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Nanosized starlike molecules. Synthesis and optical properties of 2,4, 6-tris(disilanylenebithienylene)-1,3,5-triazine derivatives

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ABSTRACT

Starlike molecules (**5**) and (**7**) that have a triazine unit as a core and arms consisting of an alterative arrangement of an Si–Si bond and bithienylene unit were prepared by the Pd-catalyzed reactions of 2,4,6-tris [5-(1,3-dioxa-4,4,5,5-tetramethyl-2-borolanyl)-2-thienyl]triazine with 5-bromothienylpentamethyldisilane and with 1-(5-bromothienyl)-2-bithienyltetramethyldisilane, respectively. In the UV–vis absorption and fluorescence spectra, **5** and **7** showed absorption maxima in a range of 398–399 nm, and revealed higher fluorescence quantum yields than that of 2,4,6-tris(bithienyl)triazine.

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1. Introduction

The nanosized starlike molecules bearing arms that extend to three directions have attracted much attention, because they show interesting behavior due to their unique molecular structures. Several types of the starlike molecules with conjugated π -electron systems in their arms have been prepared and their optical properties have been investigated so far [1]. However, little interest has been shown in the chemistry of the nanosized starlike molecules with the arms that have an alternating arrangement of an Si–Si bond and a π -electron unit, which extend to three directions, although Ponomarenko and his coworkers have reported the synthesis and optical properties of compounds including both silylene and bithienylene units in the arms [2].

We have reported the synthesis and optical properties of several types of the nanosized starlike molecules: the molecules bearing a methyltris(silyl)silane unit as a core and the arms consisting of a regular alternating arrangement of an Si–Si bond and bithieny-lene unit [3], the starlike molecules with the same core and oligothienylene units as the arms [4], and the molecules including

1,3,5-tris- and 1,2,4,5-tetrakis(silyl)benzene as a core and bithienylene—disilanylene units in the arms [5]. We have found that the starlike molecules show novel optical properties, such as high fluorescence quantum yields and long lifetimes of the excited state. We have also found that these molecules can be used as the functional device materials, such as optical recording materials [6] and semiconductors in field-effect transistors [7].

It has been reported that 1,3,5-triazine compounds show good optical and electrochemical properties, due to their electron deficiency [8]. We considered that the starlike molecules bearing triazine ring system as a core would show interesting optical behavior. In this paper, we report the synthesis and optical properties of the starlike molecules with a 1,3,5-triazine unit as a core and three arms consisting of a regular alternating arrangement of a silicon–silicon bond and a bithienylene group.

2. Results and discussion

The method used for the synthesis of the present starlike compounds bearing a 1,3,5-triazine unit as a core and an alternative arrangement of an Si–Si bond and bithienylene–disilanylene unit as arms is based on the Pd-catalyzed Suzuki–Miyaura cross-coupling reaction [9]. The starting compound, 2,4,6-tris[5-(1,3-dioxa-4,4,5,5-





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$$\begin{split} & \mathsf{MeSi}\left[\begin{array}{c} \mathsf{Me}_{2}\mathsf{Si} + \begin{pmatrix} \mathsf{S} \\ \mathsf{Ne}_{2}\mathsf{Si} + \begin{pmatrix} \mathsf{S} \\ \mathsf{Si} + \begin{pmatrix} \mathsf{Si} \\ \mathsf{Si} + \begin{pmatrix} \mathsf{Si} + \begin{pmatrix} \mathsf{S} \\ \mathsf{Si} + \begin{pmatrix} \mathsf{Si} \\ \mathsf{Si} + \begin{pmatrix} \mathsf{Si} + (\mathsf{Si} + \begin{pmatrix} \mathsf{Si}$$

tetramethyl-2-borolanyl)-2-thienyl]triazine (**4**) was prepared by a series of the reactions, as shown in Schemes 1 and 2. First, we synthesized 2,4,6-trithienyltriazine (**2**) by the Grignard crosscoupling reaction, which was developed by Kumada and Tamao [10]. Thus, the reaction of 2,4,6-trichlorotriazine (**1**) with thienylmagnesium bromide in the presence of a catalytic amount of NiCl₂(dppe) in THF afforded compound **2** in 58% yield. Treatment of **2** thus obtained with *N*-bromosuccinimide (NBS) in chloroform gave 2,4,6-tris(5-bromothienyl)triazine (**3**) in 85% yield (Scheme 1). The structures of **2** and **3** were verified by mass and ¹H, ¹³C spectrometric analysis, as well as by elemental analysis (see Experimental section).



