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Note

Synthesis and optical properties of H-shaped silicon-containing molecule with bithiophene units

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ABSTRACT

The H-shaped molecule, 5,5′-bis{[bis(5′-*tert*-butyldimethylsilyl)-2,2′-(bithiophen-5-yl)]methylsilyl}-2,2′-bithiophene (**3**) was prepared by the reaction of 5′-(*tert*-butyldimethylsilyl)-5-lithio-2,2′-bithiophene with 2-bromo-5-(dichloromethylsilyl)thiophene, followed by treatment of the resulting product (5-bromothiophen-2-yl)bis[5′-(*tert*-butyldimethylsilyl)-2,2′-bithiophen-5-yl](methyl)silane (**1**) with compound (**2**), obtained by the reaction of the lithiated derivative of **1** with 2-isopropyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, in the presence of dichlorobis(triphenylphosphine)palladium, as light yellow solids. Compound **3** showed absorption maximum (λ_{max}) at 336 nm with a molar absorption coefficient (ε) of 113,000 M^{-1} cm^{-1} in dioxane. The fluorescence spectrum of **3** excited at 336 nm in dioxane displayed the emission maxima at 377 and 387 nm, with the fluorescence quantum yield of 48%. We also carried out theoretical treatment of compound **3** to elucidate the geometrical and electronic structure, using the Gaussian 03 program package, with the 6-31G and 6-31G(d) basis sets.

1. Introduction

The nanosized conjugated molecules consisting of two or three dimensional network structures are attracting considerable attention as the materials which can be applied to the organic photo- and electro-luminescent devices [1]. Ponomarenko and his coworkers have investigated a series of bithiophenesilane dendrimers with efficient photoluminescence in the violet–blue spectrum range [2]. Recently, we have reported the synthesis and properties of some silicon-containing starlike 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 bithienylene unit [3], and those with the same core and oligothienylene units as the arms [4]. Similar star-shaped molecules composed of a 1,3,5-tris- or 1,2,4,5-tetrakis(silyl)benzene [5], or 1,3,5-triazine [6] core and bithienylene–disilanylene arms were also prepared. These starlike molecules show novel optical properties, such as high fluorescence quantum yields and long lifetimes of the excited state [3,4]. We thought that the extension of π-electron delocalization in the two or three dimensional structure might give rise to unique intra- or inter-molecular interaction and, as the result, the molecules bearing these extended π-electron delocalization can be applied to the functionality materials. In order to get more information about the chemistry of the nanosized silicon-containing molecules with the π-conjugated blocks that extend to the two or three directions, we have synthesized a new type of the H-shaped molecule with a 5,5′-bis(methylsilyl)-2,2′-bithiophene unit as a core and the silylbithienyl groups as the arms, and investigated the optical properties of this molecule.

2. Results and discussion

H-shaped compound, 5,5′-bis{[bis(5′-*tert*-butyldimethylsilyl)-2,2′-(bithiophen-5-yl)]methylsilyl}-2,2′-bithiophene (**3**) was synthesized according to the equations as shown in Scheme 1. Treatment of a lithio derivative prepared by the reaction of 5-bromo-5′-*tert*-butyldimethylsilyl-2,2′-bithiophene and *n*-butyllithium, with 2-bromo-5-(dichloromethylsilyl)thiophene gave compound, (5-bromothiophen-2-yl)bis[5′-(*tert*-butyldimethylsilyl)-2,2′-bithiophen-5-yl](methyl)silane (**1**) in 27% yield. The reaction of the lithio derivative obtained by treatment of **1** with *n*-butyllithium, with 2-isopropyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane afforded compound (**2**) in 38% yield. Suzuki–Miyaura cross-coupling reaction [7] of **1** and **2** in the presence of dichlorobis(triphenylphosphine)

