

## ORIGINAL ARTICLE

# Synthesis and characterization of poly(tetramethylsilylarylenesiloxane) derivatives bearing diphenylfluorene or diphenyldibenzosilole moieties

Kazutoshi Imai<sup>1</sup>, Yoshihiko Kihara<sup>1</sup>, Atsushi Kimoto<sup>2</sup>, Jiro Abe<sup>2</sup>, Yasufumi Tamai<sup>1</sup> and Nobukatsu Nemoto<sup>1</sup>

Poly(tetramethylsilylarylenesiloxane) derivatives having diphenylfluorene (P1) or diphenyldibenzosilole (P2) moieties were prepared via polycondensation of the corresponding disilanol monomers, that is, 2,7-bis(dimethylhydroxysilyl)-9,9-diphenylfluorene (M1) and 2,7-bis(dimethylhydroxysilyl)-9,9-diphenyldibenzosilole (M2), respectively. P1 and P2 exhibited good solubility in common organic solvents. The glass transition temperatures ( $T_g$ s) of P1 and P2 were determined by differential scanning calorimetry to be 125 and 119 °C, respectively. The melting temperature ( $T_m$ ) of P1 was observed at 276 °C; however, the  $T_m$  of P2 was not observed, indicating that the introduction of a dibenzosilole moiety decreased the crystallization tendency. The temperatures at 5% weight loss ( $T_{d5s}$ ) of P1 and P2 were 539 and 520 °C, respectively, suggesting good thermostability of P1 and P2. Bathochromic and hyperchromic effects were observed in the absorption and fluorescence spectra by introducing a dimethylsilyl substituent onto diphenylfluorene and diphenyldibenzosilole skeletons. The replacement of diphenylfluorene by the corresponding diphenyldibenzosilole also led to bathochromic shifts. The fluorescence quantum yield ( $\Phi_f$ ) of P1 was lower than that of M1, probably because of the formation of aggregates; however, the  $\Phi_f$  of P2 was higher than that of M2, indicating a decrease in the tendency toward aggregation using a dibenzosilole skeleton.

*Polymer Journal* (2011) 43, 58–65; doi:10.1038/pj.2010.104; published online 3 November 2010

**Keywords:** dibenzosilole; fluorene; heat-resistant polymer; photoluminescence; polysiloxane; poly(tetramethylsilylarylenesiloxane)

## INTRODUCTION

Fluorene derivatives have been very attractive molecules suitable for applications in electronics and optoelectronics, such as organic light emitting diodes (OLEDs). Fluorene-based conjugated polymers are also promising candidates for blue-light-emitting polymers because they have exhibited excellent quantum efficiencies in photoluminescence, as well as chemical and thermal stabilities.<sup>1–4</sup> High thermal and oxidative stabilities are also required for blue-light-emitting polymers because blue-light emissions are associated with high energy gaps and high-electrical field intensities; however, the 9-position of fluorenyl moiety is easily oxidized at high operating temperature, inducing the decline of the color stability of light emission resulting from changes in the emission spectra.<sup>5–7</sup> The introduction of bulky aryl moieties into the 9-position of fluorene has been reported to be effective in the inhibition of oxidation, although the low solubilities in common organic solvents raise another problem owing to the increase in the tendency to crystallize.<sup>8</sup>

On the other hand, conjugated polymers based on dibenzosilole, in which the vulnerable C-9 carbon in fluorene is replaced by a silicon, have been reported to be new polymeric materials for OLEDs in recent

years.<sup>9,10</sup> Dibenzosilole-based conjugated polymers have also been reported to be difficult to oxidize at high operating temperature.<sup>9</sup> The enhancement of electron affinity owing to the  $\sigma^*-\pi^*$  conjugation as observed in analogous molecular and polymeric siloles<sup>11</sup> may also attract interest in dibenzosilole-based conjugated polymers.

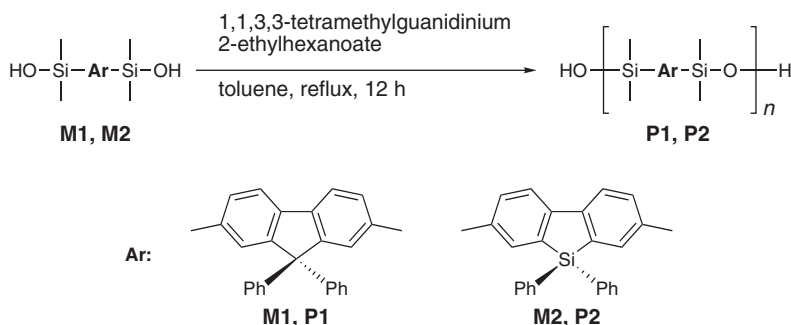
In the meantime, the incorporation of a silyl substituent onto aromatic species has been reported to result in high fluorescence quantum yield.<sup>12–17</sup> Kitamura *et al.*<sup>18</sup> reported a polysiloxane having fluorenyl moiety in the main chain; however, the obtained polysiloxane derivative was an oil product owing to the extremely low glass transition temperature ( $T_g$ ). Thus, the use of polysiloxane derivatives as polymeric OLED materials seems to be inadequate because of their extremely low  $T_g$ ,<sup>19,20</sup> which allows the formation of aggregates and/or interchain excimers to induce the decline of the color stability of light emission.<sup>5–7</sup> This is so even though the other properties of polysiloxanes such as good thermostability and stability against atomic oxygen,<sup>19</sup> which is generated by the irradiation of ultraviolet light to molecular oxygen ( $O_2$ ), would be appropriate for polymeric OLED materials. To raise  $T_g$ , we achieved the synthesis of fluorene-based polysiloxane derivatives with a bulky spirofluorenyl substituent on the

<sup>1</sup>Department of Chemical Biology and Applied Chemistry, College of Engineering, Nihon University, Tamura-machi, Fukushima, Japan and <sup>2</sup>Department of Chemistry, School of Science and Engineering, Aoyama Gakuin University, Fuchinobe, Chuo-ku, Kanagawa, Japan

Correspondence: Professor N Nemoto, Department of Chemical Biology and Applied Chemistry, College of Engineering, Nihon University, Tamura-machi, Koriyama, Fukushima 963-8642, Japan.

E-mail: nemoto@chem.ce.nihon-u.ac.jp

Received 9 August 2010; revised and accepted 19 September 2010; published online 3 November 2010



**Scheme 1** Polycondensation of 2,7-bis(dimethylhydroxysilyl)-9,9-diphenylfluorene (**M1**) and 2,7-bis(dimethylhydroxysilyl)-9,9-diphenyldibenzosilole (**M2**).

C-9 carbon.<sup>21</sup> The obtained polysiloxane derivative exhibited a  $T_g$  of 156 °C, indicating that the fluorene-based polysiloxanes with high  $T_g$  can be obtained by the introduction of bulky and rigid substituents onto the C-9 carbon of fluorene.

In this article, we report the synthesis of novel poly(tetramethylsilylenesiloxane) derivatives with fluorene or dibenzosilole moieties, at the 9-position of which the bulky phenyl substituents were attached, as shown in Scheme 1. The effects of the introduction of dibenzosilole moiety into poly(tetramethylsilylenesiloxane) derivatives on the thermal and optical properties will also be discussed.

