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Synthesis and Properties of Nanosize Starlike Silicon Compounds

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Summary: The new starlike molecules that have a regular arrangement of an Si−Si bond and bithienylene unit were synthesized by the reaction of tris(chlorodimethylsilyl)methylsilane, which was chosen as a core, with the lithiobithienylene derivatives used for construction of the arms. The starlike molecules showed high fluorescence quantum yields and long lifetimes of the excited state.

There has been significant interest in the synthesis of three-dimensional metal-containing molecules, organometallic dendrimers, which are promising for a variety of applications.[1,2] In the field of silicon chemistry, only a few dendrimers, including polysilanes,[3] polysiloxanes,[4] and carbosilanes,[5] have been reported to date. Dendrimers with a regular alternating arrangement of an Si−Si unit and π-electron system have not been reported so far.[6] We are interested in investigating the chemistry of starlike silicon compounds bearing arms that have an alternating arrangement of an Si−Si bond and π-electron system, which extend to three directions.

In this paper we report the first synthesis of starlike compounds that have a regular alternating arrangement of a disilanylene unit and bithienylene system as the arms and their optical properties. Our strategy for the synthesis of starlike compounds is based on the reaction of tris(chlorodimethylsilyl)methylsilane (**1a**), which was chosen as a core, with lithiobithienylene derivatives used for construction of the arms.

The core compound **1a** was readily prepared by the Me−Cl exchange reaction of tris(trimethylsilyl)methylsilane with a large excess of chlorotrimethylsilane in the presence of an aluminum chloride catalyst (Scheme 1).[7] The syntheses of the lithiobithienylene derivatives (**1b**,**c**,**e**,**f**) used as the arms are also shown in Scheme 1. Thus, treatment of **1a** with lithiobithiophene **1b** in ether gave tris[(5,2′-bithiophen-2-yl)dimethylsilyl]methylsilane[8] (**2**) as a bright yellow liquid in 89% yield (Scheme 2). Similar treatment of **1a** with 2-lithio-5′-(pentamethyldisilanyl)bithiophene (**1c**) in ether afforded the starlike compound[9] **3** as a bright yellow liquid in 36% yield.

Starlike molecules that have arms longer than those of **2** and **3** can be prepared by similar reactions of **1a** with lithio derivatives having longer arms. The reaction of **1a** with the lithio compound **1e**, prepared by the method shown in Scheme 1, afforded compound[10] **4** as a viscous yellow liquid in 47% yield, while **1a** reacted with lithio derivative **1f** to give product[11] **5** as a green

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(1) Newkome, G. R.; He, E.; Moorefield, C. N. *Chem. Rev.* **1999**, *99*, 1689.

(2) Fischer, M.; Vögtle, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 884.

(3) (a) Lamber, J. B.; Pflug, J. L.; Stern, C. L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 98. (b) Suzuki, H.; Kimata, Y.; Satoh, S.; Kuriyama, A. *Chem. Lett.* **1995**, 293. (c) Sekiguchi, A.; Nanjo, M.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1995**, *117*, 4195. (d) Lambert, J. B.; Pflug, J. L.; Denari, J. M. *Organometallics* **1996**, *15*, 615.

(4) (a) Rebrov, E. A.; Muzafarov, A. M.; Papkov, V. S.; Zhdanov, A. A. *Dokl. Akad. Nauk SSSR* **1989**, *309*, 376. (b) Uchida, H.; Kabe, Y.; Yoshino, K.; Kawamata, A.; Tsumuraya, T.; Masamune, S. *J. Am. Chem. Soc.* **1990**, *112*, 7077. (c) Mathias, L. J.; Carothers, T. W. *J. Am. Chem. Soc.* **1991**, *113*, 4043.

