Articles

Synthesis and Electronic Spectra of Disilatriptycene Oligomers: Evidence for Electronic Delocalization along the One-Dimensional Arrangement of Bridge-Head Disilanes

Shohei Sase, Yoen-Seok Cho, Atsushi Kawachi, Atsushi Wakamiya, Shigehiro Yamaguchi, Hayato Tsuji,* and Kohei Tamao*

International Research Center for Elements Science (IRCELS), Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan, and Department of Chemistry, Graduate School of Science, Nagoya University, Chikusa, Nagoya 464-8602, Japan

Received December 23, 2007

Reductive coupling of a 9,10-dibromo-9,10-disilatriptycene derivative followed by treatment with chlorotrimethylsilane (TMSCl) affords a series of TMS-capped 9,10-disilatriptycene oligomers **DSiT[*n*]**. Each isomer, up to the pentamer ($n = 5$), can be separated using recycling gel permeation chromatography. The X-ray structural analysis of **DSiT[2]** shows that the six silicon atoms are linearly aligned in a rigid array structure. While the ultraviolet (UV) absorption maximum remains constant at 230 nm, irrespective of the chain length, the magnetic circular dichroism (MCD) spectra exhibit a red shift band near 245 nm, and the emission maximum steadily shifts from 319 to 337 nm as the number of silicon atom increases. These spectra indicate the occurrence of electronic delocalization along the one-dimensional arrangement of bridge-head disilane moieties.

Introduction

The catenation of heavy main group elements has been extensively studied[1−3] owing to its importance in understanding the nature of chemical bonding in, and the unique electronic properties originating from, σ-electron delocalization over catenated element frameworks (σ-conjugation). One of the most striking characteristics is the absorption in the ultraviolet (UV) region, where alkanes exhibit no distinct absorption. Since silicon can form stable catenations, a variety of oligo- and polysilanes have been synthesized and extensively studied,[4] and many intriguing properties have been found, such as luminescence,[5] bulk hole-transporting capability,[6] electron- and energy-transfer capabilities,[7] and an inherent conformation dependence of the σ-conjugation.[2,8,9]

One of the unexplored subjects in silicon σ-electron systems is the orbital interaction in linearly arranged silicon arrays comprising a bicyclic cage structure,[10–12] and while various possibilities have been discussed based on theoretical calculations,[12] experimental studies have not yet been performed in this area. We now report the synthesis and isolation[13] of 9,10-disilatriptycene (hereafter denoted simply as "disilatriptycene") oligomers and their structure and photophysical properties, which provide the experimental evidence for the occurrence of electronic delocalization.

Results and Discussion

Molecular Design. To construct a linear silicon array, we chose disilatriptycene as a construction unit because of its synthetic accessibility and secure solubility by introducing substituents on the bridging benzene rings. Although the

---

* Corresponding authors. Current address (H.T.): Department of Chemistry, School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan. Phone and Fax: (+81) 3-5841-4367. E-mail: tsuji@chem.s.u-tokyo.ac.jp. Current address (K.T.): RIKEN Advanced Science Institute, 2-1 Hirosawa, Wako, Saitama 351-0981, Japan. Phone: +81-48-467-9894. Fax: +81-48-467-9895. E-mail: tamao@riken.jp.

(1) For a recent example of group 13 oligoindium, see:. Hill, M. S.; Hitchcock, P. B.; Pongtavornpinyo, R. *Science* **2006**, *311*, 1904.

(2) For recent examples of group 14 oligosilane, see: (a) Fukazawa, A.; Tsuji, H.; Tamao, K. *J. Am. Chem. Soc.* **2006**, *128*, 6800. (b) Sanji, T.; Kato, N.; Tanaka, M. *Macromolecules* **2006**, *39*, 7508.

(3) For a recent example of group 15 oligophosphane, see: Dyker, C. A.; Burford, N.; Lumsden, M. D.; Decken, A. *J. Am. Chem. Soc.* **2006**, *128*, 9632.

(4) For reviews, see: (a) Kumada, M.; Tamao, K. *Adv. Organomet. Chem.* **1968**, *6*, 19. (b) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359. (c) West, R. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; p 77. (d) Michl, J.; West, R. In *Silicon-Containing Polymers*; Jones, R. G., Ando, W., Chojnowski, J., Eds.; Kluwer Academic Publications: Dordrecht, 2000; p 499. (e) West, R. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 2001; Vol. 3, pp 541−563. (f) Tsuji, H.; Michl, J.; Tamao, K. *J. Organomet. Chem.* **2003**, *685*, 9.