## EXPERIMENTAL PROCEDURE

### Materials

9,9-Diphenylfluorene (**1**) (Wong *et al.*<sup>22</sup>) and 4,4'-dibromo-2,2'-diiodobiphenyl (**4**) (Chan *et al.*<sup>9</sup>) were prepared by the method reported in the literature. Dichlorodiphenylsilane, chlorodimethylsilane (Acros organics, Geel, Belgium), 1.6 mol l<sup>-1</sup> *t*-butyllithium in pentane, magnesium, bromine, sodium, sodium carbonate, potassium dihydrogenphosphate (KANTO KAGAKU, Tokyo, Japan) and 5% palladium on charcoal (Escat 103, from Aldrich, St Louis, MO, USA) were commercially available and used as received. The catalyst 1,1,3,3-tetramethylguanidinium 2-ethylhexanoate was prepared according to the literature.<sup>23</sup> Ethanol was used after distillation over magnesium ethoxide. Toluene and tetrahydrofuran (THF) were used after distillation over sodium. Chloroform was used after distillation over calcium hydride.

### Measurements

<sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVANCE 400F spectrometer (Bruker, Karlsruhe, Germany) in deuterated chloroform (CDCl<sub>3</sub>) or dimethylsulfoxide ((CD<sub>3</sub>)<sub>2</sub>SO) at ambient temperature. Infrared (IR) spectra were measured on a PerkinElmer Spectrum One FT-IR spectrometer (PerkinElmer, Waltham, MA, USA). Melting point ( $T_m$ ) and glass transition temperature ( $T_g$ ) were determined by differential scanning calorimetry (DSC) on a RIGAKU ThermoPlus DSC 8230 (Rigaku Co., Inc., Tokyo, Japan) at a heating rate of 10 °C min<sup>-1</sup> under a nitrogen flow rate of 10 ml min<sup>-1</sup>. Thermogravimetry was performed on a RIGAKU ThermoPlus TG8110 at a heating rate of 10 °C min<sup>-1</sup> under a nitrogen atmosphere. Number-average ( $M_n$ ) and weight-average ( $M_w$ ) molecular weights were estimated by size-exclusion chromatography on a SHOWA DENKO Shodex GPC-101 system (SHOWA DENKO K. K., Tokyo, Japan) with polystyrene gel columns (a pair of Shodex GPC LF-804), eluted with THF using a calibration curve of polystyrene standards. The purity of all prepared compounds with low-molecular weight was confirmed to be over 99% by gas chromatography (GC) analysis. Absorption and fluorescence spectra were measured on a SHIMADZU UV-2450 (Shimadzu Co., Kyoto, Japan) and a JASCO FP-6500 spectrofluorometer (JASCO Co., Tokyo, Japan), respectively, using chloroform solutions degassed by argon bubbling for 30 min with a fixed concentration of 4.0 × 10<sup>-6</sup> mol l<sup>-1</sup> for the diphenylfluorene or diphenyldibenzosilole unit. Fluorescence quantum yields were measured using a HAMAMATSU PHOTONICS C9920-02 absolute PL quantum yield measurement system (Hamamatsu Photonics K. K., Hamamatsu, Japan).<sup>24</sup>

### Monomer synthesis

**2,7-Dibromo-9,9-diphenylfluorene (2).** An aqueous solution (125 ml) of sodium carbonate (1.31 g, 12.4 mmol) was added to the chloroform solution (200 ml) of **1** (7.88 g, 24.7 mmol) at 5 °C. Iodine (0.15 g, 0.6 mmol) and bromine (9.36 g, 58.6 mmol) were added to this mixture at 5 °C, and the resulting mixture was stirred for 12 h at ambient temperature. In addition, bromine (9.36 g, 58.6 mmol) was added to the reaction mixture at 5 °C, and the resulting mixture was stirred for 12 h at ambient temperature. Then, an aqueous solution (50 ml) of sodium hydroxide (4.68 g, 117.1 mmol) was added to the reaction mixture. This was stirred for 30 min and poured into a mixture of sodium thiosulfate aqueous solution and chloroform. The crude product was washed with chloroform, and the resulting chloroform solution was washed with saturated sodium hydrogen carbonate aqueous solution, dried over anhydrous magnesium sulfate and filtered. The filtrate was concentrated under reduced pressure, and the crude product was recrystallized from toluene to afford **2** as a colorless solid with a yield of 10.62 g (90%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ (p.p.m.)=7.59 (d,  $J=7.9$  Hz, 2H, fluorenyl protons), 7.49 (s, 2H, fluorenyl protons), 7.48 (d,  $J=7.9$  Hz, 2H, fluorenyl protons), 7.24–7.27 (m, 6H, phenyl protons), 7.13–7.18 (m, 4H, phenyl protons). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ (p.p.m.)=152.9, 144.4, 138.1, 130.9, 129.4, 128.5, 128.0, 127.2, 121.8, 121.6, 65.6. Mp: 278 °C (literature<sup>22</sup>: 279 °C).

**2,7-Dibromo-9,9-diphenyldibenzosilole (5).** Under a dry argon atmosphere, 13.30 ml (21.2 mmol) of 1.6 mol l<sup>-1</sup> *t*-butyllithium in heptane was added drop wise to the THF solution (60 ml) of **4** (3.0 g, 5.32 mmol) over 2 h at –78 °C. After the reaction mixture was stirred for 1 h, dichlorodiphenylsilane (2.70 g, 10.64 mmol) was added to the mixture at –78 °C. After the reaction mixture was stirred for 12 h at ambient temperature, it was poured into 100 ml of 0.1 mol l<sup>-1</sup> HCl and the crude product was extracted with ethyl acetate. The organic layer was washed with saturated sodium hydrogen carbonate aqueous solution and brine, dried over anhydrous magnesium sulfate and filtered. The filtrate was concentrated under reduced pressure, and the crude product was purified by silica gel column chromatography eluted with the mixed solvent of hexane/chloroform (v/v=10/1). The fraction with an  $R_f$  value of 0.43 was collected and concentrated under reduced pressure. The residue was recrystallized from methanol to afford **5** as a colorless plate with a yield of 1.84 g (70%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ (p.p.m.)=7.76 (d,  $J=2.0$  Hz, 2H, dibenzosilolyl protons), 7.63 (d,  $J=8.2$  Hz, 2H, dibenzosilolyl protons), 7.51–7.54 (m, 6H, phenyl protons), 7.38 (dd,  $J=2.0, 8.2$  Hz, 2H, dibenzosilolyl protons), 7.29–7.37 (m, 4H, phenyl protons). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ (p.p.m.)=146.4, 138.5, 136.6, 135.5, 133.8, 130.9, 130.7, 128.4, 122.8, 122.7. Mp: 238 °C.

**2,7-Bis(dimethylsilyl)-9,9-diphenylfluorene (3).** Under a dry argon atmosphere, a THF solution (140 ml) of **2** (12.9 g, 27.2 mmol) and chlorodimethylsilane (6.46 g, 67.9 mmol) was added drop wise to magnesium (1.49 g, 61.1 mmol) in THF (180 ml) at 60 °C. The reaction mixture was stirred for 12 h at 60 °C and poured into the mixture of ethyl acetate (250 ml) and 0.5 mol l<sup>-1</sup> HCl aqueous solution (250 ml). The organic layer was washed successively with saturated sodium hydrogen carbonate aqueous solution and brine. The resulting ethyl acetate solution 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  $R_f$  value of 0.48 was corrected and concentrated under reduced pressure. The crude product was recrystallized from methanol to afford **3** as a colorless plate with a yield of 8.29 g (70%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (p.p.m.)=7.77 (d,  $J=7.5$  Hz, 2H, fluorenyl protons), 7.57 (s, 2H, fluorenyl protons), 7.53 (d,  $J=7.5$  Hz, 2H, fluorenyl protons), 7.19–7.25 (m, 10H, phenyl protons), 4.40 (sept,  $J=3.7$  Hz, 2H,  $-\text{Si}(\text{CH}_3)_2-\text{H}$ ), 0.31 (d,  $J=3.7$  Hz, 12H,  $-\text{Si}(\text{CH}_3)_2-\text{H}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  (p.p.m.)=150.5, 146.0, 141.1, 137.2, 133.1, 131.8, 128.2, 128.1, 126.5, 119.7, 65.5,  $-3.6$ . IR (KBr,  $\text{cm}^{-1}$ ): 2122 (Si–H). Mp: 195 °C.

