

Synthesis and properties of poly(tetramethyl-1,6-silpyrenylenesiloxane) derivative with phenyl groups on pyrenylene moiety

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Abstract Poly(tetramethyl-1,6-silpyrenylenesiloxane) derivative with phenyl groups on pyrenylene moieties (**P1**) was prepared via polycondensation of disilanol monomer, i.e. 1,6-bis(dimethylhydroxysilyl)-3,8-diphenylpyrene (**M1**). **P1** exhibited the very high glass transition temperature (T_g) of 191 °C. The temperature at 5% weight loss (T_{d5}) of **P1** was 482 °C, indicating the relatively good thermostability of **P1**. **P1** exhibited the bathochromic effect in the absorption and fluorescence spectra, indicating the expansion of π -conjugation by introducing phenyl groups onto pyrene skeleton as well as the σ – π and σ^* – π^* conjugation between pyrene and silyl moieties. In addition, **P1** exhibited relatively weak excimer emission because of the inhibition of the excimer formation of pyrene skeleton by introduction of bulky phenyl groups onto pyrene skeleton. The fluorescence quantum yields (Φ_{FS}) of **M1** and **P1** in chloroform were determined to be 0.46 and 0.37, respectively. It was revealed that **M1** and **P1** exhibited the higher fluorescence intensity than 1,6-diphenylpyrene, owing to the effect of the introduction of silyl moieties onto pyrene skeleton.

Keywords Pyrene · Poly(tetramethylsilpyrenylenesiloxane) · Heat-resistant polymer · Fluorescence emission

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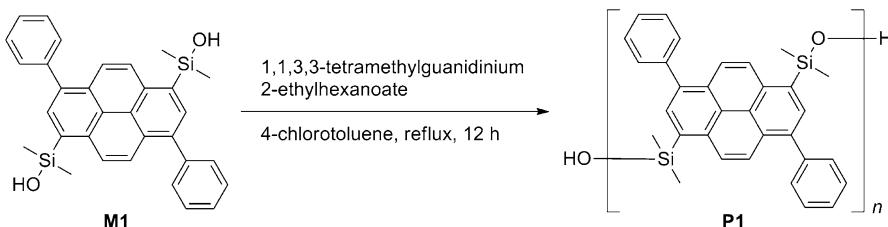
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Introduction

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, while PDMS has the low glass transition temperature (T_g : ca. $-120\text{ }^\circ\text{C}$) because of the flexible siloxane bonding [1]. On the other hand, poly(tetramethyl-silarylenesiloxane)s where the aromatic moieties are introduced into the main chain of PDMS have been reported to exhibit the excellent thermostability as well as PDMS and the T_g depending on the arylene moieties introduced. Thus, we have reported the synthesis of poly(tetramethylsilarylenesiloxane) derivatives having various aromatic moieties as arylene moieties [2–6]. It has been also reported that these derivatives show bathochromic and hyperchromic effects in the absorption spectra [5, 6] by the silyl groups introduced onto aromatic moieties owing to the $\sigma^*-\pi^*$ interaction between silyl and aromatic moieties [7–12]. On the other hand, pyrene is one of interesting compounds because it shows excimer emission in the fluorescence spectra at the high concentration and/or in the solid state [13–16]. We have reported the optical properties of poly(tetramethyl-2,7-silpyrenenesiloxane) which exhibits the excimer emission as well as good fluorescence quantum yield (Φ_F : 0.39) in chloroform solution [5].

Meanwhile, various substituted pyrene compounds such as 1,3,6,8-tetraphenyl-[17], 1,3,6,8-tetrakis(trimethylsilyl)- [18], and 1,3,6,8-tetrakis(trimethylsilyl ethynyl)-pyrene [18–20] have been reported to show the excellent fluorescence quantum yields (Φ_F : 0.56–0.99). Thus, pyrene and substituted pyrenes have much attracted interests in various fields such as biological application [13], molecular recognition chemistry [14], and organic light-emitting diodes (OLEDs) [15]. Furthermore, Kawano et al. [16] reported the synthesis and optical property of poly(2,7-pyrenylene)s which show blue emission in the fluorescence spectrum of the high concentrated solution, meaning that π – π interaction of pyrene moieties in polymer would be prevented by bulky alkylphenyl groups introduced onto pyrene.

From these of points of view, we report here the synthesis of poly(tetramethyl-1,6-silpyrenenesiloxane) with phenyl groups introduced onto 3,8-positions of pyrene skeleton as shown in Scheme 1. The thermal and optical properties of the obtained polymer are also described.