(5) Kagawa, T.; Fujino, M.; Takeda, K.; Matsumoto, N. *Solid State Commun.* **1986**, *57*, 635.

(6) (a) John, P.; Odeh, I. M.; Wood, J. *J. Chem. Soc., Chem. Commun.* **1983**, 1496. (b) Kepler, R. G.; Zeigler, J. M.; Harrah, L. A. *Bull. Am. Phys. Soc.* **1984**, *29*, 590. (c) Kepler, R. G.; Zeigler, J. M.; Harrah, L. A.; Kurtz, S. R. *Phys. Rev. B* **1987**, *35*, 2818.

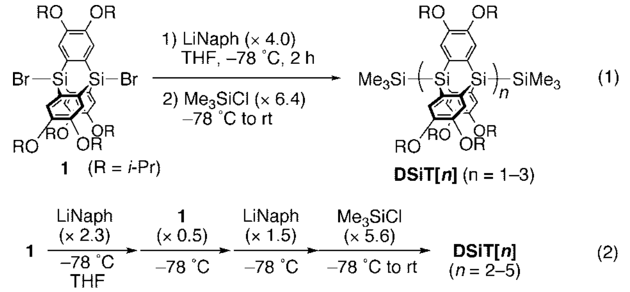
(7) (a) Tsuji, H.; Shibano, Y.; Sasaki, M.; Toganoh, M.; Kataoka, T.; Araki, Y.; Tamao, K.; Ito, O. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1338–1346. (b) Shibano, Y.; Sasaki, M.; Tsuji, H.; Araki, Y.; Ito, O.; Tamao, K. *J. Organomet. Chem.* **2007**, *692*, 356–367. (c) Sasaki, M.; Shibano, Y.; Tsuji, H.; Araki, Y.; Tamao, K.; Ito, O. *J. Phys. Chem. A* **2007**, *111*, 2973. (d) Shibano, Y.; Sasaki, M.; Kawanishi, Y.; Araki, Y.; Tsuji, H.; Ito, O.; Tamao, K. *Chem. Lett.* **2007**, *36*, 1112.

10.1021/om701283e CCC: $40.75

disilatriptycene oligomers have a phenylene-disilanylene[14] structure, the $\sigma-\pi$ conjugation between the disilane and phenylene moieties is minimal in the ground state[15−17] because the Si−Si σ-bond axis is fixed coplanar to the phenylene planes. Thus, it was expected that the photophysical aspects arising from the Si−Si σ-bond can be observed and discussed separately from those arising from the phenylene π-electrons.

Synthesis and Structural Determination. As shown in Scheme 1, the disilatriptycene[18] oligomers, **DSiT[*n*]**, were prepared by the reductive coupling of dibromodisilatriptycene **1** using lithium naphthalenide (LiNaph). The addition of a THF solution of **1** to a THF solution of LiNaph (4 molar amount), followed by treatment with chlorotrimethylsilane, afforded a mixture of a monomer, **DSiT[1]** (49%) and a dimer, **DSiT[2]** (14%), suggesting the ready formation of the dilithio species from **1** in the presence of excess reductant, which is unfavorable for the formation of longer oligomers. The degree of oligomerization was controlled by changing the sequence of the addition of the reagents. Thus, dropwise addition of the reductant to a THF solution of **1** followed by treatment with chlorotrimethylsilane afforded the dimer and trimer as the major components in a ratio of **DSiT[1]** (11%), **DSiT[2]** (53%), and **DSiT[3]** (30%). A two-step procedure proved to be more effective for preparing the longer oligomers. Thus, after the treatment of **1** with a 2.3 molar amount of LiNaph, the resulting mixture (enriched with monomer and dimer dilithio species) was treated with a 0.5 molar amount of **1** (thought to provide a mixture of bromine-terminated oligomers) and then with a 1.5 molar amount of LiNaph followed by treatment with chlorotrimethylsilane. This reaction sequence afforded **DSiT[2]**, **DSiT[3]**, **DSiT[4]**, and **DSiT[5]** in 9.8%, 14%, 29%, and 14% yields, respectively, as moisture- and air-stable white solids. These oligomers, **DSiT[*n*]** ($n = 1-5$), were separated using recycling gel permeation chromatography (GPC) using toluene as the eluent.

