Thermal and Optical Properties of Dibenzothiophene-Based Poly(tetramethylsilylenesiloxane) Derivatives

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The synthesis of dibenzothiophene derivative, i.e., 2,8-bis(trimethylsilyl)dibenzothiophene (**3a**) and dibenzothiophene-based poly(tetramethylsilylenesiloxane) derivative (**P1**) was attained. In addition, 2,8-bis(trimethylsilyl)dibenzothiophene-5,5'-dioxide (**3aO**) and oxidized dibenzothiophene-based poly(tetramethylsilylenesiloxane) derivative (**P1O**) were obtained by oxidation reaction of **3a** and **P1**, respectively. The glass transition temperature was raised by the oxidation of the dibenzothiophene-based poly(tetramethylsilylenesiloxane) derivative. The introduction of alkylsilyl groups onto dibenzothiophene derivatives induced no remarkable red shifts in the absorption as well as fluorescence spectra; however, the red shifts in the fluorescence spectra were observed by oxidation of dibenzothiophene derivatives.

Key words: dibenzothiophene, poly(tetramethylsilylenesiloxane), fluorescence, thermal properties

1. INTRODUCTION

Dibenzothiophene is a π -conjugated molecule and a typical sulfur-containing compound in light oil.^[1] Therefore, dibenzothiophene has been expected to be applied in the field of organic electronics for optical utilization; however, few studies on the utilization of dibenzothiophene derivatives have been reported.^[2-4] In addition, deviation of electric charge is generated when sulfonyl moieties as electron-withdrawing groups are derived by oxidizing the sulfur moiety at 5-position of dibenzothiophene to result in the optical properties different from those of derivatives bearing dibenzothiophene moiety.^[5]

On the other hand, the red-shifts of the wavelength in the absorption as well as emission spectra and the improvement of the fluorescence quantum yields have been reported by introducing alkylsilyl groups onto the aromatic ring.^[6-9] Our research group has also reported that poly(tetramethylsilylenesiloxane) derivatives where the aromatic moiety is introduced into the main chain component of polysiloxane improve the heat resistance and fluorescence quantum yield.^[10-15]

Based on the above background, we synthesized dibenzothiophene derivatives with trimethylsilyl groups as well as poly(tetramethylsilylenesiloxane) derivatives bearing dibenzothiophene moiety as shown in Scheme 1 in this research. In addition, oxidized compounds of the above-mentioned derivatives were also prepared. We will present the thermal and optical properties of the resulting derivatives and discuss the characteristic fluorescence properties of new dibenzothiophene derivatives with alkylsilyl groups.

2. EXPERIMENTAL

2.1. Materials

Dibenzothiophene, *m*-chloroperbenzoic acid (*m*-CPBA), chlorotrimethylsilane, chlorodimethylsilane, (Tokyo Chemical Industry Co., Ltd), bromine, 2.76 mol/L *n*-

butyllithium (*n*-BuLi) in hexane, 31 % hydrogen peroxide, acetic acid, dichloromethane, (KANTO CHEMICAL CO., INC), and 5 % palladium on charcoal (Sigma-Aldrich Co. LLC) were used as received. Tetrahydrofuran (THF) and benzene (KANTO CHEMICAL CO., INC) were used after distillation over sodium. Chloroform (KANTO CHEMICAL CO., INC) was used after distillation over calcium hydride. 2,8-Dibromodibenzothiophene was prepared by the method reported earlier.^[4] 1,1,3,3-Tetramethylguanidinium 2-ethylhexanoate was obtained from the equimolar mixture of 1,1,3,3-tetramethylguanidine and 2-ethylhexanoic acid (Tokyo Chemical Industry Co., Ltd).^[10-15]

2.2. Measurements

¹H and ¹³C NMR spectra were recorded on a JEOL ECX-400 spectrometer in deuterated dimethyl sulfoxide (DMSO-*d*₆) or chloroform (CDCl₃) at ambient temperature. FT-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 8230L 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 a 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. Emission spectra were measured on a Shimadzu RF-5300PC spectrophotometer. Fluorescence quantum yield (Φ_F) was determined in CHCl₃ using a HAMAMATSU PHOTONICS absolute PL quantum yield measured system C11347. 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).