(5) (a) van der Made, A. W.; van Leenwer, P. W. N. M. *J. Chem. Soc., Chem. Commun.* **1992**, 1400. (b) Zhou, L.-L.; Rovers, J. *Macromolecules* **1993**, *26*, 963. (c) Seyferth, D.; Son, D. Y. *Organometallics* **1994**, *13*, 2682. (d) Seyferth, D.; Kugita, T.; Rheingold, A. L.; Yap, G. P. A. *Organometallics* **1995**, *14*, 5362. (e) Ishow, E.; Gourdon, A.; Launay, J.-P.; Lecante, P.; Verelst, M.; Chiorboli, C.; Xcandole, F.; Bignozzi, C.-A. *Inorg. Chem.* **1998**, *37*, 3603. (f) Cuadrado, I.; Moran, M.; Moya, A.; Casado, C. M.; Barranco, M.; Alonso, B. *Inorg. Chim. Acta* **1996**, *251*, 5. (g) Lobete, F.; Cuadrado, I.; Casado, C. M.; Alonso, B.; Moran, M.; Losda, J. *J. Organomet. Chem.* **1996**, *509*, 109. (h) Cuadrado, I.; Casado, C. M.; Alonso, B.; Moran, M.; Losda, J.; Belsky, V. *J. Am. Chem. Soc.* **1997**, *119*, 7613. (i) Kriesel, J. W.; König, S.; Freitas, M. A.; Marshall, A. G.; Leary, J. A.; Tilley, T. D. *J. Am. Chem. Soc.* **1998**, *120*, 12207.

(6) The dendrimer composed of a silylene unit and thienylene group, hyperbranched poly(2,5-silylthiophenes), and silylacetylene dendrimers have recently been reported: (a) Nakayama, J.; Lin, J.-S. *Tetrahedron Lett.* **1997**, *38*, 6043. (b) Yao, J.; Son, D. Y. *Organometallics* **1999**, *18*, 1736. (c) Matsuo, T.; Uchida, K.; Sekiguchi, A. *Chem. Commun.* **1999**, 1799.

(7) Ishikawa, M.; Kumada, M.; Sakurai, H. *J. Organomet. Chem.* **1970**, *23*, 63.

(8) Data for compound **2**: MS m/z 712 (M^+); ^1H NMR (δ; $CDCl_3$) 0.32 (s, 3H, SiMe), 0.37 (s, 18H, $SiMe_2$), 6.92 (d, 3H, J = 3.7 Hz, thienylene protons), 6.97 (t, 3H, J = 3.7 Hz, thienylene protons), 7.11 (d, 3H, J = 3.7 Hz, thienylene protons), 7.16 (d, 3H, J = 3.7 Hz, thienylene protons), 7.18 (d, 3H, J = 5.2 Hz, thienylene protons); ^{13}C NMR (δ; $CDCl_3$) −11.88 (MeSi), −0.46 (Me_2Si), 123.71, 124.22, 125.04, 127.76, 134.97, 137.43, 138.93, 142.63 (thienylene carbons); ^{29}Si NMR (δ; $CDCl_3$) −84.8, −18.2. Anal. Calcd for $C_{31}H_{36}Si_4S_6$: C, 52.20; H, 5.09. Found: C, 52.20; H, 5.05.

(9) Data for compound **3**: MS m/z 1102 (M^+); ^1H NMR (δ; $CDCl_3$) 0.12 (s, 27H, $SiMe_3$), 0.31 (s, 3H, SiMe), 0.35 (s, 18H, $SiMe_2$), 0.37 (s, 18H, $SiMe_2$), 6.92 (d, 3H, J = 3.4 Hz, thienylene protons), 7.04 (d, 3H, J = 3.4 Hz, thienylene protons), 7.16 (d, 3H, J = 3.4 Hz, thienylene protons), 7.18 (d, 3H, J = 3.4 Hz, thienylene protons); ^{13}C NMR (δ; $CDCl_3$) −11.89 (MeSi), −2.79, −2.42, −0.49 (Me_3Si, Me_2Si), 125.05, 125.14, 134.79, 135.04, 138.63, 138.87, 142.39, 142.65 (thienylene carbons); ^{29}Si NMR (δ; $CDCl_3$) −84.9, −24.1, −19.3, −18.2. Anal. Calcd for $C_{46}H_{78}Si_{10}S_6$: C, 50.03; H, 7.12. Found: C, 49.73; H, 6.80.

