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Synthesis and characterization of poly(tetramethylsilarylenesiloxane) derivatives bearing benzodithiophene moieties

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ABSTRACT

Poly(tetramethylsilarylenesiloxane) derivatives bearing benzo[1,2-*b*;4,5-*b*′]dithiophene (**P1**) and benzo[2,1-*b*;3,4-*b*′]dithiophene (**P2**) moieties were prepared via polycondensation of the corresponding disilanol monomers, that is, 2,6-bis(dimethylhydroxysilyl)benzo[1,2-*b*;4,5-*b*′]dithiophene (**M1**) and 2,7-bis(dimethylhydroxysilyl)benzo[2,1-*b*;3,4-*b*′]dithiophene (**M2**), respectively. It was deduced that **P1** is a crystalline polymer while **P2** is an amorphous one from the results of differential scanning calorimetry (DSC). Bathochromic and hyperchromic effects were observed in the absorption and fluorescence spectra when dimethylsilyl substituents were introduced on the benzo[1,2-*b*;4,5-*b*′]dithiophene and benzo[2,1-*b*;3,4-*b*′]dithiophene skeletons. The fluorescence quantum yields (Φ_Fs) were not improved by the introduction of dimethylsilyl groups onto the benzo[1,2-*b*;4,5-*b*′]dithiophene and benzo[2,1-*b*;3,4-*b*′]dithiophene skeletons, whereas the improvement in the Φ_Fs was remarkable in the case of poly(tetramethylsilarylenesiloxane) derivatives that possessed the corresponding fused benzene ring systems, i.e., poly(tetramethyl-2,6-silanthrylenesiloxane) and poly(tetramethyl-1,8-silphenanthrylenesiloxane).

1. Introduction

Conjugated polymers [1,2] obtained via the polymerization of fused-ring derivatives have emerged as attractive materials for flexible, low-cost and low-power electro-optic devices. Thiophene-containing fused-aromatic compounds represent an interesting class of electronic materials that are used for organic conductors [3,4], narrow band gap polymers [5,6], and field-effect transistors (FET) [7,8]. Moreover, benzodithiophene (BDT) has two thiophene rings that are fused with a benzene ring. The benzene core decreases the electron richness of the flanked bithiophene unit, which provides a low-lying energy level of highest occupied molecular orbital (HOMO) [9–11]. BDT derivatives have a near-planar molecular plane, which would be conducive for establishing a close molecular π–π stacking order for efficient charge carrier transport to afford high FET mobility [7,12].

Furthermore, the incorporation of silyl substituents onto aromatic species has been reported [13–22] to result in a high fluorescence quantum yield. The use of polysiloxane derivatives as polymeric organic light-emitting diode (OLED) materials appears to be inadequate because of their low glass transition temperatures (T_gs) [23,24], which allow the formation of aggregates and/or interchain excimers to induce a decrease in the color stability of light emission. However, the other properties of polysiloxanes, such as good thermostability and stability against atomic oxygen [23–26], appear to be appropriate for polymeric OLED materials. Therefore, increasing the T_gs of polysiloxane derivatives would be desirable for overcoming their disadvantages for OLEDs. One of the methods for increasing the T_g is to incorporate bulky and rigid moieties into the main chain [27–33]. For example, the T_g of poly(dimethylsiloxane) has been reported to be −123 °C [23]; however, those of a series of poly(tetramethylsilarylenesiloxane) derivatives have been reported to range from −52 °C to 191 °C depending on the arylene moiety introduced in the main chain [17–20,28–33]. From these points of view, we have reported the synthesis of several poly(tetramethylsilarylenesiloxane) derivatives with pyrene [17], dibenzosilole [19] or cyclopentadithiophene [33] moieties that exhibited high T_gs and good thermostability and fluorescence properties. In particular, cyclopenta[2,1-*b*:3,4-*b*′]dithiophene [34,35] is regarded as an analogous compound of fluorene in which the benzene rings are replaced by thiophene rings, and it is composed of a fused bithiophene ring and an attractive compound. It has been reported that fluorene derivatives exhibit relatively high fluorescence quantum yields [36,37]; however, cyclopenta[2,1-*b*:3,4-*b*′]dithiophene exhibits a low fluorescence quantum yield [33].

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Namely, cyclopenta[2,1-*b*:3,4-*b*′]dithiophene possesses distinct fluorescence properties compared to fluorene derivatives. In addition, it has been reported that the fluorescence quantum yields of cyclopenta[2,1-*b*:3,4-*b*′]dithiophene derivatives are considerably improved by the incorporation of dimethyl-, methylphenyl-, or diphenyl-silyl substituents [33]. Therefore, we have been interested in the various properties of poly(tetramethylsilarylenesiloxane) derivatives with fused aromatic rings in which the benzene rings are replaced by thiophene rings. Moreover, benzo[1,2-*b*;4,5-*b*′]dithiophene and benzo[2,1-*b*;3,4-*b*′]dithiophene are also regarded as analogous compounds of anthracene and phenanthrene, respectively, in which two benzene rings at both ends are replaced by two thiophene rings; therefore, our attention has been focused on investigating the differences in the thermal and optical properties between poly(tetramethylsilarylenesiloxane) derivatives with BDT moieties and those with anthracene or phenanthrene moieties.