Scheme 1 Polycondensation of 1,6-bis(dimethylhydroxysilyl)-3,8-diphenylpyrene (**M1**)

Experimental part

Materials

1,6-Dibromopyrene (**1**) was prepared by the method in the literature [21]. Chloroform (CHCl_3 , KANTO KAGAKU), *N,N,N',N'*-tetramethylmethylenediamine (TMEDA, Tokyo Kasei Kogyo Co., Inc.), *N,N*-dimethylformamide (DMF, Wako Pure Chemical Industries, Ltd.), 1-bromobenzene (KANTO KAGAKU), and 4-chlorotoluene (Tokyo Kasei Kogyo Co., Inc.) were used after distillation over calcium hydride. Toluene (KANTO KAGAKU) and tetrahydrofuran (THF, KANTO KAGAKU) were used after distillation over sodium. *N*-Bromosuccinimide (NBS, Tokyo Kasei Kogyo Co., Inc.) was purified by recrystallized from distilled water. Tetrakis(triphenylphosphine)palladium [$\text{Pd}(\text{PPh}_3)_4$, Wako Pure Chemical Industries, Ltd.], 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Tokyo Kasei Kogyo Co., Inc), 1.6 and 2.6 mol/L of *n*-butyllithium in hexane solution (KANTO KAGAKU), chlorodimethylsilane (Acros organics), and 5% palladium on charcoal (Escat 103, from Aldrich) were used as received. 1,1,3,3-Tetramethylguanidinium 2-ethylhexanoate was prepared according to the literature [2].

Measurements

^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVANCE 400F spectrometer in deuterated chloroform (CDCl_3) or dimethylsulfoxide [$(\text{CD}_3)_2\text{SO}$] at ambient temperature. Infrared (IR) spectra were measured on a PerkinElmer Spectrum One FT-IR spectrometer. Melting temperature (T_m) and glass transition temperature (T_g) were determined by differential scanning calorimetry (DSC) on a RIGAKU ThermoPlus DSC 8230 at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ under a nitrogen flow rate of 10 mL min^{-1} . Thermogravimetry (TG) was performed on a RIGAKU ThermoPlus TG8110 at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ 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. The purity of all prepared compounds with low-molecular weight was confirmed to be over 99% by GC analysis. Absorption and fluorescence spectra were measured on a SHIMADZU UV-2450 and a JASCO FP-6500 spectrophotometer, respectively, using chloroform solutions degassed by argon bubbling for 30 min with the fixed concentration of $1.0 \times 10^{-6}\text{ mol/L}$ as diphenylpyrene unit. Fluorescence quantum yields were measured using a HAMAMATSU PHOTONICS C9920-02 absolute PL quantum yield measurement system [22]. The optimized geometrical structures, the highest occupied molecular orbital (HOMO), and the lowest unoccupied molecular orbital (LUMO) energies were estimated by the density functional theory (DFT) calculations (B3LYP/6-31G(d) level of theory) using Spartan'08 for Windows (Wavefunction, Inc., Irvine, CA, USA) [23].

Preparation of 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxabororane (2)

Under a dry argon atmosphere, 1.6 mol/L of *n*-butyllithium (8.48 mL, 13.56 mmol) in hexane was added to 1-bromobenzene (1.789 g, 11.39 mmol) in dry THF (50 mL) at -78°C . The reaction mixture was stirred for 1 h at -78°C , then, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxabororane (2.524 g, 13.57 mmol) was added to this reaction mixture at room temperature. After the reaction mixture was stirred for 12 h, it was poured into water. The crude product was extracted with chloroform, and the combined organic layer was dried over magnesium sulfate and filtered. The filtrate was concentrated and dried under reduced pressure to afford **2** as pale yellow liquid with the yield of 87% (2.03 g, 9.95 mmol).

^1H NMR (400 MHz, CDCl_3 , ppm): δ 7.81 (d, $J = 7.5$ Hz, 2H, phenyl protons), 7.43 (t, $J = 7.4$ Hz, 1H, phenyl proton), 7.36 (t, $J = 7.5$ Hz, 2H, phenyl protons), 1.35 (s, 12H, methyl protons). ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ 134.7 (phenyl carbons), 131.3 (phenyl carbons), 127.7 (phenyl carbons), 83.8 (boronic ester carbons), 24.9 (methyl carbons).