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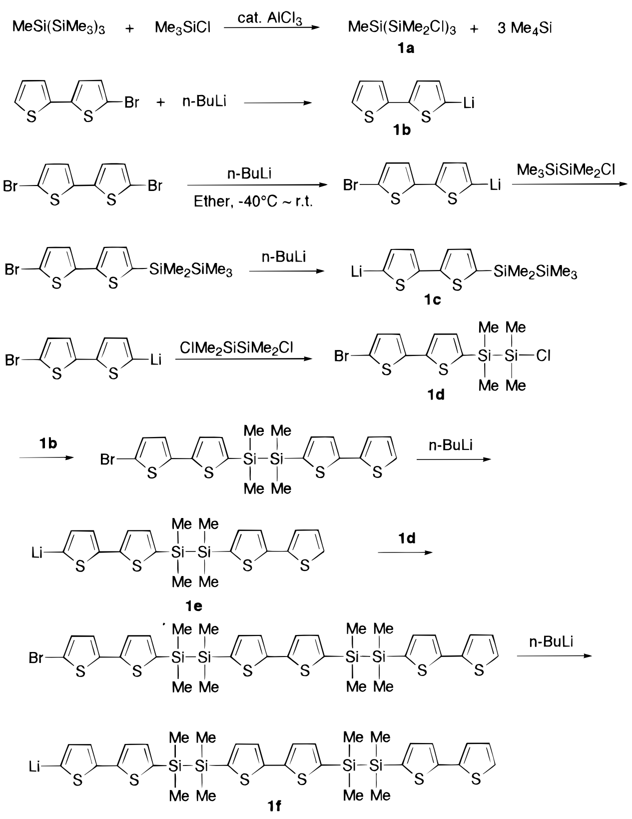
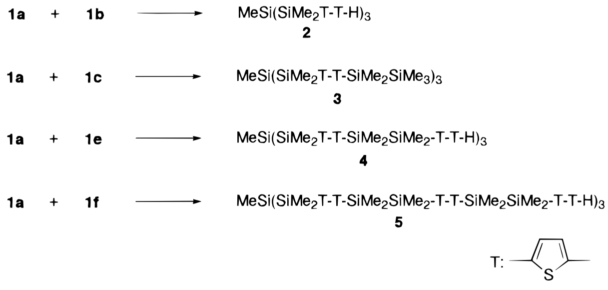
Scheme 1



Scheme 2



solid that melts at 57 °C in 42% yield. The structures of compound **2**−**5** were verified by mass and ^{1}H, ^{13}C, and ^{29}Si NMR spectrometric analysis, as well as by elemental analysis.

Strong UV absorption spectra and photoluminescence spectra for compounds **2**−**5** have been observed, and their peak positions are listed in Table 1 with those of poly[(tetraethyldisilanylene)bithiophene][12] (**6**; M_w = 53 000) for comparison. The absorption maximum for the starlike molecules **2**−**5** appears at shorter wavelength than that of polymer **6**, but fluorescence maximum wavelengths are observed at almost the same position as that of **6**. We have also measured fluorescence quantum yields (ϕ_F) and lifetimes (τ_F) in the excited states of **2**−**5**.

Table 1. Absorption and Emission Data for 2−6

	λ_{max}, nm^a			
compd	absorption (ϵ)	emission	ϕ_F ^{b}	τ_F/ns^b
2	324 (51 600)	383	0.49	0.51
3	336 (68 500)	381, 398	0.68	0.92
4	329 (106 000)	398	0.71	1.08
5	332 (211 000)	386, 398	0.75	1.12
6	343 (21 200)	383, 397	0.33	0.81

^{a} In THF. ^{b} In dioxane.