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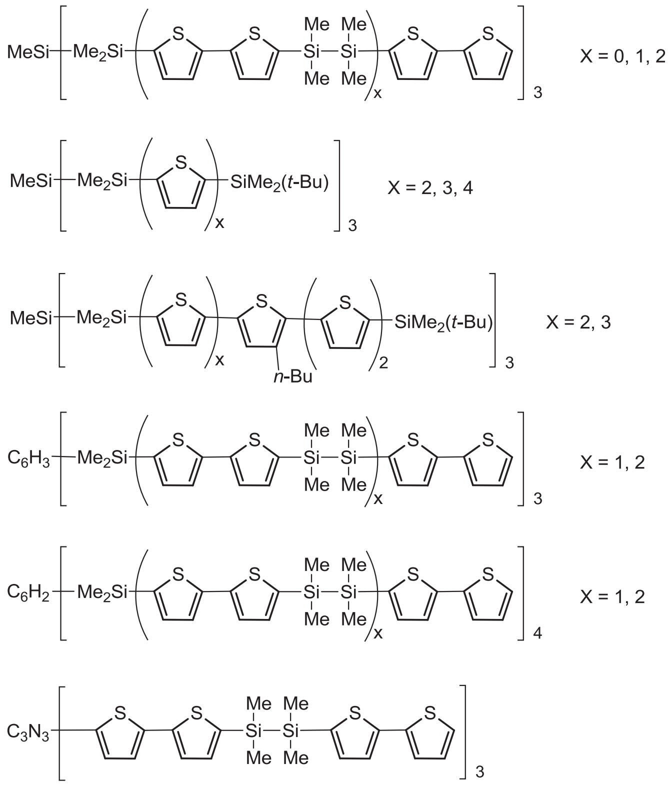


palladium gave the H-shaped molecule **3** in 52% yield as light yellow solids.

The structure of compound **3** was verified by spectrometric analysis. The mass spectrum for **3** shows the parent ion at *m*/*z* 1366, corresponding to the calculated molecular weight of $C_{66}H_{86}Si_6S_{10}$. The ^{1}H NMR spectrum for **3** shows a singlet signal at 0.30 ppm due to dimethylsilyl protons, 0.93 ppm attributable to *tert*-butyl protons and 0.96 ppm attributed to the methyl protons on the silicon atom, as well as the signals due to the thienyl ring protons. The ^{13}C NMR spectrum for **3** shows two signals at -5.0 and 0.2 ppm due to methyl carbons on the silicon atoms, two signals at 16.9 and 26.3 ppm attributable to *tert*-butyl carbons, together with twelve signals attributed to thienyl ring carbons at 125.1–144.6 ppm. The ^{29}Si NMR spectrum for **3** shows signals at -25.2 and 1.0 ppm, respectively (see Experimental section).

The absorption and fluorescence spectra of compound **3** are presented in Figs. 1–3 (see Supplementary material). Compound **3** shows the absorption maximum at $\lambda_{\max} = 336$ nm with a molar absorption coefficient (ε) of 113,000 M^{-1} cm^{-1} in dioxane. The fluorescence spectrum of **3** excited at 336 nm in dioxane displays the emission maxima at 377 and 387 nm. In the case of excitation at 336 nm, the fluorescence quantum yield of **3** in dioxane amounts to $\Phi_F = 48\%$.

We have reported the synthesis and optical properties of starlike compound **4** which is the viscous yellow liquid with an organosilicon core and bithienylene arms [4]. The absorption and fluorescence maximum wavelengths and quantum yields of **3** in solution are very similar to those of compound **4** ($\lambda_{\max,abs} = 335$ nm, $\lambda_{\max,F} = 374$ nm, $\Phi_F = 50\%$) (Chart 1).

Compound **3** in powder exhibits blue emission ($\lambda_{\max} = 392$ nm) with the quantum yield of 7%. It is well-known that the fluorophors show a strong tendency in the solid state to cause aggregations that result in fluorescence quenching in general.