2.3. Synthesis

Scheme 1. Synthesis of dibenzothiophene derivatives

2.3.1 2,8-Bis(trimethylsilyl)dibenzothiophene (**3a**)

Under a dry argon atmosphere, 2.76 mol/L *n*-BuLi (3.4 mL, 9.38 mmol) was added dropwise to 2,8-dibromodibenzothiophene (**2**, 1.20 g, 3.51 mmol) dissolved in dry THF (40 mL) at -78°C and the reaction mixture was stirred for 1 h. Then, chlorotrimethylsilane (1.55 g 14.3 mmol) was added dropwise to this solution. After the reaction mixture was stirred for 24 h at ambient temperature, it was poured into 30 mL of water. The crude product was extracted with ethyl acetate and the organic layer was washed with water and sodium chloride aqueous solution, successively, dried over anhydrous magnesium sulfate, and filtered. After the filtrate was concentrated under reduced pressure, the product was purified by silica gel column chromatography using hexane as eluent. The collected fraction with an R_f value of 0.53 was concentrated under reduced pressure to afford 2,8-bis(trimethylsilyl)dibenzothiophene as colorless liquid with the yield of 92 % (1.06 g, 3.23 mmol).

$^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ 0.37[s, 18H, $-\text{Si}(\text{CH}_3)_3$], 7.58-7.61(m, 2H, aromatic protons), 7.84-7.86 (m, 2H, aromatic protons), 8.32 (s, 2H, aromatic protons). $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz): δ 122.2 (aromatic carbon), 126.2 (aromatic carbon), 131.4 (aromatic carbon), 134.8 (aromatic carbon), 135.8 (aromatic carbon), 140.1 (aromatic carbon), $-0.82[-\text{Si}(\text{CH}_3)_3]$. FT-IR (NaCl , cm^{-1}): 878 $[-\text{Si}(\text{CH}_3)_3]$.

2.3.2 2,8-Bis(dimethylsilyl)dibenzothiophene (**3b**)

2,8-Bis(dimethylsilyl)dibenzothiophene (**3b**) was synthesized by the similar synthetic method of **3a** using chlorodimethylsilane instead of chlorotrimethylsilane and obtained as colorless liquid with the yield of 83 % (0.73 g, 2.43 mmol).

$^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ 0.46 [d, $J = 3.7$ Hz, 12H, $-\text{Si}(\text{CH}_3)_2$], 4.57-4.61 [m, 2H, $-\text{Si}(\text{CH}_3)_2\text{-H}$], 7.60-7.62 (m, 2H, aromatic protons), 7.85-7.87 (m, 2H, aromatic protons), 8.37 (s, 2H, aromatic protons). $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz): δ 122.3 (aromatic carbon), 127.1 (aromatic carbon), 131.9 (aromatic carbon), 132.9 (aromatic carbon), 134.8 (aromatic carbon), 140.5 (aromatic carbon), $-3.41[-\text{Si}(\text{CH}_3)_2]$. FT-IR (NaCl , cm^{-1}): 1248 $[-\text{Si}(\text{CH}_3)_2]$.

2.3.3 Synthesis of 2,8-bis(dimethylhydroxysilyl)dibenzothiophene (**M1**)

2,8-Bis(dimethylsilyl)dibenzothiophene (**3b**, 0.500 g, 1.66 mmol) dissolved in THF (10 mL) was added dropwise to a mixture of THF (10 mL), H_2O (90.0 mg, 5.00 mmol) and 5 % Pd-C (6.00 mg, 0.0056 mmol) at ambient temperature. The reaction mixture was stirred for 26 h at ambient temperature and filtered. The filtrate was concentrated under reduced pressure. The residue dissolved in chloroform was reprecipitated from hexane to afford 2,8-bis(dimethylhydroxysilyl)dibenzothiophene as colorless crystals with the yield of 48 % (0.26 g, 0.78 mmol).

M.p.: 164°C . $^1\text{H-NMR}$ ($\text{DMSO-}d_6$, 400 MHz): δ 0.35-0.37 [m, 12H, $-\text{Si}(\text{CH}_3)_2$], 6.07 [s, 2H, $-\text{Si}(\text{CH}_3)_2\text{-OH}$], 7.66-7.68 (m, 2H, aromatic protons), 8.01-8.03 (m, 2H, aromatic protons), 8.55 (s, 2H, aromatic protons). $^{13}\text{C-NMR}$ ($\text{DMSO-}d_6$, 100 MHz): δ 122.4 (aromatic carbon), 126.4 (aromatic carbon), 131.3 (aromatic carbon), 134.3 (aromatic carbon), 136.5 (aromatic carbon), 139.4 (aromatic carbon), 0.94 $[-\text{Si}(\text{CH}_3)_2\text{-}]$. FT-IR (KBr, cm^{-1}): 3274 ($-\text{OH}$).