To our surprise, high fluorescence quantum yields and long lifetimes are observed for the starlike molecules **2**−**5**. For example, fluorescence quantum yields ϕ_F for **3**−**5** are more than two times that of polymer **6**, whose ϕ_F value is much higher than that of bithiophene (ϕ_F = 0.018). The starlike molecules **3**−**5** also show lifetimes longer than that of **6**, as can be seen in Table 1. Rate constants of radiative and nonradiative decay pathways for the excited states can be calculated using ϕ_F and τ_F values. The results show that the high ϕ_F values observed for the starlike molecules may be ascribed to highly depressed nonradiative paths, compared with that for polymer **6**. We presumed that the slow kinetics of the nonradiative deactivation route originate from the starlike structure, as well as σ−π conjugation.

Further studies concerning various optical properties of the starlike molecules are in progress and will be reported elsewhere.

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Supporting Information Available: Text giving experimental details and characterization data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Data for compound **4**: SIMS *m/z* 1552 (M$^+$); ^{1}H NMR (δ CDCl$_3$) 0.32 (s, 3H, SiMe), 0.35 (s, 18H, SiMe$_2$), 0.42 (s, 18H, SiMe$_2$), 0.43 (s, 18H, SiMe$_2$), 6.92 (d, 3H, J = 3.7 Hz, thienylene protons), 6.98 (t, 3H, J = 3.7 Hz, thienylene protons), 7.03 (d, 3H, J = 3.7 Hz, thienylene protons), 7.05 (d, 3H, J = 3.7 Hz, thienylene protons), 7.16 (d, 6H, J = 3.7 Hz, thienylene protons), 7.18 (d, 6H, J = 3.7 Hz, thienylene protons), 7.21 (d, 3H, J = 3.7 Hz, thienylene protons); ^{13}C NMR (δ CDCl$_3$) −11.87 (MeSi), −2.79 (Me$_2$Si), −0.47 (Me$_2$Si), 123.76, 124.33, 125.19 (2C), 125.24, 127.77, 135.06, 135.30, 135.36, 137.19, 137.31, 137.35, 139.05, 142.53, 142.78, 142.81 (thienylene carbons); ^{29}Si NMR (δ CDCl$_3$) −84.8, −24.48, −24.53, −18.1. Anal. Calcd for $C_{67}H_{84}Si_{10}S_{12}$: C, 51.73; H, 5.45. Found: C, 51.67; H, 5.40.

(11) Data for compound **5**: mp 57 °C; FDMS *m/z* 2393 (MH$^+$); ^{1}H NMR (δ; CDCl$_3$) 0.32 (s, 3H, SiMe), 0.35 (s, 18H, SiMe$_2$), 0.41 (br s, 72H, SiMe$_2$), 6.92 (d, 3H, J = 3.7 Hz, thienylene protons), 6.99 (t, 3H, J = 3.7 Hz, thienylene protons), 7.02−7.05 (m, 12H, thienylene protons), 7.16−7.19 (m, 12H, thienyl ring protons), 7.21−7.22 (m, 9H, thienyl ring protons); ^{13}C NMR (δ; CDCl$_3$) −11.89 (MeSi), −2.84 (2C) (Me$_2$Si), −2.80 (Me$_2$Si), −2.78 (Me$_2$Si), −0.48 (Me$_2$Si), 123.75, 124.32, 125.17 (2C), 125.24 (3C), 127.77, 135.05, 135.30, 135.35 (3C), 137.18, 137.28 (2C), 137.31, 137.34, 139.02, 142.51, 142.71 (2C), 142.75, 142.78 (thienylene carbons); ^{29}Si NMR (δ; CDCl$_3$) −84.8, −24.53 (2Si), −24.48 (2Si), −18.1. Anal. Calcd for $C_{103}H_{132}Si_{16}S_{18}$: C, 51.61; H, 5.55. Found: C, 51.30; H, 5.32.

(12) (a) Kunai, A.; Ueda, T.; Horata, K.; Toyoda, E.; Nagamoto, I.; Ohshita, J.; Ishikawa, M.; Tanaka, K. *Organometallics* **1996**, *15*, 2000. (b) Tang, H.; Zhu, L.; Harima, Y.; Yamashita, K.; Ohshita, J.; Kunai, A. *J. Polym. Sci., Part B, Polym. Phys.* **1999**, *37*, 1873.