Scheme 1. Synthesis of Disilatriptycene Oligomers DSiT[*n*]



Each of the oligomers **DSiT[*n*]** ($n = 1-5$) was characterized using ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy, FAB mass spectrometry, and elemental analysis. The aromatic protons of **DSiT[2]** resonated at δ_H 8.07 and 7.72, which were assigned to the inside and outside protons, respectively, with the latter being almost identical to the chemical shift of the aromatic protons of **DSiT[1]** (δ_H 7.66). Such deshielding of the inside protons was attributed to the effect of the ring current of the benzene rings of the neighboring disilatriptycene unit and is a common feature of **DSiT[*n*]** ($n \geq 2$).

The molecular structure of **DSiT[2]** was unambiguously determined using X-ray crystallography. Each unit cell contains two crystallographically independent molecules having similar structures and both with an inversion center. Figure 1 shows the molecular structure of one of these molecules. The linear arrangement of six silicon atoms comprises a rigid array structure, and the Si−Si bond axes are located on the same plane as the benzene rings. The Si−Si bond lengths are within the normal range.[19] The interatomic distance of the bridgehead silicon atoms (3.02 Å) is significantly shorter than the sum of their van der Waals radii (4.00 Å).[19]

Photophysical Properties. The UV absorption, magnetic circular dichroism (MCD),[20] and emission spectra of **DSiT[*n*]**

---

(8) For oligosilanes: (a) Imhof, R.; Teramae, H.; Michl, J. *Chem. Phys. Lett.* **1997**, *270*, 500. (b) Mazières, S.; Raymond, M. K.; Raabe, G.; Prodi, A.; Michl, J. *J. Am. Chem. Soc.* **1997**, *119*, 6682. (c) Obata, K.; Kabuto, C.; Kira, M. *J. Am. Chem. Soc.* **1997**, *119*, 11345. (d) Obata, K.; Kira, M. *Organometallics* **1999**, *18*, 2216. (e) Tanaka, R.; Unno, M.; Matsumoto, H. *Chem. Lett.* **1999**, 595. (f) El-Sayed, I.; Hatanaka, Y.; Muguruma, C.; Shimada, S.; Tanaka, M.; Koga, N.; Mikami, M. *J. Am. Chem. Soc.* **1999**, *121*, 5095. (g) Tamao, K.; Tsuji, H.; Terada, M.; Asahara, M.; Yamaguchi, S.; Toshimitsu, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3287. (h) Tsuji, H.; Toshimitsu, A.; Tamao, K.; Michl, J. *J. Phys. Chem. A* **2001**, *105*, 10246. (i) El-Sayed, I.; Hatanaka, Y.; Onozawa, S.; Tanaka, M. *J. Am. Chem. Soc.* **2001**, *123*, 3597. (j) Fogarty, H. A.; Tsuji, H.; David, D. E.; Ottosson, C. H.; Ehara, M.; Nakatsuji, H.; Tamao, K.; Michl, J. *J. Phys. Chem. A* **2002**, *106*, 2369. (k) Tsuji, H.; Terada, M.; Toshimitsu, A.; Tamao, K. *J. Am. Chem. Soc.* **2003**, *125*, 7686. (l) Hatanaka, Y. *J. Organomet. Chem.* **2003**, *685*, 207. (m) Rooklin, D. W.; Schepers, T.; Raymond-Johansson, M. K.; Michl, J. *Photochem. Photobiol. Sci.* **2003**, *2*, 511. (n) Tsuji, H.; Fukazawa, A.; Yamaguchi, S.; Toshimitsu, A.; Tamao, K. *Organometallics* **2004**, *23*, 3375. (o) Mallesha, H.; Tsuji, H.; Tamao, K. *Organometallics* **2004**, *23*, 1639.

(9) For polysilanes: (a) Fujiki, M. *J. Am. Chem. Soc.* **1994**, *116*, 11976. (b) Koe, J. R.; Fujiki, M.; Nakashima, H. *J. Am. Chem. Soc.* **1999**, *121*, 9734. (c) Fujiki, M. *J. Am. Chem. Soc.* **2000**, *122*, 3336.

(10) For the synthesis of 1,3-disilabicyclo[1.1.1]pentane-related compounds: (a) Driel, M.; Gleiter, R.; Janoschek, R.; Pritzkow, H.; Reisgys, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1484. (b) Choi, N.; Asano, K.; Ando, W. *Organometallics* **1995**, *14*, 3146. (c) Choi, N.; Asano, K.; Sato, N.; Ando, W. *J. Organomet. Chem.* **1996**, *516*, 155.