2.3.4 Polycondensation of **M1**

To 2,8-bis(dimethylhydroxysilyl)dibenzothiophene (**M1**, 0.200 g, 0.60 mmol) dissolved in benzene (5 mL), was added a few drops 1,1,3,3-tetramethylguanidinium 2-ethylhexanoate. After the reaction mixture was refluxed for 12 h, it was concentrated under reduced pressure. The resulting residue dissolved in chloroform was reprecipitated from methanol to afford dibenzothiophene-based poly(tetramethylsilylarylenesiloxane) (**P1**) as colorless solids with the yield of 32 % (0.060 g, 0.20 mmol).

^1NMR (CDCl_3 , 400 MHz): δ 0.36 [s, 12H, $-\text{Si}(\text{CH}_3)_2$], 7.46-7.53 (m, 2H, aromatic protons), 7.67-7.72 (m, 2H, aromatic protons), 8.24 (s, 2H, aromatic protons). $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz): δ 122.2 (aromatic carbon), 126.0 (aromatic carbon), 131.0 (aromatic carbon), 134.7 (aromatic carbon), 135.1 (aromatic carbon), 140.6 (aromatic carbon), 1.12 $[-\text{Si}(\text{CH}_3)_2\text{-}]$. FT-IR (KBr, cm^{-1}): 1053 $[\text{Si-O-Si}]$.

2.3.5 Dibenzothiophene-5,5'-dioxide (**10**)^[16]

Under a dry argon atmosphere, dibenzothiophene (**1**, 0.800 g, 4.34 mmol), acetic acid (13 mL), and 31 % hydrogen peroxide (2.0 mL, 21.7 mmol) were mixed. After the resulting reaction mixture was refluxed for 4 h, it was poured into water and filtered. The resulting precipitate was recrystallized from chloroform to afford dibenzothiophene-5,5'-dioxide as colorless crystals with the yield of 57 % (0.537 g, 2.5 mmol).

M.p.: 230°C . $^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ 7.51-7.55 (m, 2H, aromatic protons), 7.63-7.67 (m, 2H, aromatic protons), 7.79-7.84 (m, 4H, aromatic protons). $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz): δ 121.6 (aromatic carbon), 122.2 (aromatic carbon), 130.4 (aromatic carbon), 131.6 (aromatic carbon), 133.9 (aromatic carbon), 137.7 (aromatic carbon). FT-IR (KBr, cm^{-1}): 1288 (S=O).

2.3.6 2,8-Bis(trimethylsilyl)dibenzothiophene-5,5'-dioxide (**3aO**)

2,8-Bis(trimethylsilyl)dibenzothiophene-5,5'-dioxide (**3aO**) was synthesized by the similar synthetic method of **10** using **3a** as the substrate. Recrystallization from the mixed solvent of ethyl acetate and hexane afforded **3aO** as

colorless crystals with the yield of 53 % (0.463 g, 1.3 mmol).

M.p.: 230 °C. ¹H-NMR (CDCl₃, 400 MHz): δ 0.37 [s, 18H, -Si(CH₃)], 7.67 (m, 2H, aromatic protons), 7.78 (m, 2H, aromatic protons), 7.92 (s, 2H, aromatic protons). ¹³C-NMR (CDCl₃, 100 MHz): δ -1.11 [-Si(CH₃)], 121.2 (aromatic carbon), 125.9 (aromatic carbon), 130.9 (aromatic carbon), 135.4 (aromatic carbon), 138.2 (aromatic carbon), 148.7 (aromatic carbon). FT-IR (KBr, cm⁻¹): 1303 (S=O).

2.3.7 Oxidation of **P1**

P1 (0.325 g, 1.0 mmol), *m*-CPBA (0.534 g, 3.1 mmol), and dichloromethane (40 mL) were mixed. The resulting reaction mixture was stirred for 18 h at ambient temperature shielded from light. Then, the reaction solution was poured into sodium thiosulfate aqueous solution and the crude product was extracted with chloroform and washed with sodium hydrogen carbonate aqueous solution. The organic layer was concentrated under reduced pressure. The crude product dissolved in chloroform was reprecipitated from methanol to afford dibenzothiophene-5,5'-oxide-based poly(tetramethylsilylenesiloxane) (**P10**) as colorless solids with the yield of 78 % (0.091 g, 0.26 mmol).