Previously, we investigated X-ray crystallographic analysis of a starlike molecule, tris[(5′-bromo-2,2′-bithiophen-5-yl)dimethylsilyl]methylsilane, and found that this compound has the interesting molecular structure, that is, two of the three arms, bromobithienyl units are located in a parallel fashion to adopt π-stacking in the crystal structure (Chart 2). Therefore, we had interest in the crystal structure of compound **3**, and attempted to carry out X-ray crystallographic analysis. However, all attempts to obtain single crystals that can be used for X-ray analysis by recrystallization of **3** were unsuccessful. The fine powder, but not single crystal was always obtained. Accordingly, we focused on theoretical treatment to elucidate the structure of **3**.

2.1. Theoretical calculations

To examine stable structures of **3** illustrated in Scheme 1, the density functional theory (DFT) calculations were carried out using the Gaussian 03 program package [8]. The Becke-three-parameter-Lee–Yang–Parr hybrid functional [9–11] was employed. The 6-31G and 6-31G(d) basis sets were used for C and H atoms and Si and S atoms, respectively. With the optimized structure, the singlet excitation energy was evaluated with the time-dependent DFT method.

It has been found that many stable conformations are present for this molecule. For example, in a bithiophene unit arising from bonding of two thienyl groups, *syn* and *anti* conformations are generated per a bithiophene unit. We calculated all-*syn* and all-*anti* conformers as the representative, and their optimized structures are shown in Fig. 4 (see Supplementary material). The all-*anti* conformer is more stable by 22 kJ mol^{-1} than the all-*syn* conformer. The energies for the other intermediate conformers (including both *syn* and *anti* parts) are expected to be laid in this range.