(11) For the synthesis of 1,4-disilabicyclo[2.2.2]octane-related compounds: Zoch, H. G.; Szeimies, G.; Butkowskyj, T.; Van.Meerssche, M.; Germain, G.; Declercq, J. P. *Chem. Ber.* **1981**, *114*, 3896.

(12) For theoretical studies on 1,3-disilabicyclo[1.1.1]pentane and related compounds: (a) Nagase, S.; Kudo, T.; Kurakake, T. *J. Chem. Soc., Chem. Commun.* **1988**, 1063. (b) Streitwieser, A. *J. Chem. Soc., Chem. Commun.* **1989**, 1261. (c) Kitchen, D. B.; Jackson, J. E.; Allen, L. C. *J. Am. Chem. Soc.* **1990**, *112*, 3408. (d) Nguyen, K. A.; Carroll, M. T.; Gordon, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 7924. (e) Sandstroem, N.; Ottosson, H. *Chem.−Eur. J.* **2005**, *11*, 5067.

(13) For the preparation of a mixture of a disilatriptycene dimer and a disiloxane, see: Aizawa, K. Hatano, D. Terunuma. *Abstracts of the 8th Symposium of the Society of Silicon Chemistry*; Japan, Kyoto, Japan, Oct 2003; p 29.

(14) (a) Nate, K.; Ishikawa, M.; Ni, H.; Watanabe, H.; Saheki, Y. *Organometallics* **1987**, *6*, 1673. (b) Kyushin, S.; Kitahara, T.; Tanaka, R.; Takeda, M.; Matsumoto, T. *Chem. Commun.* **2001**, 2714. (c) Tsuji, H.; Shibano, Y.; Takahashi, T.; Kumada, M.; Tamao, K. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 1334.

(15) Pitt, G. C.; Carey, R. N.; Toren, E. C. *J. Am. Chem. Soc.* **1972**, *94*, 3806.

(16) Reviews see: (a) Sakurai, H. *J. Organomet. Chem.* **1980**, *200*, 261. (b) Sakurai, H. *Pure Appl. Chem.* **1987**, *59*, 1637. (c) Brook, A. G. In *The Chemistry of Organosilicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1989; Part 2, p 965. (d) Kira, M.; Miyazawa, T. In *The Chemistry of Organosilicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, 1998; Vol. 2, p 1311. (e) Brook, A. G. In *The Chemistry of Organosilicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, 1998; Vol. 2, p 1233.

(17) Sakurai, H.; Tasaka, S.; Kira, M. *J. Am. Chem. Soc.* **1972**, *94*, 9285.

(18) (a) Al-Jabar, N. A. A.; Massey, A. G. *J. Organomet. Chem.* **1985**, *287*, 57. (b) Takahashi, M.; Hatano, K.; Kawada, Y.; Koga, G.; Tokitoh, N.; Okazaki, R. *J. Chem. Soc., Chem. Commun.* **1993**, 1850. (c) Dam, M. A.; Akkerman, O. S.; de.Kanter, F. J. J.; Bickelhaupt, F.; Veldman, N.; Spek, A. L. *Chem.−Eur. J.* **1996**, *2*, 1139. (d) Kubota, M.; Hatano, K.; Takahashi, M.; Kawada, Y.; Kobayashi, T. *J. Electron Spectrosc. Relat. Phenom.* **1997**, *83*, 165.

(19) Emsley, J. *The Elements*, 3rd ed.; Oxford University Press: New York, 1998.

(20) MCD spectra can provide useful information about transitions that are forbidden in UV spectra. For details, see: Klessinger, M.; Michl, J. *Excited States and Photochemistry of Organic Molecules*; VCH Publishers: New York, 1995.

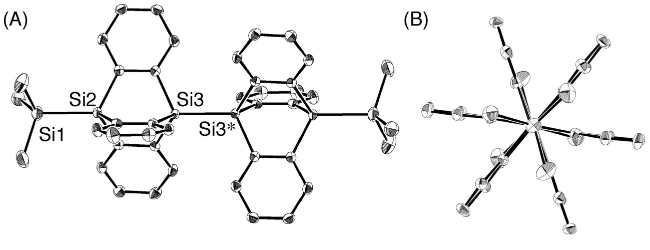


Figure 1. ORTEP drawings of the dimer **DSiT[2]** (50% probability; isopropoxy groups and hydrogen atoms are omitted for clarity): (A) Side and (B) top views. Selected interatomic distances (Å) and bond angles (deg): Si(1)−Si(2) = 2.3448(9), Si(2)···Si(3) = 3.0221(8), Si(3)−Si(3)* = 2.3385(11), Si(1)−Si(2)···Si(3) = 175.62(3), Si(2)···Si(3)−Si(3)* = 178.19(4).