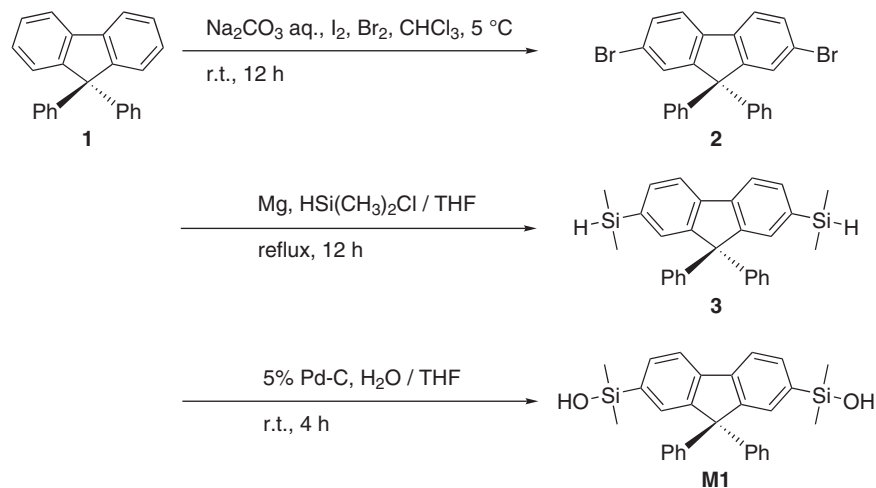
**2,7-Bis(dimethylsilyl)-9,9-diphenyldibenzosilole (6).** The silole **6** was prepared by a method similar to that used in the preparation of **3**, using **5** as the raw material. Yield: 13.76 g (74%) obtained as a colorless plate.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (p.p.m.)=7.94 (s, 2H, dibenzosilolyl protons), 7.89 (d,  $J=7.6$  Hz, 2H, dibenzosilolyl protons), 7.65–7.66 (m, 6H, phenyl protons), 7.37 (d,  $J=7.6$  Hz, 2H, dibenzosilolyl protons), 7.34–7.38 (m, 4H, phenyl protons), 4.45 (sept,  $J=3.7$  Hz, 2H,  $-\text{Si}(\text{CH}_3)_2-\text{H}$ ), 0.36 (d,  $J=3.7$  Hz, 12H,  $-\text{Si}(\text{CH}_3)_2-\text{H}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  (p.p.m.)=149.6, 139.6, 137.1, 136.5, 135.6, 135.3, 132.7, 130.1, 128.1, 120.7,  $-3.66$ . IR (KBr,  $\text{cm}^{-1}$ ): 2124 (Si–H). Mp: 121 °C.

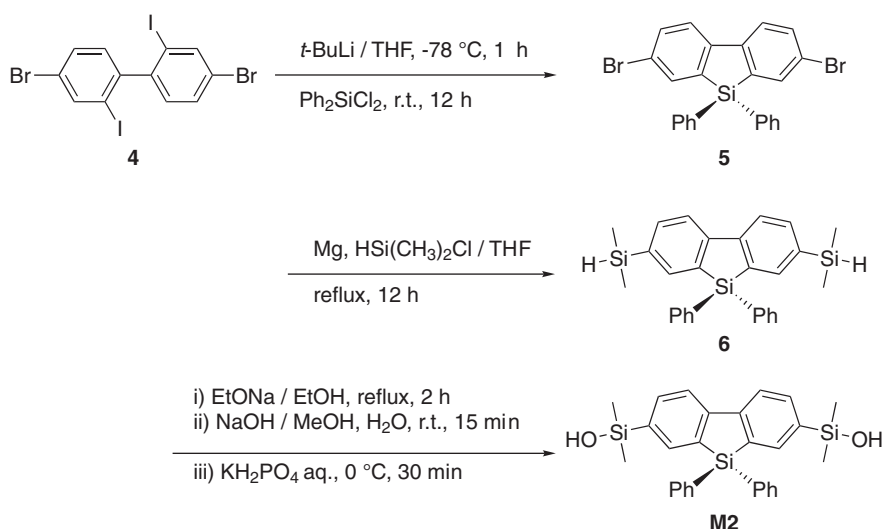
**2,7-Bis(dimethylhydroxysilyl)-9,9-diphenylfluorene (M1).** A THF solution (50 ml) of 2,7-bis(dimethylsilyl)-9,9-diphenylfluorene (**3**, 6.01 g, 13.8 mmol) was added to a mixture of 0.05 g of 5% palladium on charcoal in THF (30 ml) and water (0.67 g, 38.5 mmol) at room temperature. After the reaction mixture was stirred for 4 h, it was filtered using celite. The filtrate was concentrated under reduced pressure. The crude product was recrystallized from toluene to afford **M1** as a colorless solid with a yield of 5.68 g (88%).

$^1\text{H}$  NMR ( $(\text{CD}_3)_2\text{SO}$ , 400 MHz):  $\delta$  (p.p.m.)=7.91 (d,  $J=7.5$  Hz, 2H, fluorenyl protons), 7.60 (s, 2H, fluorenyl protons), 7.56 (d,  $J=7.5$  Hz, 2H, fluorenyl protons), 7.28–7.21 (m, 6H, phenyl protons), 7.09–7.11 (m, 4H, phenyl protons), 5.91 (s, 2H,  $-\text{Si}(\text{CH}_3)_2-\text{OH}$ ), 0.20 (s, 12H,  $-\text{Si}(\text{CH}_3)_2-\text{OH}$ ).  $^{13}\text{C}$  NMR ( $(\text{CD}_3)_2\text{SO}$ , 100 MHz):  $\delta$  (p.p.m.)=149.7, 145.6, 140.5, 132.2, 130.2, 128.3, 128.2, 127.5, 126.5, 119.8, 64.9, 0.6. IR (KBr,  $\text{cm}^{-1}$ ): 3401 (–OH). Mp: 209 °C. Anal. Calcd for  $\text{C}_{29}\text{H}_{30}\text{O}_2\text{Si}_2$ : C, 74.63; H, 6.48. Found: C, 74.63; H, 6.50.

**2,7-Bis(dimethylhydroxysilyl)-9,9-diphenyldibenzosilole (M2).** Under a dry argon atmosphere, sodium (0.5 g) was added to 15 ml of ethanol at room temperature. To the resulting clear solution **6** (2.32 g, 5.15 mmol) was added in ethanol (30 ml). After the reaction mixture was refluxed for 2 h, a solution of sodium hydroxide (0.75 g, 18.75 mmol) in a mixture of water (0.5 ml) and methanol (3.75 ml) was added to the solution, and the reaction mixture was stirred for 15 min. After the reaction mixture was poured into an aqueous solution (50 ml) of potassium dihydrogen phosphate (5.50 g, 40.41 mmol) in



**Scheme 2** Synthetic pathways for 2,7-bis(dimethylhydroxysilyl)-9,9-diphenylfluorene (**M1**).



**Scheme 3** Synthetic pathways for 2,7-bis(dimethylhydroxysilyl)-9,9-diphenyldibenzosilole (**M2**).

an ice bath, it was stirred for 30 min. The crude product was extracted with ethyl acetate, dried over anhydrous magnesium sulfate and filtered. The filtrate was concentrated under reduced pressure. The crude product was recrystallized from the mixed solvent of toluene and hexane to afford **M2** as a colorless powder with a yield of 1.98 g (80%).