We synthesized compound **4** by the two-step reaction using the bromo compound **3** in 72% yield: conversion of **3** into the lithio derivative by treating with *n*-BuLi, and the reaction of the resulting lithio derivative with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Scheme 2). All spectral data including mass



spectrum and also its elemental analysis are wholly consistent with those of the structure proposed for compound **4** (see Experimental section).

Compound **4** was used as the starting compound for the synthesis of the starlike molecules with the arms extended to the three directions. The starlike compound, 2,4,6-tris(5'-pentamethyl-disilanylbithienyl)triazine (5) was prepared by the Pd-catalyzed crosscoupling reaction of 2-(5-bromothienvl)pentamethyldisilane with 4. The product 5 was isolated from the resulting reaction mixture, using a silica gel column in 30% yield. The structure of 5 was confirmed by mass and, ¹H, ¹³C, and ²⁹Si NMR spectrometric analysis. In fact, mass spectrometric analysis for **5** indicates the molecular ion at m/z 963, corresponding to the calculated value for C₄₂H₅₇N₃Si₆S₆. The ¹H NMR spectrum of **5** shows two signals at 0.14 and 0.41 ppm due to the two kinds of methylsilyl protons, and thienyl ring protons. The ¹³C NMR spectrum of **5** reveals two resonances at -2.8 and -2.4 ppm, attributed to the methylsilyl carbons, eight resonances at 124.6, 126.3, 132.4, 135.0, 139.4, 140.7, 142.0, and 144.0 ppm due to the thienyl ring carbons and a single resonance at 167.0 ppm attributable to the triazine carbon. The ²⁹Si NMR spectrum reveals two signals at -23.7, -19.2 ppm, due to the two different kinds of the silicon atoms. These results are wholly consistent with the structure proposed for 5 (Schemes 3 and 4).

Similar methods were used for the synthesis of the molecules, which have more elongated π -electron systems than those of **5**. Thus, the Suzuki–Miyaura coupling of compound **4** with 1-(5-bromothienyl)-2-bithienyltetramethyldisilane (**6**) [11] in MeOH gave 2,4,6-tris(bithienyltetramethyldisilanylenebithienylene)triazine (**7**) in 23% yield (Scheme 4). The structure of **7** was verified by mass and, ¹H, ¹³C, and ²⁹Si NMR spectrometric analysis (see Experimental section).

2.1. Optical properties of starlike molecules 5 and 7

The UV-visible absorption spectra and fluorescence spectra of compounds **5** and **7** are summarized in Table 1, where the data for relevant compounds, bithiophene, 2,4,6-tris(bithienyl)-1,3,5-(8), the starlike molecules having a 1,3,5triazine dimethylsilvlphenyl moiety as a core and the arms consisting of a regular alternating arrangement of a silicon-silicon bond and bithienylene unit (9 and 10), and a linear polymer with an alternative arrangement of a disilanylenebithienylene unit, poly[(tetraethyldisilanylene)bithienylene] (11) reported previously [12], are also included for comparison (Figs. 1-3). The present starlike molecules 5 and 7 show absorption maxima in the range of 398–399 nm. These bands are red-shifted by 60–80 nm from those of the starlike molecules **9** and **10**. In the fluorescence spectra, the emission maximum of **5** and **7** display a marked red shift of about 60 nm compared with those of compounds 9 and 10. The quantum yields of compounds 5 and 7 are much higher than those of 9 and 10, bithiophene, and poly[(tetraethyldisilanylene)bithienylene] 11. The absorption bands and emission maxima of compounds 5 and 7 with the disilarly groups shift bathochromically in comparison with those of 8, which has no silyl groups. The electronic effects of the silvl groups on the thiophene ring have been studied in terms of the molecular orbital calculations by Kyushin et al. [13]. The bathochromic shift of the absorption band may be explained by $\sigma - \pi$ and $\sigma^* - \pi^*$ conjugation between the Si-C(methyl) orbitals and thiophene orbitals. The quantum yields of compounds 5 and 7 are higher than that of **8**. Compound **7** has a quantum vield of 0.96. Mizuno et al. [14] have reported that the fluorescence intensities of silvl-substituted aromatic compounds are stronger than those of unsubstituted ones.