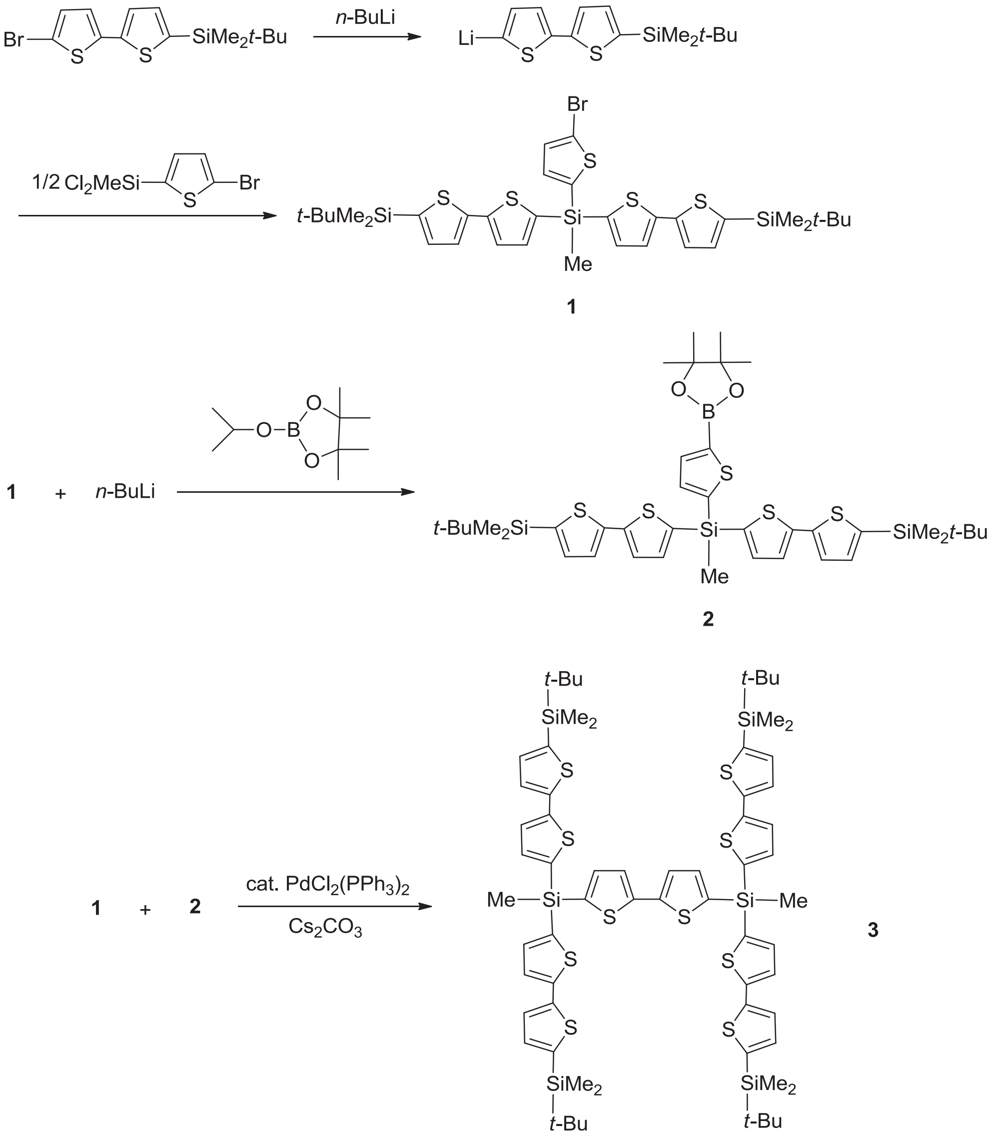
For the all-*anti* conformer, the singlet excitation energies were evaluated for ten of the lowest excitations between the occupied and vacant MO's, as shown in Table 1. The excitations with oscillation strength smaller than 0.1 are omitted. For the ten excitations, the excitation energies ranges from 353.2 to 334.7 nm, and well agree with the experimental value of 336 nm. The third excitation has the largest oscillation strength (0.94), which is composed of five electron transfers from the occupied MO's to the vacant MO's. Fig. 5 shows the orbital contour plots for the four typical MO's (MO#359, #360, #361, and #364) which have larger coefficients, i.e., leading contribution to this excitation (see Supplementary material). Among the four MO's, the destination MO of excitation is solely the LUMO (#364), whereas the origin MO's of excitation are distributed to #359, #360, and #361, and the HOMO (#363) is not included. As can be seen in Fig. 5, this excitation is the π–π type, and the electron transfer occurs from the central bithiophene unit (#359), left units (#360) and right units (#361) to the central bithiophene unit (#364). The Si atoms are not contributed to the excitation, and the contribution from S atoms seems to be smaller than that from C atoms.

In conclusion, the H-shaped molecule **3** with the silylbithienylene groups was synthesized by using Suzuki–Miyaura cross-coupling reaction. Compound **3** showed the absorption maximum at 336 nm and the emission maxima at 377 and 387 nm in dioxane. In powder, it exhibited the emission at 392 nm. The excitation energies calculated for the all-*anti* conformer well reproduced the experimental value.

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 LTQ Orbitrap XL. UV–visible absorption spectra were measured with a JASCO V-560 spectrometer. Fluorescence spectra were measured with a JASCO FP-777



Scheme 1. Synthesis of compound 3.

spectrometer and JASCO FP-8300 spectrometer. Melting point was measured with a Yanaco-MP-S3 apparatus. Column chromatography was performed by using Wakogel C-300 (WAKO). THF used as a solvent was distilled from sodium/benzophenone ketyl, just before use.

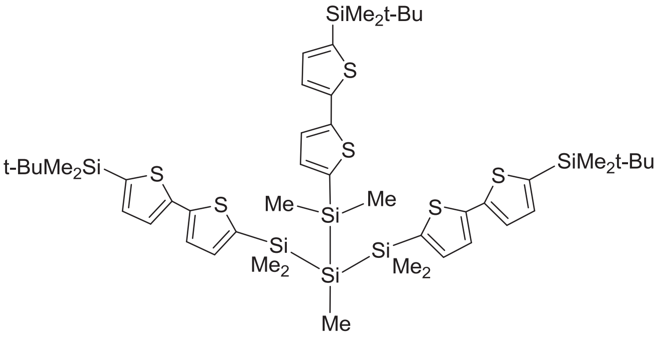


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Chart 1.