$^1\text{H}$  NMR ( $(\text{CD}_3)_2\text{SO}$ , 400 MHz):  $\delta$  (p.p.m.)=8.03 (s, 2H, dibenzosilyllyl protons), 8.02 (d,  $J=7.5$  Hz, 2H, dibenzosilyllyl protons), 7.70 (d,  $J=7.5$  Hz, 2H, dibenzosilyllyl protons), 7.60 (d,  $J=8.2$  Hz, 4H, phenyl protons), 7.46–7.39 (m, 6H, phenyl protons), 5.94 (s, 2H,  $-\text{Si}(\text{CH}_3)_2-\text{OH}$ ), 0.27 (s, 12H,  $-\text{Si}(\text{CH}_3)_2-$

OH).  $^{13}\text{C}$  NMR ( $(\text{CD}_3)_2\text{SO}$ , 100 MHz):  $\delta$  (p.p.m.)=149.1, 140.8, 138.6, 136.0, 135.2, 134.4, 132.5, 130.5, 128.6, 121.0, 0.91. IR (KBr,  $\text{cm}^{-1}$ ): 3367 ( $-\text{OH}$ ). Mp: 188 °C. Anal. Calcd for  $\text{C}_{28}\text{H}_{30}\text{O}_2\text{Si}_3$ : C, 69.66; H, 6.26. Found: C, 69.43; H, 6.57.

### Polymerization procedure

**Synthesis of poly(tetramethyl-9,9-diphenyl-2,7-silfluorenylenesiloxane) (P1).** The catalyst 1,1,3,3-tetramethylguanidinium 2-ethylhexanoate (0.09 g) was added to **M1** (0.957 g, 1.98 mmol) dissolved in toluene (43.5 ml) and the reaction mixture was refluxed for 12 h. The reaction mixture was filtered and poured into 900 ml of methanol to isolate the corresponding polymer as white precipitates. Yield: 0.67 g (73%) as a white solid.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (p.p.m.)=7.62 (d,  $J=7.5$  Hz, 2H, fluorenyl protons), 7.57 (s, 2H, fluorenyl protons), 7.41 (d,  $J=7.5$  Hz, 2H, fluorenyl protons), 7.17–7.11 (m, 10H, phenyl protons), 0.17 (s, 12H,  $-\text{Si}(\text{CH}_3)_2-$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  (p.p.m.)=150.4, 146.1, 141.1, 139.6, 132.1, 130.8, 128.1, 127.4, 126.5, 119.6, 65.6, 0.8. IR (KBr,  $\text{cm}^{-1}$ ): 1000–1100 (Si-O).

**Synthesis of poly(tetramethyl-9,9-diphenyl-2,7-silidibenzosilylenesiloxane) (P2).** **P2** was prepared by a method similar to that used in the preparation of **P1** using **M2** as the monomer. Yield: 0.26 g (90%), obtained from 0.319 g (0.66 mmol) of **M2**.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  (p.p.m.)=7.96 (s, 2H, dibenzosilyllyl protons), 7.76 (d,  $J=7.5$  Hz, 2H, dibenzosilyllyl protons), 7.62 (d,  $J=8.0$  Hz, 6H, phenyl protons), 7.34 (d,  $J=7.5$  Hz, 2H, dibenzosilyllyl protons), 7.27–7.29 (m, 4H, phenyl protons), 0.31 (s, 12H,  $-\text{Si}(\text{CH}_3)_2-$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  (p.p.m.)=149.7, 139.4, 138.6, 135.6, 135.5, 135.2, 132.8, 130.0, 128.1, 120.6, 0.96. IR (KBr,  $\text{cm}^{-1}$ ): 1000–1100 (Si-O).

**Table 1** Results of polycondensation and thermal properties of the obtained polymers

Polymer	Yield (%) <sup>a</sup>	$M_n^b$	$M_w/M_n^c$	$T_g^d$ (°C)	$T_m^e$ (°C)	$T_{d5}^f$ (°C)
<b>P1</b>	73	67 000	1.56	125	276	539
<b>P2</b>	90	52 000	2.36	119	— <sup>g</sup>	520

Abbreviations: **P1**, poly(tetramethyl-9,9-diphenyl-2,7-silfluorenylenesiloxane); **P2**, poly(tetramethyl-9,9-diphenyl-2,7-silidibenzosilylenesiloxane).

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

<sup>b</sup>Number-average molecular weight estimated from size-exclusion chromatography eluted with tetrahydrofuran based on polystyrene standards.

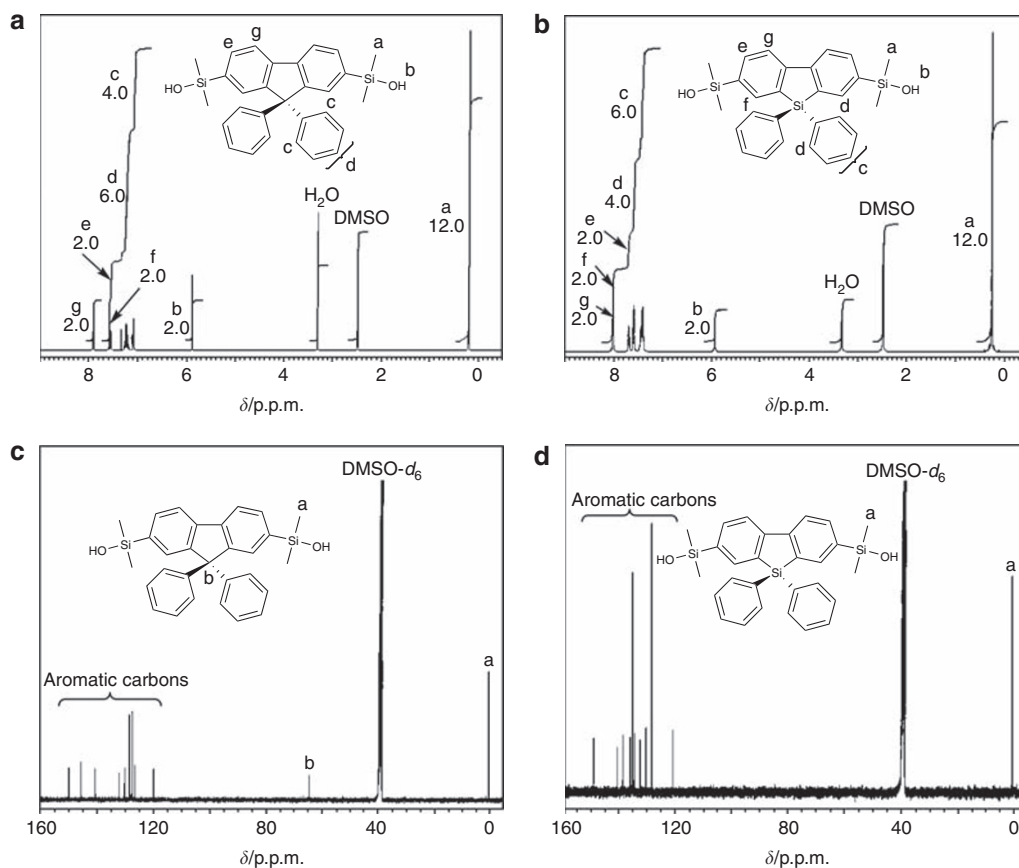
<sup>c</sup>Polydispersity index.