Table 1
Absorption and emission data (in dioxane) for compounds 5 and 7 in comparison
with related compounds.

Compd	$\lambda_{max,Abs}$ (nm)	$\lambda_{\max,F}(nm)$	${\Phi_{\mathrm{F}}}^{\mathrm{a}}$
5	398	451	0.67
7	399	452	0.96
Bithiophene	303	362	0.018
8	386	437	0.57
9	321	388	0.39
10	335	381, 394	0.41
11	343	383, 397	0.33

^a Based on quinine sulfate ($\phi_{366} = 0.546$) as a standard.

In conclusion, the starlike molecules that have a triazine unit as a core and arms consisting of an alterative arrangement of an Si–Si bond and bithienylene unit were synthesized by the Pd-catalyzed reactions of 2,4,6-tris[5-(1,3-dioxa-4,4,5,5-tetramethyl-2-borolanyl)-2-thienyl]triazine with 5-bromothienyldisilanyl derivatives. In the UV–vis absorption and fluorescence spectra, **5** and **7** show absorption maxima in a range of 398–399 nm, and reveal high fluorescence quantum yields.

3. Experimental

3.1. General procedures

All reactions were performed under an atmosphere of dry nitrogen. NMR spectra were recorded on a JNM-LA300 spectrometer and JNM-LA500 spectrometer. Low-resolution mass spectra were measured on a JEOL Model JMS-700 instrument. High-resolution mass spectra were obtained from a Thermo Fisher Scientific LTQ Orbitrap XL. UV–visible absorption spectra were measured with a JASCO V-560 spectrometer in dioxane. Fluorescence spectra were measured with a JASCO V-560 spectrometer in dioxane. Fluorescence spectra were measured with a JASCO FP-777 spectrometer in dioxane. Melting points were measured with a Yanaco-MP-S3 apparatus. Column chromatography was performed by using Wakogel C-300 (WAKO). Diethyl ether and THF used as the solvents were distilled from sodium/benzophenone ketyl, just before use.

3.1.1. 2,4,6-Trithienyl-1,3,5-triazine (2)

In a 300 mL two-necked flask equipped with a stirrer, reflux condenser, and dropping funnel was placed a solution of 2-thienylmagesium bromide prepared from 3.768 g (0.155 mol) of magnesium and 25.340 g (0.155 mol) of 2-bromothiophene in 200 mL of THF. To this was added 0.831 g (1.59 mmol) of NiCl₂(dppe) and then 6.466 g (34.5 mmol) of 2,4,6-trichloro-1,3,5-triazine in 30 mL of THF. The mixture was heated to reflux for 12 h and hydrolyzed with dilute aqueous hydrochloric acid. The organic layer was separated, washed with water and dried over anhydrous



Fig. 1. UV–vis spectra of **5** and **7** in 10^{-5} M dioxane solution.



Fig. 2. Fluorescence spectra of **5** and 7 in 10^{-5} M dioxane solution ($\lambda_{ex} = \lambda_{UV-max}$).

magnesium sulfate. After the solvent was evaporated, compound **2** (6.607 g, 58% yield) was isolated by recrystallization with hexane–chloroform (5:1) as an orange solid. Anal. Calcd for C₁₅H₉N₃S₃: C, 55.02; H, 2.77; N, 12.83. Found: C, 55.04; H, 2.49; N, 12.47. Mp. 187 °C; MS *m*/*z* 327 (M⁺); ¹H NMR (δ CDCl₃) 7.22 (t, 3H, *J* = 4.6 Hz, thienyl ring protons) 7.63 (d, 3H, *J* = 4.6 Hz, thienyl ring protons); ¹³C NMR (δ CDCl₃) 128.4, 131.7, 132.3, 141.5 (thienylene carbons), 167.7 (triazine carbon).

