temperature at 5% weight loss ( $T_{d5}$ ) of the present **P1** was determined by TGA to be 454 °C, which was somewhat lower than that of **Pa**, plausibly owing to the increase in molecular mobility of the main chain of **P1** as deduced from the relatively low  $T_g$  of **P1**.

## 3.3. Optical properties

The optical properties of the obtained CPDT derivatives, including monomers and polymers, were also studied. Fig. 5 shows the absorption and fluorescence spectra of CPDT derivatives and the optical properties of CPDT derivatives are summarized in Table 2. The introduction of dimethylsilyl groups onto CPDT skeleton induced the bathochromic and hyperchromic effects in the absorption spectra of CPDT derivatives as shown in Fig. 5(a) through  $\sigma^* - \pi^*$  conjugations between the dimethylsilyl groups and aromatic moieties [7–13]. It has been reported [8,9,27] that lowering the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) causes the bathochromic effects by stabilization of the LUMO state through  $\sigma^* - \pi^*$  conjugation. In addition, the increase in the dipole moments of the HOMO and LUMO states owing to the  $\sigma - \pi$  conjugation in the HOMO and the  $\sigma^* - \pi^*$  conjugation in the LUMO [7–13] would cause the enhancement of the transition moment to result in the hyperchromic effects.

Table 3 summarizes the HOMO and LUMO energy levels as well as the energy gap between LUMO and HOMO for **M1** and **5** calculated by the DFT method at the B3LYP/6-31G(d) level of theory for the confirmation of the effects of the introduction of dimethylsilyl moieties on the absorption spectra. The introduction of dimethylsilyl moieties onto CPDT skeleton was confirmed to lower the LUMO energy level by comparison of the LUMO energy level of **M1** (-1.47 eV) with that of **5** (-1.15 eV), probably owing to the stabilization of LUMO state through  $\sigma^* - \pi^*$  conjugation. Thus, the introduction of dimethylsilyl moieties caused the decrease in the energy gap between LUMO and HOMO, resulting in the bathochromic shift of the maximum absorption.



Fig. 5. Absorption (a) and fluorescence (b) spectra of CPDT derivatives in CHCl<sub>3</sub> at ambient temperature (conc.:  $2.0 \times 10^{-6}$  mol/L,  $\lambda_{ex}$ : 317 nm).



Fig. 6. Structure of 4,4-dimethylcyclopentadithiophene derivatives. 4,4-dimethylCPDT; CPDT1, 2,6-bis(dimethylsilyl)-4,4-dimethylcyclopentadithiophene; CPDT2, 2,6-bis(dimethylsilyl)-4,4-dimethylcyclopentadithiophene; Pb, 4,4-dimethylCPDT based poly(tetramethylsilarylenesiloxane).

Optical properties	of CPDT	derivatives.	

Compound	$\lambda_{abs}/nm \ (\epsilon/L \ mol^{-1} \ cm^{-1})$	λ <sub>em</sub> /nm	$\Phi_F^{a}$
5	323 (12700) 332 (10500)	373	0.03
7	340 (23700) 351 (19400)	387	0.41
M1	338 (21000) 351 (17900)	385	0.36
P1	340 (22200) 352 (19200)	387	0.39
4,4-dimethylCPDT <sup>b</sup>	317 (15000) 329 (11800)	382	0.01
CPDT1 <sup>c</sup>	336 (24500) 348 (19200)	382	0.09
CPDT2 <sup>d</sup>	335 (24300) 346 (19200)	381	0.09
Pb <sup>e</sup>	336 (23700) 348 (19200)	381	0.09

<sup>a</sup> Fluorescence quantum yield ( $\Phi_F$ ) was determined by using pyrene ( $\Phi_F$ : 0.19) [8] as a standard in CHCl<sub>3</sub>.

<sup>b</sup> 4,4-Dimethylcyclopentadithiophene (as shown in Fig. 6) [27].

<sup>c</sup> 2,6-Bis(dimethylsilyl)-4,4-dimethylcyclopentadithiophene (as shown in Fig. 6) [27].

<sup>d</sup> 2,6-Bis(dimethylhydroxysilyl)-4,4-dimethylcyclopentadithiophene (as shown in Fig. 6) [27].

<sup>e</sup> 4,4-DimethylCPDT based poly(tetramethylsilarylenesiloxane) (as shown in Fig. 6) [27].

#### Table 3

Table 3

Results of DFT calculation for CPDT derivatives.