Preparation of 1,6-diphenylpyrene (3)

Under a dry argon atmosphere, 2.0 mol/L of potassium carbonate aqueous solution (127.6 mL) was added dropwise to a mixture of **1** (1.493 g, 4.147 mmol), tetrakis(triphenylphosphine)palladium (0.479 g, 0.415 mmol), and **2** (2.03 g, 9.95 mmol) at 60°C . After the reaction mixture was stirred for 12 h at 60°C , it was poured into water. The crude product was extracted with ethyl acetate, and the combined organic layer was washed 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 the mixed solvent of chloroform/hexane (v/v = 1/1). The fraction with an R_f value of 0.82 was collected and concentrated under reduced pressure. The residue was recrystallized from the mixed solvent of toluene and methanol to afford **3** as pale yellow plates with the yield of 73% (1.07 g, 3.02 mmol).

^1H NMR (400 MHz, CDCl_3 , ppm): δ 8.22–8.18 (m, 4H, pyrenyl protons), 8.04 (d, $J = 9.2$ Hz, 2H, pyrenyl protons), 7.99 (d, $J = 7.8$ Hz, 2H, pyrenyl protons), 7.66–7.63 (m, 4H, phenyl protons), 7.59–7.55 (m, 4H, phenyl protons), 7.52–7.48 (m, 2H, phenyl protons). ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ 141.27 (phenyl carbons), 137.82 (pyrenyl carbons), 130.61 (pyrenyl carbons), 130.38 (phenyl carbons), 128.82 (pyrenyl carbons), 128.36 (phenyl carbons), 127.76 (phenyl carbons), 127.45 (pyrenyl carbons), 127.23 (pyrenyl carbons), 124.46 (pyrenyl carbons), 125.27 (pyrenyl carbons), 125.17 (pyrenyl carbons), T_m : 220 °C.

Preparation of 1,6-dibromo-3,8-diphenylpyrene (4)

Under a dry argon atmosphere, after a mixture of **3** (0.100 g, 0.282 mmol), DMF (3.92 mL) and NBS (0.121 g, 0.680 mmol) was stirred for 8 h at 80°C , water (2 mL) was added to this reaction mixture. Then, the reaction mixture was filtered.

After the obtained precipitate was washed with water and methanol, it was recrystallized from toluene to afford **4** as pale yellow needles with the yield of 62% (0.090 g, 0.176 mmol).

¹H NMR (400 MHz, CDCl₃, ppm): δ 8.45 (d, J = 9.5 Hz, 2H, pyrenyl protons), 8.04 (s, 2H, pyrenyl protons), 8.24 (d, J = 9.5 Hz, 2H, pyrenyl protons), 7.8–7.5 (m, 10H, phenyl protons).

Preparation of 1,6-bis(dimethylsilyl)-3,8-diphenylpyrene (**5**)

Under a dry argon atmosphere, after 2.6 mol/L *n*-butyllithium (0.376 mL, 0.978 mmol) in hexane was added dropwise to a mixture of **4** (0.100 g, 0.195 mmol), THF (5 mL) and *N,N,N',N'*-tetramethylethylenediamine (0.114 g, 0.980 mmol), the reaction mixture was stirred for 2 h at –78 °C. Chlorodimethylsilsilane (0.046 g, 0.486 mmol) was added to this reaction mixture at room temperature and stirred overnight. The reaction mixture was poured into 0.2 mol/L of HCl aqueous solution (100 mL), and the crude product was extracted with chloroform. The combined organic layer was washed with saturated sodium hydrogen carbonate aqueous solution, 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 the mixed solvent of chloroform/hexane (v/v = 1/2). The fraction with an R_f value of 0.66 was collected and concentrated under reduced pressure. The residue was recrystallized from the mixed solvent of toluene and hexane to afford **5** as colorless needles with the yield of 40% (0.037 g, 0.079 mmol).

¹H NMR (400 MHz, CDCl₃, ppm): δ 8.36 (d, J = 9.4 Hz, 2H, pyrenyl protons), 8.22 (d, J = 9.4 Hz, 2H, pyrenyl protons), 8.17 (s, 2H, pyrenyl protons), 7.7–7.6 (m, 4H, phenyl protons), 7.6–7.5 (m, 4H, phenyl protons), 7.5–7.4 (m, 2H, phenyl protons), 5.06 [sept, J = 3.8 Hz, 2H, –Si(CH₃)₂–H], 0.58 [d, J = 3.8 Hz, 12H, –Si(CH₃)₂–]. ¹³C NMR (100 MHz, CDCl₃, ppm): δ 141.4 (phenyl carbons), 137.1 (pyrenyl carbons), 135.0 (pyrenyl carbons), 134.0 (phenyl carbons), 132.6 (pyrenyl carbons), 130.7 (phenyl carbons), 129.6 (phenyl carbons), 128.4 (pyrenyl carbons), 127.7 (pyrenyl carbons), 127.3 (pyrenyl carbons), 125.4 (pyrenyl carbons), 125.0 (pyrenyl carbons), –2.88 [–Si(CH₃)₂–]. IR (KBr, cm^{–1}): 2153 (Si–H), T_m : 255 °C.