3.1.2. 2,4,6-Tris(bromothienyl)-1,3,5-triazine (3)

In a 100 mL two-necked flask was placed 1.023 g (3.10 mmol) of compound **1** in 50 mL of chloroform. To this was added 6.563 g (36.9 mmol) of *N*-bromosuccinimide (NBS). The mixture was stirred for 6 days at room temperature and hydrolyzed with dilute aqueous hydrochloric acid. The organic layer was separated, washed with water and dried over anhydrous magnesium sulfate. After the solvent was evaporated, compound **3** (1.485 g, 85% yield) was isolated by recrystallization from chloroform as a white solid. Anal. Calcd for C₁₅H₆N₃S₃Br₃: C, 31.94; H, 1.07; N, 7.45. Found: C, 32.03; H, 1.00; N, 7.38. Mp. 243 °C; MS *m*/*z* 561 (M⁺); ¹H NMR (δ CDCl₃) 7.17 (d, 3H, *J* = 4.0 Hz, thienyl ring protons) 7.96 (d, 3H, *J* = 4.0 Hz, thienyl ring protons), 132.0, 142.1 (thienylene carbons), 166.7 (triazine carbon).

3.1.3. Synthesis of compound 4

In a 200 mL two-necked flask equipped with a stirrer, reflux condenser, and dropping funnel was placed 1.721 g (3.05 mmol) of compound 2 in 100 mL of THF. To this was added 3.45 mL (13.78 mmol) of a 1.54 M n-butyllithium-hexane solution at -80 °C. The mixture was stirred for 1 h at -80 °C, and then to this was added 2.456 g (13.27 mmol) of 2-isopropoxy-4,4,5,5tetramethy-1,3,2-dioxaborolane in 5 mL of THF. The mixture was stirred overnight at room temperature and hydrolyzed with dilute aqueous hydrochloric acid. The organic layer was separated, washed with water and dried over anhydrous magnesium sulfate. After the solvent was evaporated, compound 4 (1.613 g, 72% yield) was isolated by recrystallization from hexane as a yellow solid. Anal. Calcd for C₃₃H₄₂B₃N₃O₆S₃: C, 56.19; H, 6.00; N, 5.96. Found: C, 56.60; H, 6.21; N, 5.69. Mp. >300 °C; MS m/z 705 (M⁺); ¹H NMR (δ $CDCl_3$) 1.38 (s, 36H, CH_3), 7.68 (d, 3H, J = 3.4 Hz, thienyl ring protons), 8.28 (d, 3H, J = 3.4 Hz, thienyl ring protons); ¹³C NMR (δ CDCl₃) 24.8 (CH₃), 84.8 (CO), 132.2, 137.6, 147.5 (thienylene carbons), 167.7 (triazine carbon).

3.1.4. Synthesis of compound 5

In a 200 mL two-necked flask was placed 1.012 g (1.43 mmol) of compound **3**, 1.529 g (5.21 mmol) of 2-(5-bromothienyl)pentamethyldisilane, 0.107 g (0.152 mmol) of bis(triphenylphosphine)



Fig. 3. Structures of compounds 8-11.

dichloropalladium and 1.708 g (5.20 mmol) of cesium carbonate in 50 mL MeOH. The mixture was heated to reflux for 3 h and hydrolyzed with dilute aqueous hydrochloric acid. The organic layer was separated, washed with water and dried over anhydrous magnesium sulfate. After the solvent was evaporated, compound **5** (0.415 g, 30% yield) was isolated by a silica gel column eluting with hexane–chloroform (1:1) as a green yellow solid. Exact mass calcd for C₄₂H₅₈N₃Si₆S₆: 964.15558, found: 964.15651. Mp. >300 °C; MS *m*/*z* 964 (M⁺); ¹H NMR (δ CDCl₃) 0.14 (s, 27H, Me₃Si), 0.41 (s, 18H, Me₂Si), 7.13 (d, 3H, *J* = 3.4 Hz, thienyl ring protons), 7.27 (d, 3H, *J* = 3.4 Hz, thienyl ring protons), 8.16 (s, 3H, 3.4 Hz, thienyl ring protons); ¹³C NMR (δ CDCl₃) –2.8, –2.4 (MeSi), 124.6, 126.3, 132.4, 135.0, 139.4, 140.7, 142.0, 144.0 (thienylene carbons), 167.0 (triazine carbon); ²⁹Si NMR (δ CDCl₃) –23.7, –19.2.