¹H-NMR (CDCl₃, 400 MHz): δ 0.36-0.44 [m, 18H, -Si(CH₃)], 7.67-7.68 (m, 2H, aromatic protons), 7.76-7.78 (m, 2H, aromatic protons), 7.92 (s, 2H, aromatic protons). ¹³C-NMR (CDCl₃, 100 MHz): δ 121.5 (aromatic carbon), 125.5 (aromatic carbon), 130.9 (aromatic carbon), 135.0 (aromatic carbon), 138.7 (aromatic carbon), 147.1 (aromatic carbon), 0.988 [-Si(CH₃)]. FT-IR (KBr, cm⁻¹): 1171 (S=O).

3. RESULTS AND DISCUSSION

3.1 Synthesis of monomer and polymer

Scheme 1 shows the synthetic pathways for dibenzothiophene derivatives (**3a**, **P1**, **10**, **3aO**, and **P10**). Dibenzothiophene (**1**) was brominated using bromine to afford 2,8-dibromodibenzothiophene (**2**).^[4] 2,8-Bis(trimethylsilyl)dibenzothiophene (**3a**) and 2,8-bis(dimethylsilyl)dibenzothiophene (**3b**) were synthesized via lithiation reaction of **2** using *n*-BuLi and successive reaction with chlorotrimethylsilane and chlorodimethylsilane, respectively. 2,8-Bis(dimethylhydroxysilyl)dibenzothiophene (**M1**) was obtained by the hydrolysis of **3b** catalyzed by 5 % Pd-C. **M1** underwent polycondensation catalyzed by 1,1,3,3-tetramethylguanidinium 2-ethylhexanoate to afford the corresponding dibenzothiophene-based poly(tetramethylsilylenesiloxane) (**P1**). Dibenzothiophene-5,5'-dioxide (**10**) and 2,8-bis(trimethylsilyl)dibenzothiophene-5,5'-dioxide (**3aO**) were synthesized by oxidation reaction of **1** and **3a**, respectively, using 31 % hydrogen peroxide as the oxidant. Dibenzothiophene-5,5'-dioxide-based poly(tetramethylsilylenesiloxane) (**P10**) was synthesized by oxidation reaction of **P1** using *m*-CPBA as the oxidant. The results of the polycondensation of **M1** and the oxidation of **P1** are summarized in Table I.

Each structure of the obtained compounds was confirmed by the NMR as well as FT-IR spectroscopy. The formation of **P1** and **P10** was also confirmed by SEC measurement and NMR as well as FT-IR spectroscopy. All NMR spectra of the obtained compounds were consistent with their structures. In addition, the SEC

profile of **P1** was bimodal, indicating that a small amount of relatively low-molecular weight species such as a cyclic dimer or trimer were involved in the resulting polymer; however, that of **P10** was unimodal to confirm that the removal of the low-molecular weight species such as a cyclic dimer or trimer was achieved by reprecipitation procedures. The obtained **P1** and **P10** exhibited the good solubility in common organic solvents such as THF, chloroform, dichloromethane, toluene, and so on.

3.2 Thermal characterization of polymer

Table I summarizes the thermal properties of each polymer together with the results of polycondensation. The glass transition temperatures (*T_g*) of **P1** and **P10** were 73 °C and 150 °C, respectively. The higher *T_g* of **P10** than that of **P1** would be due to the polarity of dibenzothiophene-5,5'-dioxide moiety higher than that of dibenzothiophene one that increased the inter- and/or intramolecular interactions and that inhibited the mobility of the main chain. No clear endothermal peaks based on melting behavior were observed in the range of -50 °C to 400 °C, plausibly indicating that **P1** and **P10** were amorphous polymers. The temperatures at 5% weight loss (*T_{d5}*) of **P1** and **P10** were 496 °C and 440 °C, respectively. This finding would suggest that the polarity of dibenzothiophene-5,5'-dioxide moiety higher than that of dibenzothiophene one promotes the inter- and/or intramolecular interactions to decrease the thermal stability.

Table I. Characterization of **P1** and **P10**.

Polymer	Yield(%)	<i>M_n</i> ^{a)}	<i>M_w</i> / <i>M_n</i> ^{a)}	<i>T_g</i> (°C) ^{b)}	<i>T_{d5}</i> (°C) ^{c)}
P1	32	26000	1.44	73	496
		7000	1.05		
P10	78	17000	1.77	150	440

- a) Estimated from SEC eluted with THF based on polystyrene standards.
 b) Glass transition temperature determined by DSC at a heating rate of 10 °C/min under a nitrogen atmosphere.
 c) Temperature at 5 % weight loss determined by TG at a heating rate of 10 °C/min under a nitrogen atmosphere.