Preparation of 1,6-bis(dimethylhydroxysilyl)-3,8-diphenylpyrene (**M1**)

A THF solution (20 mL) of **5** (0.215 g, 0.457 mmol) was added to a mixture of 5% palladium on charcoal (0.002 g) in THF (5 mL) and water (0.022 g, 0.112 mmol) at room temperature. After the reaction mixture was stirred for 12 h, it was filtered using Celite. The filtrate was concentrated under reduced pressure. The residue was purified by recrystallization from the mixed solvent of toluene and hexane to afford **M1** as colorless plates with the yield of 75% (0.172 g, 0.342 mmol).

¹H NMR [400 MHz, (CD₃)₂SO, ppm]: δ 8.56 (d, J = 9.5 Hz, 2H, pyrenyl protons), 8.21 (s, 2H, pyrenyl protons), 8.14 (d, J = 9.5 Hz, 2H, pyrenyl protons), 7.6–7.3 (m, 10H, phenyl protons), 6.37 [s, 2H, –Si(CH₃)₂–OH], 0.53 [s, 12 H, –Si(CH₃)₂–]. ¹³C NMR [100 MHz, (CD₃)₂SO, ppm]: δ 140.93 (phenyl carbons),

136.51 (pyrenyl carbons), 136.17 (pyrenyl carbons), 134.31 (phenyl carbons), 133.68 (pyrenyl carbons), 128.36 (phenyl carbons), 127.76 (phenyl carbons), 127.45 (pyrenyl carbons), 130.56 (pyrenyl carbons), 129.09 (pyrenyl carbons), 128.81 (pyrenyl carbons), 128.40 (pyrenyl carbons), 2.31 [−Si(CH₃)₂−]. IR (KBr, cm^{−1}): 3310 (−OH).

Polycondensation

To **M1** (0.120 g, 0.239 mmol) dissolved in 4-chlorotoluene (1.89 mL), was added 1,1,3,3-tetramethylguanidinium 2-ethylhexanoate (0.09 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 52% (0.060 g).

¹H NMR (400 MHz, CDCl₃, ppm): δ 8.43 (d, *J* = 9.5 Hz, 2H, pyrenyl protons), 8.08 (s, 2H, pyrenyl protons), 7.93 (d, *J* = 9.5 Hz, 2H, pyrenyl protons), 7.5–7.0 (m, 10H, phenyl protons), 0.62 [s, 12H, −Si(CH₃)₂−]. ¹³C NMR (100 MHz, CDCl₃, ppm): δ 141.2 (phenyl carbons), 136.7 (pyrenyl carbons), 134.6 (pyrenyl carbons), 134.2 (phenyl carbons), 133.4 (pyrenyl carbons), 130.4 (phenyl carbons), 129.4 (phenyl carbons), 128.4 (pyrenyl carbons), 128.0 (pyrenyl carbons), 126.8 (pyrenyl carbons), 125.2 (pyrenyl carbons), 124.9 (pyrenyl carbons), 2.61 [−Si(CH₃)₂−]. IR (KBr, cm^{−1}): 1000–1100 (Si–O).