*3.1.1. Preparation of compound **1***

In a 100 mL two-necked flask was placed 3.1416 g (8.74 mmol) of 5-bromo-5′-*tert*-butyldimethylsilyl-2,2′-bithiophene in 50 mL of THF. To this was added 5.6 mL (8.79 mmol) of a 1.57 M *n*-butyllithium-hexane solution at −78 °C. After the mixture was stirred at room temperature for 1 h, 1.2055 g (4.37 mmol) of 2-bromo-5-(dichloromethylsilyl)thiophene was added at −78 °C. The mixture was stirred for 12 h at room temperature, and then hydrolyzed with water. The organic layer was separated, washed with water, and dried over anhydrous magnesium sulfate. After the solvent was evaporated, compound **1** (0.9104 g, 27% yield) was isolated by a silica gel column eluting with hexane as a yellow viscous liquid: Anal. Calcd for $C_{33}H_{43}Si_3S_5Br$: C, 51.87; H, 5.67. Found: C, 51.66; H, 5.53. MS m/z 762 (M^+); ^1H NMR (δ $CDCl_3$) 0.30 (s, 12H, Me_2Si), 0.92

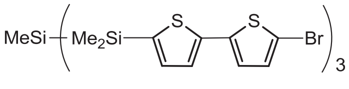

Chart 2.

Table 1
Excitation energy, relating MO's, and oscillation strength.

Ex. #	MO# (origin → dest.)[a]	MO coeff.	Energy (eV)	Energy (nm)	Oscillation strength
2	362 → 364	0.689	3.52	352.1	0.13
	362 → 365	−0.103			
3	359 → 364	0.169	3.57	347.2	0.94
	360 → 364	−0.291			
	360 → 365	0.106			
	361 → 364	0.548			
	363 → 367	−0.118			
4	360 → 364	0.151	3.59	345.5	0.26
	361 → 367	0.101			
	363 → 365	0.582			
	363 → 366	−0.028			
6	359 → 364	−0.171	3.61	343.2	0.28
	360 → 366	0.135			
	361 → 364	0.108			
	362 → 365	0.271			
	362 → 366	0.549			
	363 → 367	0.104			
7	359 → 364	0.387	3.63	341.9	0.56
	360 → 364	0.218			
	360 → 366	0.129			
	361 → 364	−0.137			
	362 → 366	0.143			
	362 → 368	0.281			
	363 → 367	−0.334			
8	359 → 364	0.231	3.64	340.3	0.18
	360 → 365	0.139			
	361 → 364	−0.124			
	361 → 365	0.399			
	361 → 366	−0.226			
	362 → 368	0.165			
	363 → 367	0.375			
9	359 → 364	−0.161	3.67	338.1	0.19
	360 → 365	−0.202			
	360 → 366	−0.374			
	361 → 366	0.200			
	362 → 368	0.455			
10	359 → 365	−0.138	3.70	334.7	0.34
	360 → 367	0.177			
	360 → 368	−0.153			
	361 → 367	0.593			

[a] The HOMO and LUMO are 363th and 364th MO's, respectively.

(s, 3H, MeSi), 0.93 (s, 18H, Me_3C), 7.13 (d, 2H, $J = 3.7$ Hz, thienylene protons), 7.14 (d, 2H, $J = 3.7$ Hz, thienylene protons), 7.16 (d, 1H, $J = 3.7$ Hz, thienylene proton), 7.27–7.28 (m, 5H, thienylene protons); ^{13}C NMR (δ $CDCl_3$) −5.0 (Me_2Si), −0.3 (MeSi), 16.9 ($\underline{C}Me_3$), 26.3 ($\underline{Me}_3C$), 119.2, 125.1, 125.4, 131.5, 133.1, 135.9, 137.4, 137.5, 137.8, 140.0, 141.9, 144.8 (thienylene carbons); ^{29}Si NMR (δ $CDCl_3$) −25.5, 1.0.