In this article, we report the syntheses of novel poly(tetramethylsilarylenesiloxane) derivatives bearing benzo[1,2-*b*;4,5-*b*′]dithiophene (**P1**) or benzo[2,1-*b*;3,4-*b*′]dithiophene (**P2**) moieties, as shown in Scheme 1. The effects of introducing benzo[1,2-*b*;4,5-*b*′]dithiophene (**P1**) or benzo[2,1-*b*;3,4-*b*′]dithiophene (**P2**) moieties into poly(tetramethylsilarylenesiloxane) derivatives on the thermal and optical properties were investigated. In addition, the distinct fluorescence properties of poly(tetramethylsilarylenesiloxane) derivatives bearing benzo[1,2-*b*;4,5-*b*′]dithiophene (**P1**) or benzo[2,1-*b*;3,4-*b*′]dithiophene (**P2**) moieties from poly(tetramethyl-2,6-silanthrylenesiloxane) or poly(tetramethyl-1,8-silphenanthrylenesiloxane), respectively, will also be discussed.

2. Experimental

2.1. Materials

Benzo[1,2-*b*;4,5-*b*′]dithiophene (**1**) [38] and benzo[2,1-*b*;3,4-*b*′]dithiophene [39] (**3**) were prepared using the method reported in the literature. *n*-Butyllithium in hexane (1.6 mol/L) (KANTO KAGAKU), 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) and benzene were used after distilling over sodium. 1,1,3,3-Tetramethylguanidinium 2-ethylhexanoate was obtained from an equimolar mixture of 1,1,3,3-tetramethylguanidine and 2-ethylhexanoic acid (Tokyo Kasei Kogyo Co., Inc.) [29–33]. 2,6-Bis(dimethylsilyl)anthracene (**ANT1**), 2,6-bis(dimethylhydroxysilyl)anthracene (**Ma**), poly(tetramethyl-2,6-silanthrylenesiloxane) (**Pa**), 1,8-(dimethylsilyl)phenanthrene (**PHN1**), 1,8-bis(dimethylhydroxysilyl)phenanthrene (**Mb**), and poly(tetramethyl-1,8-silphenanthrylenesiloxane) (**Pb**) were prepared using a previously reported method [30].

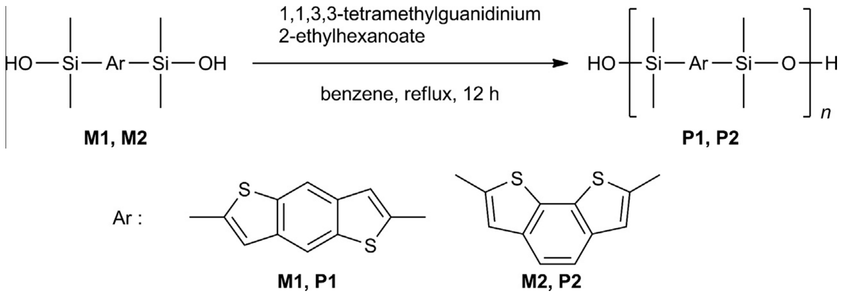
2.2. Measurements

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 400F spectrometer in deuterated chloroform ($CDCl_3$) or dimethylsulfoxide [$(CD_3)_2SO$] at ambient temperature. IR spectra were measured on a Perkin–Elmer Spectrum One FT-IR spectrometer. The 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/cooling rate of 10 °C/min under nitrogen at a flow rate of 10 mL/min. Thermogravimetric analysis (TGA) was performed on a RIGAKU ThermoPlus TG8110 at a heating rate of 10 °C/min under a nitrogen atmosphere. The 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), eluting with THF and using a calibration curve of polystyrene standards. Gas chromatography mass spectroscopy (GC/MS) was conducted 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 using a solution that was degassed by argon bubbling for 30 min. The fluorescence quantum yields (Φ_Fs) were determined using anthracene (Φ_F: 0.27) [40] 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 through density functional theory (DFT) calculations at the B3LYP/6-31G(d) level of theory using Spartan ’08 for Windows (Wavefunction, Inc., Irvine, CA, USA) [41].

2.3. Synthesis of 2,6-bis(dimethylsilyl)benzo[1,2-b;4,5-b′]dithiophene (2)

Under a dry argon atmosphere, 1.6 mol/L *n*-butyllithium in hexane (3.8 mL, 6.31 mmol) was added dropwise to **1** (0.400 g, 2.10 mmol) in dry THF (21 mL) at 0 °C, and the mixture was stirred for 30 min. After the mixture was stirred for 1 h at ambient temperature, chlorodimethylsilane (0.796 g, 8.41 mmol) was added to this solution. The reaction mixture was stirred for 22 h at ambient temperature and poured into 20 mL of water with stirring. The crude product was extracted with ethyl acetate. The combined organic layer was washed several times with water, dried over anhydrous sodium sulfate and filtered. The filtrate was concentrated under reduced pressure and purified by silica gel chromatography using hexane as the eluent. The collected fraction with an R_f value of 0.40 was concentrated under reduced pressure, and the residue was recrystallized from a mixed solvent of chloroform/methanol to afford **2** as colorless crystals with a yield of 81% (0.52 g, 1.70 mmol).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.29 (s, 2H, aromatic protons), 7.53 (s, 2H, aromatic protons), 4.63 (m, 2H, $-Si(CH_3)_2-H$),



Scheme 1. Polycondensation of 2,6-bis(dimethylhydroxysilyl)benzo[1,2-*b*;4,5-*b*′]dithiophene (**M1**) and 2,7-bis(dimethylhydroxysilyl)benzo[2,1-*b*;3,4-*b*′]dithiophene (**M2**).