<sup>d</sup>Glass transition temperature determined by differential scanning calorimetry (DSC) at a heating rate of  $10\text{ °C min}^{-1}$  under a nitrogen atmosphere.

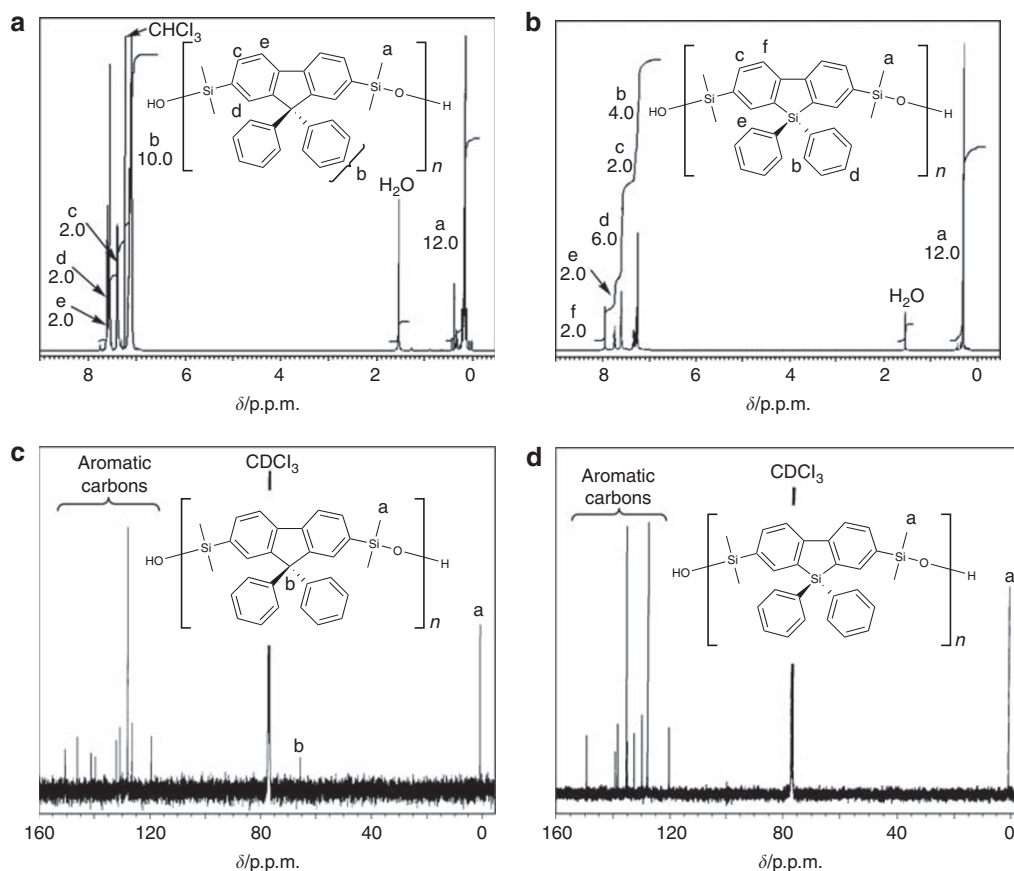
<sup>e</sup>Melting temperature determined by DSC at a heating rate of  $10\text{ °C min}^{-1}$  under a nitrogen atmosphere.

<sup>f</sup>Temperature at 5% weight loss determined by thermogravimetry at a heating rate of  $10\text{ °C min}^{-1}$  under a nitrogen atmosphere.

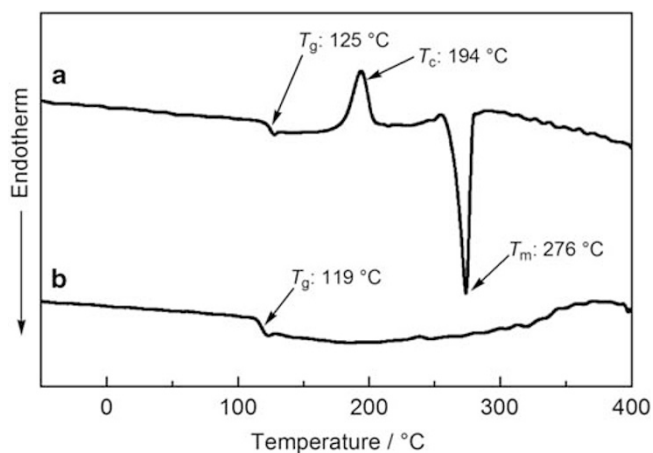
<sup>g</sup>Not observed from  $-50$  to  $400\text{ °C}$ .



**Figure 1**  $^1\text{H}$  nuclear magnetic resonance (NMR; 400 MHz) spectra of (a) 2,7-bis(dimethylhydroxysilyl)-9,9-diphenylfluorene (**M1**) and (b) 2,7-bis(dimethylhydroxysilyl)-9,9-diphenyldibenzosilole (**M2**), and  $^{13}\text{C}$  NMR (100 MHz) spectra of (c) **M1** and (d) **M2** in  $(\text{CD}_3)_2\text{SO}$  at ambient temperature. DMSO, dimethyl sulfoxide.



**Figure 2**  $^1\text{H}$  nuclear magnetic resonance (NMR; 400 MHz) spectra of (a) poly(tetramethyl-9,9-diphenyl-2,7-silfluorenylenesiloxane) (**P1**) and (b) poly(tetramethyl-9,9-diphenyl-2,7-silidibenzosilolylenesiloxane) (**P2**), and  $^{13}\text{C}$  NMR (100 MHz) spectra of (c) **P1** and (d) **P2** in  $\text{CDCl}_3$  at ambient temperature.



**Figure 3** Differential scanning calorimetry traces of (a) poly(tetramethyl-9,9-diphenyl-2,7-silfluorenylenesiloxane) (**P1**) and (b) poly(tetramethyl-9,9-diphenyl-2,7-silidibenzosilolylenesiloxane) (**P2**) during a second heating scan at a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$  under  $\text{N}_2$  flow rate of  $10\text{ ml min}^{-1}$ .

## RESULTS AND DISCUSSION

### Synthesis of monomer and polymer

Scheme 2 and Scheme 3 show the synthetic pathways for disilanol monomers, that is, **M1** and **M2**, respectively.