3.1.2. *Preparation of compound* ***2***

In a 100 mL two-necked flask equipped with a stirrer, reflux condenser, and dropping funnel was placed 1.0955 g (1.43 mmol) of compound **1** in 40 mL of THF. To this was added 1.5 mL (2.48 mmol) of a 1.65 M *n*-butyllithium-hexane solution at −78 °C, and the mixture was stirred for 1 h at −78 °C. To this was added 0.5294 g (2.845 mmol) of 2-isopropoxy-4,4,5,5-tetramethy-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 **2** (0.4370 g, 38% yield) was isolated by a silica gel column eluting with hexane–acetone (10:1) as a light yellow liquid. Exact mass calcd for $C_{39}H_{55}O_2BNaSi_3S_5$ $[M + Na]^+$: 833.20987, found: 833.21051. MS *m/z* 810 (M^+); ^{1}H NMR (δ $CDCl_3$) 0.30 (s, 12H, Me_2Si), 0.93 (s, 18H, Me_3C), 0.95 (s, 3H, MeSi), 1.34 (s, 12H, CH_3), 7.13 (d, 2H, $J = 3.4$ Hz, thienylene protons), 7.27–7.29 (m, 6H, thienylene protons), 7.50 (d, 1H, $J = 3.4$ Hz, thienylene proton), 7.73 (d, 1H, $J = 3.4$ Hz, thienylene proton); ^{13}C NMR (δ $CDCl_3$) −5.0 (Me_2Si), −0.2 (MeSi), 16.9 ($\underline{C}Me_3$), 24.7 (CH_3), 26.3 ($\underline{Me}_3C$), 84.2 (CO), 125.1, 125.3, 133.8, 135.9, 137.3, 137.8, 137.9, 138.0, 142.0, 142.5, 144.5 (thienylene carbons); ^{29}Si NMR (δ $CDCl_3$); −25.1, 1.0.

3.1.3. *Preparation of compound* ***3***

In a 100 mL two-necked flask was placed 0.4347 g (0.569 mmol) of compound **1**, 0.4370 g (0.539 mmol) of compound **2**, 0.0389 g (0.055 mmol) of dichlorobis(triphenylphosphine)palladium and 0.2246 g (0.689 mmol) of cesium carbonate in 30 mL THF. 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 **3** (0.3851 g, 52% yield) was isolated by subjecting to a silica gel column eluting with hexane–chloroform (5:1) as light yellow solids. Anal. calcd for $C_{66}H_{86}Si_6S_{10}$: C, 57.92; H, 6.33%. Found: C, 57.63; H, 6.48%. Exact mass calcd for $C_{66}H_{86}Si_6S_{10}$: 1366.25467, found 1366.25281. Mp. 173 °C; MS *m/z* 1366 (M^+); IR (cm^{-1}, KBr) 3059, 2952, 2925, 2854, 1637, 1460, 1420, 1260, 1197, 1076, 988, 875, 795, 739. ^{1}H NMR (δ $CDCl_3$) 0.30 (s, 24H, Me_2Si), 0.93 (s, 36H, Me_3C), 0.96 (s, 6H, MeSi), 7.13 (d, 4H, $J = 3.7$ Hz, thienylene protons), 7.27–7.30 (m, 16H, thienylene protons); ^{13}C NMR (δ $CDCl_3$) −5.0 (Me_2Si), 0.2 (MeSi), 16.9 ($\underline{C}Me_3$), 26.3 ($\underline{Me}_3C$), 125.1, 125.4, 125.7, 133.7, 134.5, 135.9, 137.4, 137.8, 137.9, 142.0, 144.1, 144.6 (thienylene carbons); ^{29}Si NMR (δ $CDCl_3$) −25.2, 1.0.

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Appendix A. Supplementary material

Supplementary material related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2013.05.024.

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