Figs. 1 and 2 show the absorption and fluorescence spectra of each derivative, respectively. Table II summarizes the optical properties of the obtained dibenzothiophene derivatives. The slight red-shifts owing to the introduction of alkylsilyl groups onto dibenzothiophene and dibenzothiophene-5,5'-dioxide skeletons were observed in the absorption spectra as shown in Fig. 1. On the other hand, the introduction of alkylsilyl groups onto dibenzothiophene skeleton induced the very slight red-shifts in the fluorescence spectra; however, the introduction of alkylsilyl groups onto dibenzothiophene-5,5'-dioxide skeleton did the relatively remarkable red-shifts in the fluorescence spectra as shown in Fig. 2. In the previous studies, it was indicated that the introduction of alkylsilyl groups onto aromatic moieties caused the red-shifts in the absorption and fluorescence wavelengths mainly owing to the effects of σ*-π* conjugation.^[7] Thus, the present results would indicate that no remarkable σ*-π* conjugation is induced between dibenzothiophene moiety and substituted alkylsilyl groups. Fig. 3 shows the molecular orbitals of **1**, **3a**, **10**, and **3aO** calculated using the DFT method at the B3LYP/6-31G(d) level. There were no remarkable changes in the orbital shapes of the HOMO and LUMO by the introduction of trimethylsilyl groups, suggesting that the σ*-π* conjugation is not induced by the σ* orbital of silicon and the π* orbital of

carbon at 1 and 9 positions of dibenzothiophene.

Table II. Optical properties of dibenzothiophene derivatives.

Compound	$\lambda_{\text{abs}}(\text{nm})^{\text{a}}$	$\lambda_{\text{em}}(\text{nm})^{\text{a}}$	$\Phi_{\text{F}}^{\text{b)}$
1	287	332	0.06 ± 0.01
3a	291	335	0.03
P1	292	334	0.01
1O	290	358	0.09
3aO	295	368	0.07
P1O	298	370	0.06

a) In CHCl_3 at ambient temperature (conc.: 5.0×10^{-6} mol/L, λ_{ex} : 288 nm).

b) Fluorescence quantum yields (Φ_{F}) of **1**, **3a**, **P1**, **1O**, **3aO** and **P1O** derivatives were measured in CHCl_3 using a HAMAMATSU PHOTONICS absolute PL quantum yield measurement system (λ_{ex} : 288 nm).

These calculation results are consistent with the spectroscopic results as mentioned above.

As seen in Table II, the improvement in fluorescence quantum yield (Φ_{F}) was not observed by introducing alkylsilyl groups onto dibenzothiophene and dibenzothiophene-5,5'-dioxide skeletons. It has been reported^[8] that the introduction of alkylsilyl groups onto aromatic moieties make the intersystem crossing rate constants negligible owing to the energy stabilization of the first single excited state (S_1) to result in the change of the relative energy position against the second triplet state (T_2). As a result, Φ_{F} is increased; however, the introduction of alkylsilyl groups onto dibenzothiophene and dibenzothiophene-5,5'-dioxide skeletons plausibly induced little energy stabilization of S_1 to result in no remarkable improvement of Φ_{F} .

In conclusion, we achieved the synthesis of new dibenzothiophene-based poly(tetramethylsilylarylene-siloxane) derivative (**P1**) as well as new oxidized dibenzothiophene-based poly(tetramethylsilylarylene-siloxane) derivative (**P1O**) through the oxidation reaction of **P1**. It was revealed from the absorption and fluorescence spectroscopy as well as the calculation using the DFT method that the present dibenzothiophene derivatives having alkylsilyl moieties exhibit the specific fluorescent property owing to no remarkable appearance of $\sigma^*-\pi^*$ conjugation between dibenzothiophene and alkylsilyl groups.

Fig. 1. Absorption spectra of **1**, **3a**, **P1**, **1O**, **3aO**, and **P1O** in CHCl_3 at ambient temperature (conc.: 5.0×10^{-6} mol/L).

Fig. 2. Fluorescence spectra of **1**, **3a**, **P1**, **1O**, **3aO**, and **P1O** in CHCl_3 at ambient temperature (conc.: 5.0×10^{-6} mol/L, λ_{ex} : 288 nm).

Fig.3. Molecular orbitals of **1** (a), **3a** (b), **1O** (c) and **3aO** (d) calculated using the DFT method at the B3LYP/6-31G(d) level.

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