Results and discussion

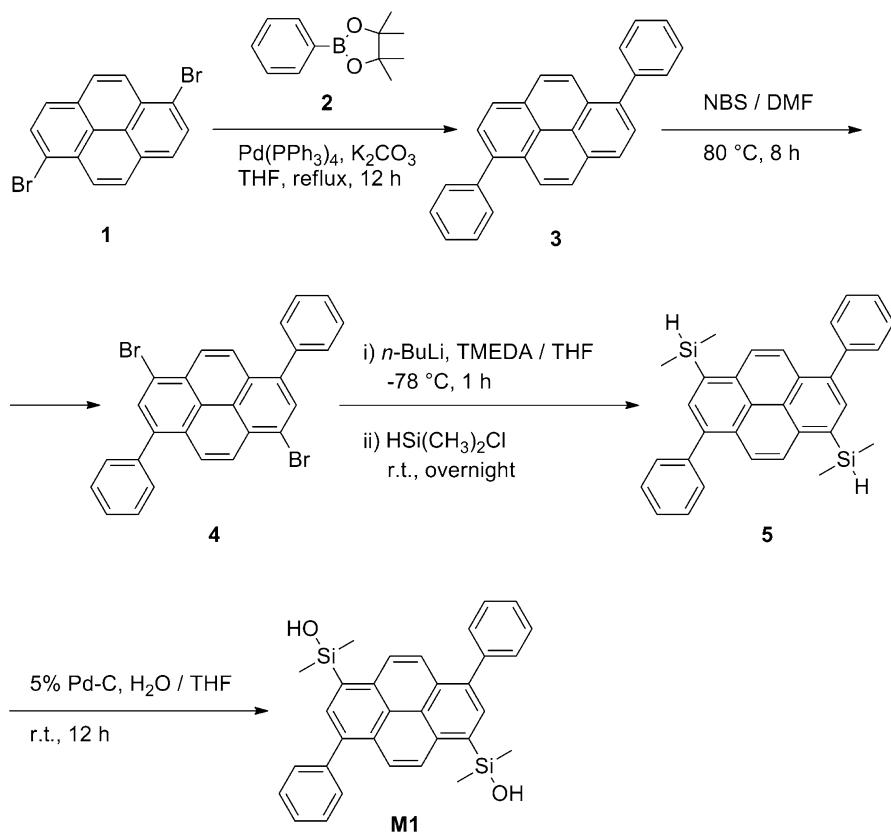
Synthesis of monomer

Scheme 2 shows the synthetic pathway of a disilanol monomer (**M1**). 1,6-Diphenylpyrene (**3**) was synthesized by the Suzuki cross coupling reaction between 1,6-dibromopyrene (**1**) and phenyl boronic acid pinacol ester (**2**) using Pd(PPh₃)₄ as a catalyst. 1,6-Dibromo-3,8-diphenylpyrene (**4**) was synthesized by bromination reaction of **3** using *N*-bromosuccinimide (NBS). 1,6-Bis(dimethylsilyl)-3,8-diphenylpyrene (**5**) was synthesized by lithiation reaction of **4** using *n*-butyllithium at −78 °C and successive reaction with chlorodimethylsilane. **M1** was synthesized by the hydrolysis reaction of **5** using 5% palladium on charcoal. Thus, the structure of the obtained **M1** was confirmed by the ¹H and ¹³C NMR spectra as described in Fig. 1, where each signal was consistently assigned.

Synthesis and thermal characterization of polymer

Poly(tetramethyl-1,6-silpyrenylenesiloxane) derivative with phenyl groups (**P1**) was synthesized by polycondensation reaction of **M1** using 1,1,3,3-tetramethylguanidinium 2-ethylhexanoate as a catalyst [2–6]. Results of polycondensation and characterization of **P1** are summarized in Table 1.

In general, any solvents forming azeotropic mixtures with water and dissolving both monomer and the resulting polymer, such as benzene and toluene, can be used



Scheme 2 Synthetic pathway of disilanol monomer (**M1**)

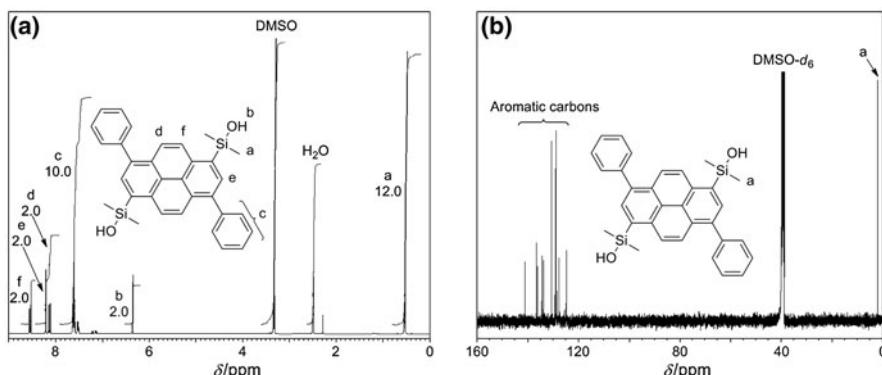


Fig. 1 **a** ^1H NMR (solvent: $(\text{CD}_3)_2\text{SO}$, 400 MHz, numerals at signal's side are the integral values of each signal) and **b** ^{13}C NMR spectra (solvent: $(\text{CD}_3)_2\text{SO}$, 100 MHz) of **M1** at ambient temperature