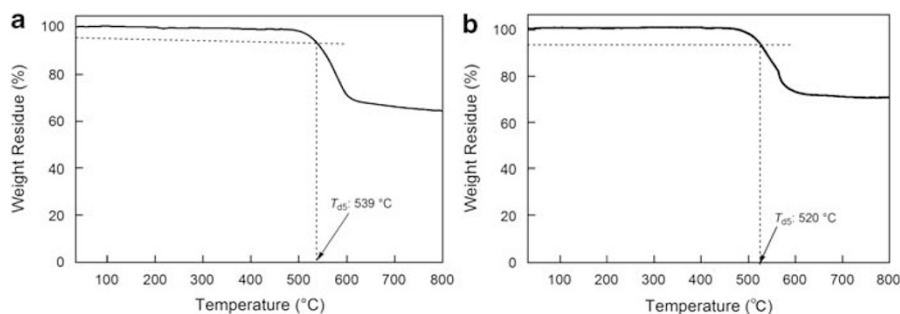
**M1** was obtained by the hydrolysis reaction catalyzed by 5% palladium on charcoal using **3**. The hydrolysis of **6** to afford **M2**

was carried out using sodium ethoxide.<sup>25</sup> We have attempted to obtain **M2** by the hydrolysis reaction using 5% palladium on charcoal as a manner similar to that used in the preparation of **M1**; however, the hydrolysis reaction hardly proceeded and the yield of **M2** was extremely low plausibly because the dimerization reaction<sup>26</sup> would be inclined to occur in the hydrolysis of **6**.

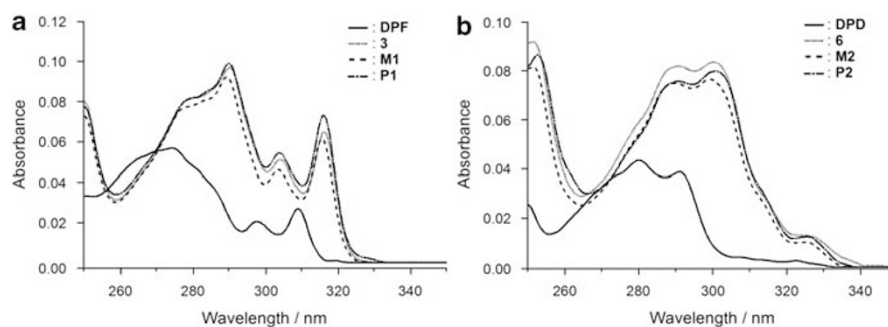
The obtained **M1** and **M2** underwent polycondensation using 1,1,3,3-tetramethylguanidinium 2-ethylhexanoate as a catalyst to afford the corresponding poly(tetramethylsilylarylenesiloxane) derivatives **P1** and **P2**, respectively, as shown in Scheme 1. As reported previously,<sup>21,23</sup> any 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. The results of the polycondensation of **M1** and **M2** are summarized in Table 1.

**P1** and **P2** were obtained with good yields via polycondensation of **M1** and **M2**, respectively, and exhibited good solubility in common organic solvents such as toluene, benzene, chloroform, dichloromethane and THF, although the rigid phenyl substituents were introduced at the 9-position of fluorene or dibenzosilole moiety.

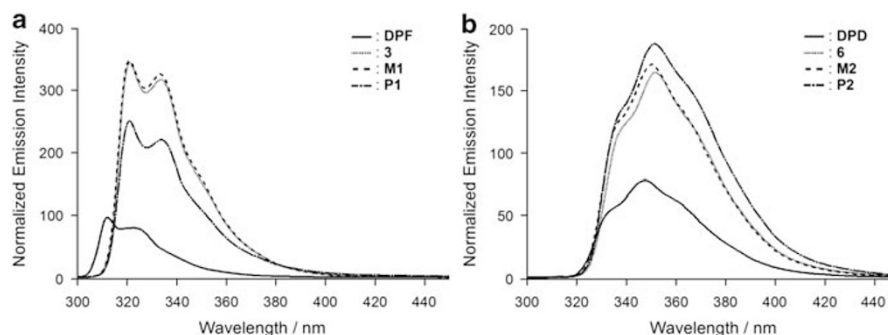
The formation of **P1** and **P2** was confirmed by size-exclusion chromatography measurement and NMR spectroscopy. The size-exclusion chromatography profiles of **P1** and **P2** indicated that the obtained polymers were unimodal and that the low-molecular weight species such as a cyclic dimer or trimer were almost completely removed by reprecipitation in methanol. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **M1** and **M2** are shown in Figure 1, and those of **P1** and **P2** are shown in Figure 2.



**Figure 4** Thermogravimetry curves of (a) poly(tetramethyl-9,9-diphenyl-2,7-silfluorenylenesiloxane) (**P1**) and (b) poly(tetramethyl-9,9-diphenyl-2,7-sildibenzosilolylenesiloxane) (**P2**) at heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  in a nitrogen atmosphere.



**Figure 5** Absorption spectra of (a) diphenylfluorene and (b) diphenyldibenzosilole derivatives in  $\text{CHCl}_3$  solution (conc.  $4.0 \times 10^{-6} \text{ mol l}^{-1}$ ). DPF, 9,9-diphenylfluorene; DPD, 9,9-diphenyldibenzosilole; **3**, 2,7-(dimethylsilyl)-9,9-diphenylfluorene; **6**, 2,7-(dimethylsilyl)-9,9-diphenyldibenzosilole; **M1**, 2,7-bis(dimethylhydroxysilyl)-9,9-diphenylfluorene; **M2**, 2,7-bis(dimethylhydroxysilyl)-9,9-diphenyldibenzosilole; **P1**, poly(tetramethyl-9,9-diphenyl-2,7-silfluorenylenesiloxane); **P2**, poly(tetramethyl-9,9-diphenyl-2,7-sildibenzosilolylenesiloxane).



**Figure 6** Fluorescence spectra of (a) diphenylfluorene and (b) diphenyldibenzosilole derivatives in  $\text{CHCl}_3$  solution (conc.  $4.0 \times 10^{-6} \text{ mol l}^{-1}$ ,  $\lambda_{\text{ex}}$ ; 285 nm) at ambient temperature. The value of the vertical axis in the case of the fluorescence spectra was normalized using the molar extinction coefficient at  $\lambda_{\text{ex}}$ ; 285 nm. DPF: 9,9-diphenylfluorene; DPD: 9,9-diphenyldibenzosilole; **3**, 2,7-(dimethylsilyl)-9,9-diphenylfluorene; **6**, 2,7-(dimethylsilyl)-9,9-diphenyldibenzosilole; **M1**, 2,7-bis(dimethylhydroxysilyl)-9,9-diphenylfluorene; **M2**, 2,7-bis(dimethylhydroxysilyl)-9,9-diphenyldibenzosilole; **P1**, poly(tetramethyl-9,9-diphenyl-2,7-silfluorenylenesiloxane); **P2**, poly(tetramethyl-9,9-diphenyl-2,7-sildibenzosilolylenesiloxane).

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **P1** and **P2** were almost similar to those of **M1** and **M2**, respectively, except the disappearance of a signal at 5.91 or 5.94 p.p.m. based on  $-\text{OH}$  groups as observed in the  $^1\text{H}$  NMR spectrum of **M1** or **M2**. The integrated ratio of each  $^1\text{H}$  NMR signal was consistent with the structure of **P1** and **P2** as described in Figure 2. These results strongly support that no side-reactions occurred during polycondensation.

#### Thermal characterization of polymer

Table 1 also summarizes the thermal characterization of **P1** and **P2**. Figure 3 depicts the DSC thermograms for **P1** and **P2** on a second heating scan.

The glass transition temperatures ( $T_g$ s) of **P1** and **P2** were 125 and  $119\text{ }^{\circ}\text{C}$ , respectively, indicating no remarkable difference in  $T_g$  between **P1** and **P2**. In the meantime, the melting temperature ( $T_m$ ) of **P1** was observed at  $276\text{ }^{\circ}\text{C}$  after the exothermal crystallization at  $194\text{ }^{\circ}\text{C}$  ( $T_c$  in Figure 3); however, neither  $T_m$  nor  $T_c$  was observed in the DSC thermogram of **P2**. This result indicates that **P1** exhibits crystallinity, and the introduction of dibenzosilole moiety in the main chain decreased the crystallization tendency of polymer chains.