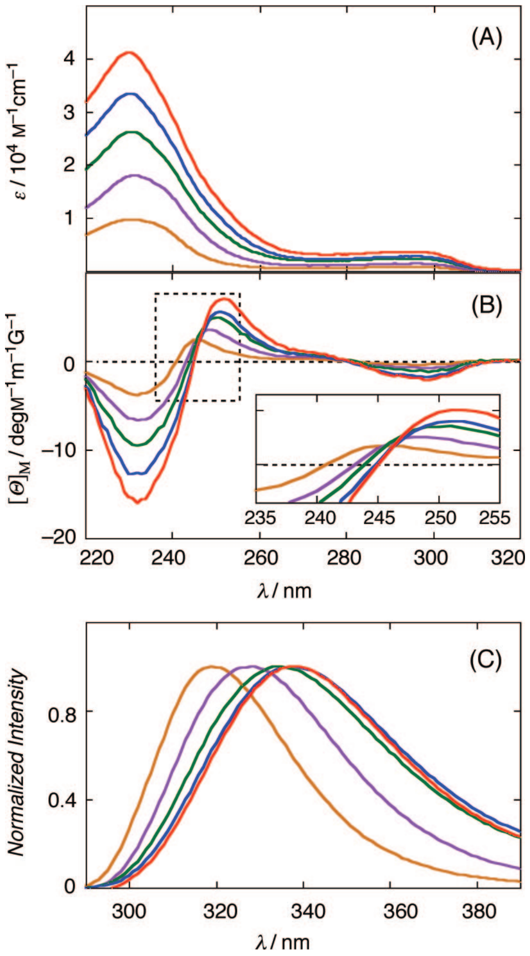


Figure 2. Electronic spectra of **DSiT[*n*]** in cyclohexane. (A) UV absorption, (B) MCD (inset: enlargement of the region bounded by dotted-line square), and (C) emission (excitation at 250 nm, normalized at the emission maximum): **DSiT[1]** (pale brown), **DSiT[2]** (purple), **DSiT[3]** (green), **DSiT[4]** (blue), and **DSiT[5]** (red).

(n = 1−5) are shown in Figure 2, and the data are summarized in Table 1. In the series of **DSiT[*n*]**, the wavelength of the transitions occurring near 230 and 295 nm observed in both the UV and MCD spectra remain almost constant, regardless of the array length, while only the extinction coefficients of these bands increases as the value of n increases. These bands were attributed to the π(aryl) → π^*(aryl) transitions of the phenylene moieties within each triptycene unit. In contrast, the MCD spectra show a dispersive pattern from 220 to 270 nm, and the peak occurring at 245−250 nm shows a slight, but noticeable, red shift as the length of the array increases. We assume that this red shift demonstrates the existence of electronic delocalization along the DSiT array.

Table 1. Summary of UV Absorption and Fluorescence Measurements of DSiT[*n*] in Cyclohexane at Room Temperature

compound	UV abs λ/nm (ε/10^4 M^{-1} cm^{-1})	emission λ/nm
DSiT[1]	230 (9.76), 297 (0.84)	319
DSiT[2]	231 (18.0), 297 (1.45)	328
DSiT[3]	231 (26.2), 296 (2.37)	335
DSiT[4]	230 (33.4), 297 (2.77)	337
DSiT[5]	230 (41.1), 296 (3.66)	337

The emission of **DSiT[*n*]** (n = 1−5) (Figure 2C) shows broad and structureless spectra similar to emission bands of diaryldisilanes.[16] The emission maximum also shifts from 319 to 337 nm as the number of the silicon atoms increases. This red shift of the emission maximum obviously indicates the existence of electronic delocalization. The origin of the delocalization effect and the nature of the excited state are unclear at this stage. Detailed experimental and computational studies are future subjects.

Conclusions

A series of disilatriptycene oligomers with a one-dimensional array have been found to show a small, but steady, red shift in the MCD and emission spectra. The chain-length dependence of the spectra has been observed for the first time by introducing triptycene units, suggesting the existence of electronic delocalization over the silicon array structure.