Table 1 Results of polycondensation of **M1** and characterization of **P1**

Polymer	Yield (%) ^a	M_n^b	M_w/M_n^c	T_g^d (°C)	T_m^e (°C)	T_{d5}^f (°C)
P1	52	13000	1.70	191	— ^g	482

^a Insoluble part in methanol

^b Number-average molecular weight estimated from SEC eluted with tetrahydrofuran based on polystyrene standards

^c Molecular-weight dispersity

^d Glass transition temperature determined by DSC at a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere

^e Melting temperature determined by DSC at a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere

^f Temperature at 5% weight loss determined by thermogravimetry at a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere

^g Not observed from –50 to 400 °C on the DSC thermogram

for the similar polycondensation of **M1** as reported previously [2–6]; however, **M1** exhibits the relatively poor solubility in benzene and toluene. Thus, 4-chlorotoluene, in which both **M1** and **P1** exhibit the relatively good solubility, was used for the present polycondensation of **M1**. In addition, too low concentration of monomer resulted in the formation of not polymer but the corresponding cyclic compounds [2–6]. In contrast, too high concentration of **M1** in polycondensation resulted in the low yield of **P1**, presumably because **P1** with the very high molecular weight would exhibit the relatively low solubility in the solvent used and resulted in the low yield of **P1** [24]. The number-average molecular weight (M_n) and molecular-weight dispersity (M_w/M_n) of **P1** were determined by SEC measurement to be 13,000 and 1.70, respectively. The SEC profile of **P1** indicated that the obtained polymer was unimodal and that the low molecular-weight species as a cyclic dimer or trimer were almost completely removed by reprecipitation in methanol.

Figure 2 depicts the ¹H and ¹³C NMR spectra of **P1**, where each signal was also assigned consistently. The ¹H and ¹³C NMR spectra of **P1** were almost similar to those of **M1**, except the disappearance of a signal of 6.37 ppm based on hydroxy groups as observed in the ¹H NMR spectrum of **M1**. The integrated ratio of each ¹H NMR signal was consistent with the structure of **P1** as described in Fig. 2a. These results support that no side-reactions occurred during the polycondensation of **M1**.

On the other hand, glass transition temperature (T_g) of **P1** was determined to be 191 °C from DSC measurement as depicted in Fig. 3, and no melting temperature (T_m) of **P1** was observed in the DSC thermogram, indicating that the obtained **P1** would be an amorphous polymer. As far as we know, the T_g of poly(tetramethylsilsil-fluorenylenesiloxane) derivative having spirofluorenyl moiety at 9-position of fluorenylene moiety has been reported to be 156 °C [4] and highest among those of poly(tetramethylsilsilarylenesiloxane) derivatives reported so far. Thus, the present **P1** was revealed to exhibit extremely high T_g , plausibly because the bulky diphenylpyrenylene moieties would inhibit the motion of the main chain. In addition, the temperature at 5% weight loss (T_{d5}) of **P1** was determined to be 482 °C from thermogravimetry (TG), indicating the relatively good thermostability of **P1**.

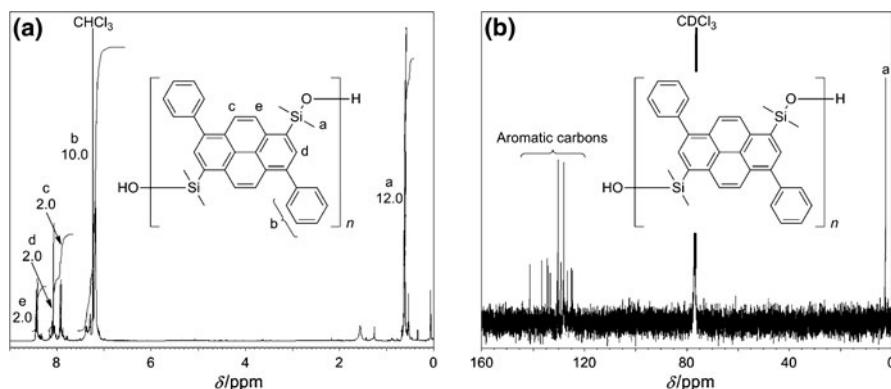
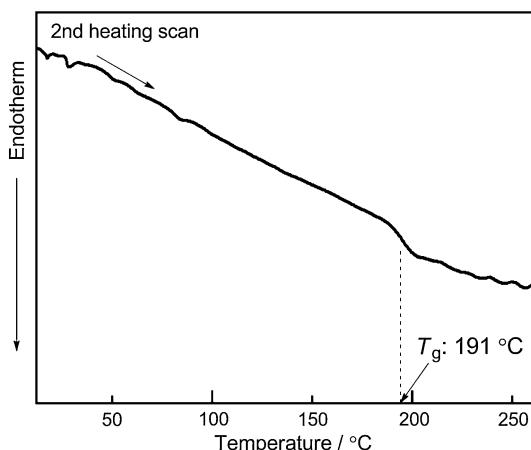