Compound	LUMO/eV <sup>a</sup>	HOMO/eV <sup>a</sup>	LUMO-HOMO gap/eV
5	-1.15	-5.25	4.10
M1	-1.47	-5.36	3.89

 $^{\rm a}\,$  Calculated with density-functional theory (DFT) method at the B3LYP/6-31G(d) level.

Table 2 also provides the wavelength at maximum emission  $(\lambda_{em})$  and fluorescence quantum yields  $(\Phi_{FS})$  of CPDT derivatives. The introduction of dimethylsilyl groups onto 4,4-diphenylCPDT skeleton was revealed to induce bathochromic effects also in the fluorescence spectra of CPDT derivatives as well as the improvement of the  $\Phi_F$ . The  $\Phi_F$ s of unsubstituted 4,4-diphenylCPDT (5) and dimethylsilylated adducts (7, M1, P1) were 0.03, 0.41, 0.36, and 0.39, respectively, indicating that the introduction of dimethylsilyl moieties onto 4,4-diphenylCPDT skeleton rather increased  $\Phi_{F}$ . 9,9-Diphenylfluorene-based poly(tetramethylsilarylenesiloxane) (Pa as shown in Fig. 1) is regarded as the analogous polymer of P1 where the thiophene rings are replaced by phenyl rings. The  $\Phi_F$  of Pa has been reported to be 0.19 [8] and smaller than that of P1 (0.39) in chloroform solution, indicating a decrease in the tendency to aggregate by use of a CPDT skeleton. This result may also be supported by the observation that the introduction of CPDT moiety in the main chain decreases the crystallization tendency of polymer chains. The use of CPDT skeletons was confirmed to be effective in the inhibition of aggregate formation and to result in improved emission intensity.

On the other hand, the  $\Phi_{\rm FS}$  of 4,4-diphenylCPDT with dimethylsilyl groups (7, M1, P1) are higher than those of 4,4dimethylCPDT with dimethylsilyl groups (CPDT1, CPDT2, Pb) as shown in Table 2 [27]. The introduction of dimethylsilyl moieties onto 2- and 6-position of 4,4-dimethylCPDT skeleton was not so effective to improve the  $\Phi_F$  that is, the  $\Phi_F$  of 4,4-dimethylCPDT was 0.01 and those of CPDT1, CPDT2 and Pb were the almost constant values of 0.09 [27]. On the other hand, the introduction of dimethylsilyl moieties onto 4,4-diphenylCPDT skeleton effectively improve the  $\Phi_F$ , that is, the  $\Phi_F$  of 4,4-diphenylCPDT was 0.03 and those of 7, M1 and P1 were 0.41, 0.36 and 0.39, respectively, as mentioned above. It would be probably because the interaction and molecular mobility of 4,4-diphenylCPDT would be inhibited by bulky diphenyl moieties on spiro carbon and result in the inhibition of non-radiative transition that the improvement of  $\Phi_F$  was observed by the introduction of dimethylsilyl moieties onto 4,4diphenylCPDT. It would be remarkable that the cooperative effects of the introduction of diphenyl groups onto spiro carbon of CPDT as well as dimethylsilyl moieties onto 2- and 6-position of CPDT skeleton appears and improves the  $\Phi_F$ 

## 4. Conclusions

We achieved the synthesis of poly(tetramethylsilary lenesiloxane) derivative with diphenylcyclopentadithiophene moiety (P1). P1 exhibited the good solubility in common organic solvents such as benzene, toluene, chloroform, dichloromethane and THF. The  $T_g$  of **P1** was determined by DSC to be 109 °C. The  $T_{d5}$ of P1 was 454 °C, indicating the relatively good thermostability of P1. As for the optical properties of the obtained 4,4-diphenylCPDT derivatives, the bathochromic and hyperchromic effects were observed by introducing dimethylsilyl moieties onto 4,4diphenvlCPDT. The bathochromic shifts of wavelength at the maximum absorption and fluorescence were induced by stabilization of LUMO state through  $\sigma^* - \pi^*$  conjugation. It was remarkable that the cooperative effects of the introduction of diphenyl groups onto spiro carbon of CPDT as well as dimethylsilyl moieties onto 2and 6-position of CPDT skeleton are revealed to be much effective for the increase in fluorescence quantum yield, as deduced from the low fluorescence quantum yields of both unsubstituted 4,4diphenylCPDT and 2,6-bis(dimethylsilyl)substituted-4,4-dimethy ICPDT.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2014.10.048.

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