In addition, Figure 4 depicts the thermogravimetry curves for **P1** and **P2**.

The 5% weight loss temperatures ( $T_{d5s}$ ) of **P1** and **P2** were determined to be 539 and  $520\text{ }^{\circ}\text{C}$ , respectively, indicating the excellent

**Table 2** Optical properties of diphenylfluorene and diphenyldibenzosilole derivatives

Compound	$\lambda_{abs}/nm$ ( $\epsilon/l mol^{-1}cm^{-1}$ )	$\lambda_{em}/nm^a$	$\Phi_F^b$
9,9-diphenylfluorene	273 (14 300)	310	0.04
	297 (5500)	323	
	309 (7800)		
<b>5</b>	291 (25 300)	310	0.26
	304 (13 500)	321	
	316 (17 800)	334	
<b>M1</b>	290 (24 000)	309	0.27
	304 (12 300)	320	
	316 (17 000)	333	
<b>P1</b>	290 (25 800)	309	0.19
	304 (14 300)	321	
	316 (20 000)	334	
9,9-diphenyldibenzosilole	281 (11 000)	348	0.06
	292 (10 000)		
	320 (750)		
<b>6</b>	253 (23 800)	352	0.19
	300 (21 000)		
	324 (3250)		
<b>M2</b>	252 (21 300)	351	0.20
	300 (19 000)		
	324 (2500)		
<b>P2</b>	253 (22 300)	352	0.23
	300 (20 000)		
	324 (3000)		

Abbreviations: **5**, 2,7-bis(dimethylsilyl)-9,9-diphenylfluorene; **6**, 2,7-bis(dimethylsilyl)-9,9-diphenyldibenzosilole; **M1**, 2,7-bis(dimethylhydroxysilyl)-9,9-diphenylfluorene; **M2**, 2,7-bis(dimethylhydroxysilyl)-9,9-diphenyldibenzosilole; **P1**, poly(tetramethyl-9,9-diphenyl-2,7-silfluorenylenesiloxane); **P2**, poly(tetramethyl-9,9-diphenyl-2,7-silidibenzosilylenesiloxane).

<sup>a</sup>Excited at 285 nm. The concentration was fixed at  $4.0 \times 10^{-6} mol l^{-1}$  as diphenylfluorene or diphenyldibenzosilole unit.

<sup>b</sup>Fluorescence quantum yields ( $\Phi_F$ ) of diphenyldibenzosilole and diphenylfluorene derivatives were measured in  $CHCl_3$  using a HAMAMATSU PHOTONICS absolute PL quantum yield measurement system C9920-02 ( $\lambda_{ex}=285 nm$ ).<sup>24</sup>

thermal stabilities of **P1** and **P2**. Poly(tetramethyl-9,9-dimethyl-2,7-silfluorenylenesiloxane)<sup>21</sup> has been reported to show a  $T_g$  of 67 °C and  $T_{d5}$  of 464 °C; therefore, the introduction of bulky and rigid phenyl substituents onto a fluorene or dibenzosilole skeleton turned out to be effective in the improvement of thermal stability.

### Optical properties

Fluorene-based conjugated polymers have attracted much attention in the field of OLEDs in recent years as mentioned above. Dibenzosilole-based conjugated polymers have also been expected to be new materials for the substitution of fluorene-based conjugated polymers. Therefore, we investigated the optical properties of the obtained diphenylfluorene and diphenyldibenzosilole derivatives, including both monomers and polymers. The absorption and fluorescence spectra of diphenylfluorene and diphenyldibenzosilole derivatives are shown in Figures 5 and 6, respectively.

Table 2 summarizes the optical properties of diphenylfluorene and diphenyldibenzosilole derivatives.

In all present absorption spectra, bathochromic and hyperchromic effects were observed after the introduction of silylene groups onto diphenylfluorene and diphenyldibenzosilole skeletons, presumably because of  $\sigma-\pi$  and  $\sigma^*-\pi^*$  conjugations between the silylene groups and aromatic moieties.<sup>12–17</sup> The bathochromic effect has been known to be induced by lowering the energy gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied

molecular orbital (LUMO) states because of destabilization of the HOMO state through  $\sigma-\pi$  conjugation and stabilization of the LUMO state through  $\sigma^*-\pi^*$  conjugation. The hyperchromic effects result from the enhancement of the transition moment based on 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.<sup>12–17</sup>

On the other hand, the 0–0 electronic transition was observed at around 316 nm in the case of silyl-substituted diphenylfluorene derivatives (**5**, **M1** and **P1**), as shown in Figure 5a, whereas it was observed at around 324 nm in the case of silyl-substituted diphenyldibenzosilole derivatives (**6**, **M2**, and **P2**), as shown in Figure 5b. This bathochromic shift would be due to the stabilization of the LUMO state through  $\sigma^*-\pi^*$  conjugation induced by the replacement of the C-9 carbon in fluorene by silicon. In addition, the absorbance of the 0–0 electronic transition band in the case of silyl-substituted diphenylfluorene derivatives was larger than that of the vibronic band at around 304 nm; meanwhile, the absorbance of the 0–0 electronic transition band in the case of silyl-substituted diphenyldibenzosilole derivatives was smaller than that of the vibronic band at around 313 nm as a shoulder peak. This finding suggests that the molecular structure in the  $S_1$  state for silyl-substituted diphenyldibenzosilole derivatives tends to change. Differences in the shape of the absorption and fluorescence spectra between a series of diphenylfluorene derivatives and those of diphenyldibenzosilole ones are as shown in Figures 5 and 6, that is, the relatively structureless shapes of the absorption and fluorescence spectra of a series of dibenzosilole derivatives were observed. This result also suggests the difference in the tendency for change of molecular structure in the  $S_1$  state between diphenylfluorene and diphenyldibenzosilole derivatives.

In addition, the fluorescence quantum yield ( $\Phi_F$ ) was improved by the introduction of silylene groups into aromatic moieties for both diphenylfluorene and diphenyldibenzosilole derivatives. The  $\Phi_F$  of **P1** was lower than that of **M1**, probably because the crystallization tendency in **P1** results in a relatively strong interaction between the diphenylfluorene units in **P1** that leads to the aggregation of diphenylfluorene units. In addition, the concentration of diphenylfluorene units was so low ( $4.0 \times 10^{-6} mol l^{-1}$  as diphenylfluorene unit) that the aggregate formation may occur through the intramolecular interactions between the diphenylfluorene units. On the other hand, the fluorescence quantum yield of **P2** was higher than that of **M2**, indicating a decrease in the tendency to aggregate using a dibenzosilole skeleton. This result may also be supported by the observation that the introduction of dibenzosilole moiety in the main chain decreases the crystallization tendency of polymer chains. The use of dibenzosilole skeletons was confirmed to be effective in the inhibition of aggregate formation and to result in improved emission intensity.