Fig. 2 **a** ^1H NMR (solvent: CDCl_3 , 400 MHz, numerals at signal's side are the integral values of each signal) and **b** ^{13}C NMR spectra (solvent: CDCl_3 , 100 MHz) of **P1** at ambient temperature

Fig. 3 DSC thermogram of **P1** on a second heating scan under a nitrogen flow rate of 10 mL/min and heating or cooling rate of 10 $^{\circ}\text{C}/\text{min}$



Optical characterization of the obtained 1,6-diphenylpyrene derivatives

Next, the optical properties of the obtained 1,6-diphenylpyrene derivatives in the present study were investigated. Figure 4 depicts the absorption and fluorescence spectra of 1,6-diphenylpyrene derivatives, and the optical properties of the obtained 1,6-diphenylpyrene derivatives are summarized in Table 2.

In the absorption spectra of 1,6-diphenylpyrene (**3**), the wavelength of maximum absorption (λ_{abs}) was red-shifted from that of pyrene, meaning the expansion of the π -conjugation system by the introduction of phenyl groups onto pyrene skeleton.

In addition, bathochromic effect was observed in the absorption spectra of silyl-substituted compounds such as **5** and **M1**, owing to $\sigma-\pi$ and $\sigma^*-\pi^*$ interaction between silyl and aromatic moieties [5–9]. It has been known that the bathochromic effect is induced by lowering the energy gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) states

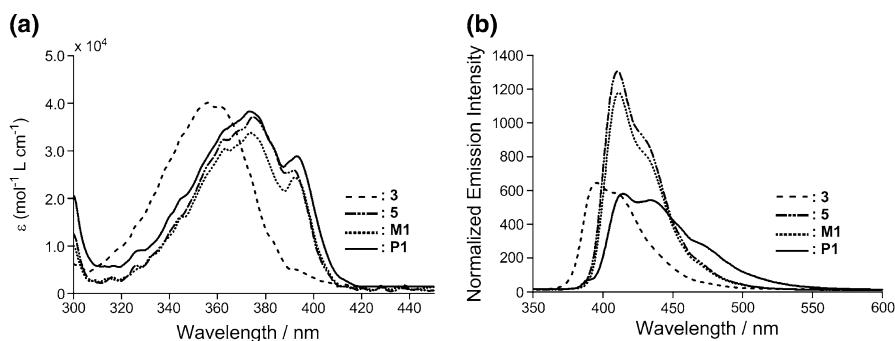


Fig. 4 **a** Absorption spectra (in CHCl_3 ; conc. 1.0×10^{-6} mol/L) and **b** fluorescence spectra of diphenylpyrene derivative (in CHCl_3 ; conc. 1.0×10^{-6} mol/L; $\lambda_{\text{ex}} = 338$ nm) at ambient temperature. The value of the vertical axis in the case of the fluorescence spectra was normalized using the molar extinction coefficient at $\lambda_{\text{ex}} = 338$ nm

Table 2 Optical characterization of diphenylpyrene derivatives in CHCl_3 solution

Compound	$\lambda_{\text{abs}}/\text{nm} (\varepsilon/\text{L mol}^{-1} \text{cm}^{-1})$	$\lambda_{\text{em}}/\text{nm}^{\text{a}}$	Φ_F^{b}
Pyrene	309 (8000)	374	0.19 ^c
	322 (24000)	385	
	338 (38000)	393	
3	356 (40000)	395	0.29
5	375 (37000)	411	0.52
	393 (25000)		
M1	374 (34000)	411	0.46
	392 (24000)		
P1	374 (38000)	413	0.37
	393 (29000)		

^a Excited at 338 nm. The concentration was fixed at 1.0×10^{-6} mol L^{-1} as diphenylpyrene unit

^b Fluorescence quantum yields (Φ_F) of diphenylpyrene derivatives were measured in CHCl_3 using a HAMAMATSU PHOTONICS absolute PL quantum yield measurement system C9920-02 ($\lambda_{\text{ex}} = 338$ nm) [22]

^c From Ref. [5]

because of both destabilization of HOMO state through σ – π conjugation and stabilization of LUMO state through σ^* – π^* conjugation [7–12].