3.1.5. Synthesis of 1-(5-bromothienyl)-2-bithienyltetramethyldisilane (6)

In a 100 mL two-necked flask was placed 4.69 g (19.14 mmol) of 2,5-dibromothiophene in 50 mL of diethyl ether. To this was added 11.5 mL (19.00 mmol) of a 1.65 M *n*-butyllithium–hexane solution at -40 °C. After the addition was complete, the mixture was

warmed to room temperature and stirred for 2 h. To this was slowly added 5.81 g (18.52 mmol) of 2-(5,2'-bithiophen-2-yl)-1-chloro-1,1,2,2-tetramethyldisilane at room temperature. This mixture was stirred overnight and hydrolyzed with dilute aqueous hydrochloric acid. The organic layer was separated, washed with water and dried over anhydrous magnesium sulfate. After the solvent was evaporated, compound 6 (5.122 g, 62% yield) was isolated by a silica gel column eluting with hexane as a yellow liquid. Anal. Calcd for C₁₆H₁₉Si₂S₃Br: C, 43.32; H, 4.32. Found: C, 43.08; H, 4.15. MS *m*/*z* 442 (M⁺); ¹H NMR (δ CDCl₃) 0.38 (s, 6H, Me₂Si), 0.41 (s, 6H, Me₂Si), 6.90 (d, 1H, J = 3.7 Hz thienyl ring protons), 7.01 (t, 1H, J = 3.7 Hz thienyl ring protons), 7.04 (d, 1H, J = 3.7 Hz thienyl ring protons), 7.08 (d, 1H, J = 3.7 Hz thienyl ring protons), 7.18 (d, 1H, J = 3.7 Hz thienyl ring protons), 7.21 (d, 1H, J = 3.7 Hz thienyl ring protons), 7.23 (d, 1H, J = 3.7 Hz thienyl ring protons); ¹³C NMR (δ CDCl₃) -3.0, -2.9 (MeSi), 116.8, 123.7, 124.3, 125.1, 127.7, 131.3, 134.9, 135.3, 136.7, 137.2, 140.7, 142.8 (thienylene carbons); ²⁹Si NMR(δ CDCl₃) -24.5, -24.1.

3.1.6. Synthesis of compound 7

In a 100 mL two-necked flask was placed 0.507 g (0.719 mmol) of compound **4**, 1.197 g (2.70 mmol) of compound **6**, 0.054 g

(0.08 mmol) of bis(triphenylphosphine)dichloropalladium and 0.853 g (2.59 mmol) of cesium carbonate in 50 mL MeOH. The mixture was heated to reflux for 3 h and hydrolyzed with dilute aqueous hydrochloric acid. The organic layer was separated, washed with water and dried over anhydrous magnesium sulfate. After the solvent was evaporated, compound 7 (0.230 g, 23% yield) was isolated by a silica gel column eluting with hexane-chloroform (2:1) as a green vellow solid. Exact mass calcd for $C_{63}H_{64}N_3Si_6S_{12}$: 1414.03308, found: 1414.03588. Mp. >300 °C; MS *m*/*z* 1413 (M⁺); ¹H NMR (δ CDCl₃) 0.45 (s, 18H, Me₂Si), 0.46 (s, 18H, Me₂Si) 7.01 (t, 3H, I = 3.4 Hz, thienyl ring protons), 7.07 (d, 3H, I = 3.4 Hz, thienyl ring protons), 7.12 (d, 3H, I = 3.4 Hz, thienyl ring protons), 7.19 (d, 3H, I = 3.4 Hz, thienyl ring protons), 7.21 (d, 3H, I = 3.4 Hz, thienyl ring protons), 7.25 (d, 3H, J = 3.4 Hz, thienyl ring protons), 7.28 (d, 3H, J = 3.4 Hz, thienyl ring protons), 7.43 (d, 3H, J = 3.4 Hz, thienyl ring protons), 8.17 (d, 3H, I = 3.4 Hz, thienyl ring protons); ¹³C NMR (δ CDCl₃) -2.9, -2.8 (MeSi), 123.8, 124.4, 124.8, 125.2, 126.4, 127.8, 132.5, 135.4, 135.5, 137.1, 137.3, 139.4, 139.5, 142.3, 142.9, 144.0 (thienylene carbons), 167.1 (triazine carbon); 29 Si NMR(δ CDCl₃) -24.4, -24.2.

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