### CONCLUSION

The syntheses of poly(tetramethylsilylenesiloxane) derivatives with diphenylfluorene and diphenyldibenzosilole moieties were achieved. **P1** and **P2** exhibited good solubility in common organic solvents such as benzene, toluene, chloroform, dichloromethane and THF. There was no significant difference in  $T_g$  between **P1** and **P2**; however, the  $T_m$  of **P1** was observed in spite of the absence of  $T_m$  in the case of **P2**, indicating that the introduction of a dibenzosilole moiety in the main chain decreased the crystallization tendency of polymer chains. The  $T_{d5}$ s of **P1** and **P2** were 539 and 520 °C, respectively, suggesting the excellent thermostability of **P1** and **P2**. As for the optical properties of the obtained diphenylfluorene and diphenyldibenzosilole derivatives, the bathochromic and hyperchromic effects were observed

by introducing dimethylsilyl substituents onto diphenylfluorene and diphenyldibenzosilole skeletons in both the absorption and the fluorescence spectra. The fluorescence quantum yield of **P1** was lower than that of **M1** probably because of the formation of aggregates; however, the fluorescence quantum yield of **P2** was higher than that of **M2**, indicating a decrease in the tendency to aggregate using a dibenzosilole skeleton.

## ACKNOWLEDGEMENTS

This work was partly supported by the Japan Science and Technology Agency through Research for Promoting Technological Seeds 2009 (No. 03-072). We would like to express our appreciation to Dr Yasushi Numata, College of Engineering, Nihon University, for the helpful discussion about optical properties; Ms Satoko Tokiwa and Ms Nami Sugashima, Nihon University College of Engineering Worldwide Research Center for Advanced Engineering and Technology (NEWCAT), for performing NMR measurements and Dr Miki Hasegawa, School of Science and Engineering, Aoyama Gakuin University, for performing the fluorescence quantum yield measurement.

- Andrew, C. G. & Klaus, M. Polyphenylene-type emissive materials: poly(para-phenylene)s, polyfluorenes, and ladder polymers. *Adv. Polym. Sci.* **199**, 1–82 (2006).
- Leclerc, M. Polyfluorenes: twenty years of progress. *J. Polym. Sci., Part A: Polym. Chem.* **39**, 2867–2873 (2001).
- Neher, D. Polyfluorene homopolymers: conjugated liquid-crystalline polymers for bright blue emission and polarized electroluminescence. *Macromol. Rapid Commun.* **22**, 1365–1385 (2001).
- Scherf, U. & List, E. J. W. Semiconducting polyfluorenes: towards reliable structure-property relationship. *Adv. Mater.* **14**, 477–487 (2002).
- Gaal, M., List, E. J. W. & Scherf, U. Excimer or emissive on-chain defects? *Macromolecules* **36**, 4236–4237 (2003).
- List, E. J. W., Guentner, R., Guentner, R., Scanducci de, F. P. & Scherf, U. The effect of keto defect sites on the emission properties of polyfluorene-type materials. *Adv. Mater.* **14**, 374–378 (2002).
- Cho, S. Y., Grimsdale, A. C., Jones, D. J., Watkins, S. E. & Holmes, A. B. Polyfluorenes without monoalkylfluorene defects. *J. Am. Chem. Soc.* **129**, 11910–11911 (2007).
- Trimpin, S., Grimsdale, A. C., Räder, H. J. & Müllen, K. Characterization of an insoluble poly(9,9-diphenyl-2,7-fluorene) by solvent-free sample preparation for MALDI-TOF mass spectrometry. *Anal. Chem.* **74**, 3777–3782 (2002).
- Chan, K. L., McKiernan, M. J., Towns, C. R. & Holmes, A. B. Poly(2,7-dibenzosilole): a blue light emitting polymer. *J. Am. Chem. Soc.* **127**, 7662–7663 (2005).
- Wong, W. W. H. & Holmes, A. B. Poly(dibenzosilole)s. *Adv. Polym. Sci.* **212**, 85–98 (2008).
- Yamaguchi, S., Endo, T., Uchida, M., Izumizawa, T., Furukawa, K. & Tamao, K. Toward new materials for organic electroluminescent devices: synthesis, structures, and properties of a series of 2,5-diaryl-3,4-diphenylsiloles. *Chem. Eur. J.* **6**, 1683–1692 (2000).
- Shizuka, H., Sato, Y., Ueki, Y., Ishikawa, M. & Kumada, M. The  $2p\pi^* - 3d\pi$  interaction in aromatic silanes. Fluorescence from the  ${}^1(2p\pi, 3d\pi)$  intramolecular charge-transfer state. *J. Chem. Soc., Faraday Trans. 1* **80**, 341–357 (1984).
- Declercq, D., Delbeke, P., De Schryver, F. C., Van Meervelt, L. & Miller, R. D. Ground- and excited-state interaction in di-1-pyrenyl substituted oligosilanes. *J. Am. Chem. Soc.* **115**, 5702–5708 (1993).
- Kyushin, S., Ikuragi, M., Goto, M., Hiratsuka, H. & Matsumoto, H. Synthesis and electronic properties of 9,10-disilylanthracenes. *Organometallics* **15**, 1067–1070 (1996).
- Maeda, H., Inoue, Y., Ishida, H. & Mizuno, K. UV absorption and fluorescence properties of pyrene derivatives having trimethylsilyl, trimethylgermyl, and trimethylstannyl groups. *Chem. Lett.* **30**, 1224–1225 (2001).
- Imai, K., Sasaki, T., Abe, J., Kimoto, A., Tamai, Y. & Nemoto, N. Synthesis of novel poly(tetramethyl-2,7-silpyrenylenesiloxane) and its thermal and optical properties. *Polym. J.* **41**, 584–585 (2009).
- Imai, K., Hatano, S., Kimoto, A., Abe, J., Tamai, Y. & Nemoto, N. Optical and electronic properties of siloxane-bridged cyclic dimers with naphthylene or pyrenylene moieties. *Tetrahedron* **66**, 8012–8017 (2010).
- Kitamura, N. & Yamamoto, T. Carbon-silicon coupling between fluorenyl Grignard reagents and dichlorosilanes for synthesis of novel copolymers and chemical properties of the copolymers. *Appl. Organomet. Chem.* **17**, 840–842 (2003).
- Mark, J. E. in *Silicon-Based Polymer Science* (ed. Ziegler, J.M. & Gordon, F.W.), Ch. 2 47–68 (American Chemical Society, 1990).
- Brook, M. A. *Silicon in Organic, Organometallic, and Polymer Chemistry* 256–308 (John Wiley & Sons, Inc, New York, 2000).
- Nemoto, N., Yamaguchi, T., Ozawa, Y., Nigorikawa, M., Yanai, Y. & Nagase, Y. Synthesis and thermal characterization of novel fluorene-based polysiloxane derivatives. *Polym. Bull.* **61**, 165–175 (2008).
- Wong, K.-T., Wang, Z.-J., Chien, Y.-Y. & Wang, C.-L. Synthesis and properties of 9,9-diarylfuorene-based triaryldiamines. *Org. Lett.* **3**, 2285–2288 (2001).
- Otomo, Y., Nagase, Y. & Nemoto, N. Synthesis and properties of novel poly(tetramethylsilylnaphthylenesiloxane) derivatives. *Polymer* **46**, 9714–9724 (2005).
- Kawamura, Y., Sasabe, H. & Adachi, C. Simple accurate system for measuring absolute photoluminescence quantum efficiency in organic solid-state thin films. *Jpn. J. Appl. Phys.* **43**, 7729–7730 (2004).
- Merker, R. L. & Scott, M. J. Preparation and properties of poly(tetramethyl-*p*-silylphenylene-siloxane). *J. Polym. Sci.: Part A* **2**, 15–29 (1964).
- Barnes Jr, G. H. & Daughenbaugh, N. E. The preparation of organosilanol by the metal-catalyzed reaction of organosilicon hydrides with water. *J. Org. Chem.* **31**, 885–887 (1966).