We calculated the HOMO and LUMO energy levels of pyrene, **3** and **M1** with density functional theory (DFT) method at the B3LYP/6-31G(d) level of theory for the confirmation of the effects of the introduction of phenyl groups and silyl moieties on the absorption spectra. Table 3 summarizes the HOMO and LUMO energy levels of pyrene, **3** and **M1**. The difference in the LUMO energy level between pyrene (-1.48 eV) and **3** (-1.60 eV) and that in the HOMO energy level between pyrene (-5.33 eV) and **3** (-5.15 eV) mean that stabilization of LUMO

Table 3 Results of DFT calculation for pyrene derivatives

Compound	LUMO/eV ^a	HOMO/eV ^a	LUMO–HOMO gap/eV
Pyrene	−1.48	−5.33	3.85
3	−1.60	−5.15	3.55
M1	−1.73	−5.13	3.40

^a Calculated with density-functional theory (DFT) method at the B3LYP/6-31G(d) level of theory

state and destabilization of HOMO state through the expansion of π -conjugation are induced by the introduction of phenyl groups on pyrene skeleton. In addition, the difference in the LUMO energy level between **3** (−1.60 eV) and **M1** (−1.73 eV) and that in the HOMO energy level between **3** (−5.15 eV) and **M1** (−5.13 eV) mean that stabilization of LUMO state through $\sigma^*-\pi^*$ conjugation and destabilization of HOMO state through $\sigma-\pi$ conjugation are induced by the introduction of silyl moieties. Thus, the introduction of silyl moieties onto diphenylpyrene caused the decrease in the energy gap between LUMO and HOMO, resulting in the bathochromic shift of the maximum absorption.

The wavelength at maximum emission (λ_{em}) and fluorescence quantum yield (Φ_F) of the obtained pyrene derivatives are also summarized in Table 2. In the fluorescence spectra of pyrene derivatives, bathochromic effects were observed by the introduction of phenyl groups onto pyrene skeleton, and further bathochromic effects were observed in the fluorescence spectra of **5** and **M1**. In addition, **P1** exhibited relatively weak excimer emission, comparing the excimer emission of **P1** with that of poly(tetramethyl-2,7-silypyrenylene)siloxane) [5], plausibly because of the inhibition of the excimer formation of pyrene skeleton by introduction of bulky phenyl groups onto pyrene skeleton.

The fluorescence quantum yield (Φ_F) of silyl-substituted diphenylpyrene was improved. Further detailed analysis of photochemical processes including the determination of the rate constants as radiative rate constant, intersystem crossing rate constant, and non-radiative rate constant would be necessary for the clarification of the reason for the increase in Φ_F ; however, the plausible reasons for the increase in Φ_F are as follows [11]. The intersystem crossing rate constant becomes negligible owing to the energy stabilization of the first singlet excited state (S_1) by silyl substitution to result in the change of the relative energy position against the second triplet excited state (T_2) as observed in the case of silyl-substituted certain aromatic compounds [7, 8, 10, 11]. On the other hand, the Φ_F of **P1** was lower than that of **M1**, probably because the interactions between the diphenylpyrene units in **P1**, which are not so strong to form the excimers, lead to the aggregation of diphenylpyrene units. In addition, the concentration of diphenylpyrene units was so low (1.0×10^{-6} mol/L as diphenylpyrene unit) that the aggregate formation may occur through the intramolecular interactions between the diphenylpyrene units in **P1** [6]. Namely, it is plausibly because the intramolecular energy transfer in **P1** that the Φ_F of **P1** is lower than that of **M1**.

Conclusions

We achieved synthesis of poly(tetramethyl-1,6-silpyrenylenesiloxane) derivative with phenyl groups on the pyrenylene moieties (**P1**), which was obtained by polycondensation of 1,6-bis(dimethylhydroxysilyl)-3,8-diphenylpyrene (**M1**). **P1** exhibited the very high T_g and the relatively good thermostability. **P1** also exhibited the bathochromic effect in the absorption and fluorescence spectra as well as the higher fluorescence emission intensity than pyrene, indicating the expansion of conjugation by introducing phenyl groups and silyl moieties onto pyrene skeleton. The Φ_{fs} of **M1** and **P1** in chloroform solution were 0.46 and 0.37, respectively.

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