Experimental Section

General Comments. Ether, THF, and hexane were freshly distilled from sodium benzophenone ketyl before use unless otherwise noted. Anhydrous-grade DMF, ether, and THF were purchased from Wako Pure Chemical Industries. Butyllithium and *tert*-butyllithium were purchased from Wako Pure Chemical Industries and Kanto Chemical, respectively. Lithium naphthalenide was prepared from the reaction of naphthalene with lithium granular (CHMETALL) in THF at 0 °C before use. Recycling gel permeation chromatography (GPC) was performed on an LC-908 instrument with JAIGEL 1H+2H columns (Japan Analytical Industry) with toluene as eluent at the flow rate of 3.5 mL/min. Elemental analyses and mass spectroscopy were performed at the Micro Analysis Division of Institute for Chemical Research, Kyoto University, and the Mass Spectrum Division of Institute for Chemical Research, Kyoto University, respectively. 1,2-Dibromo-4,5-diisopropoxybenzene was prepared according to the literature.[21]

Tris(2-bromo-4,5-diisopropoxyphenyl)silane. This compound was prepared in a similar manner to similar compounds.[22] Under a nitrogen atmosphere, to a solution of 1,2-dibromo-4,5-diisopropoxybenzene (61.0 g, 0.173 mol) in ether (anhydrous, 270 mL) and THF (anhydrous, 180 mL) was added n-butyllithium (1.6 M in hexane, 114 mL, 0.18 mol) at −110 °C over 2.5 h. After being stirred at −110 °C for 1 h, a solution of trichlorosilane (5.8 mL, 0.057 mol) in ether (anhydrous, 45 mL) was added over 15 min at the same temperature. The reaction mixture was slowly allowed to warm to room temperature to give a yellow suspension. After

---

(21) (a) Tsuji, H.; Inoue, T.; Sase, S.; Tamao, K. *Acta Crystallogr. E* **2006**, *E62*, m535. (b) Tsuji, H.; Inoue, T.; Kaneta, Y.; Sase, S.; Kawachi, A.; Tamao, K. *Organometallics* **2006**, *25*, 6142.

(22) (a) Chen, L. S.; Chen, G. J.; Tamborski, C. *J. Organomet. Chem.* **1980**, *193*, 283. (b) Kyushin, S.; Shinnai, T.; Kubota, T.; Matsumoto, H. *Organometallics* **1997**, *16*, 3800.

evaporation, hexane (400 mL) was added to the residue, and the resulting yellow suspension was passed through a pad of Celite. The filtrate was concentrated in vacuo to give a yellow oil. Recrystallization from hexane afforded the title compound (16.0 g, 33% yield) as a white solid (hexane), which was used in the next step without further purification: mp 109−111 °C (dec): ^{1}H NMR (300 MHz, C_6D_6) δ 1.05 (d, $J = 6.0$ Hz, 18H), 1.16 (d, $J = 6.0$ Hz, 18H), 4.06 (sept, $J = 6.0$ Hz, 3H), 4.32 (sept, $J = 6.0$ Hz, 3H), 6.50 (s, 1H), 7.39 (s, 3H), one signal due to protons on the benzene rings was not observed because the signal overlapped with the signal of residual benzene in C_6D_6; ^{13}C{^{1}H} NMR (68 MHz, C_6D_6) δ 22.03, 22.24, 71.30, 71.97, 120.51, 123.01, 126.24, 127.41, 148.32, 152.24; ^{29}Si NMR (53 MHz, INEPT, C_6D_6) δ −19.11; HRMS-EI (*m/z*) M$^+$ calcd for $C_{36}H_{49}O_6{}^{79}Br_2{}^{81}BrSi$, 844.0828; found, 844.0801; calcd for $C_{36}H_{49}O_6{}^{79}Br{}^{81}Br_2Si$, 846.0808; found, 846.0801.

2,3,6,7,14,15-Hexa(isopropoxy)-9,10-disilatriptycene. Under an argon atmosphere, to a solution of tris(2-bromo-4,5-diisopropoxyphenyl)silane (7.94 g, 9.39 mmol) in ether (360 mL) was added *tert*-butyllithium (1.56 M in pentane, 36 mL, 56 mmol) over 15 min at −78 °C. After being stirred for 2 h at −78 °C, trichlorosilane (1.00 mL, 9.82 mmol) was added to the reaction mixture, which was slowly allowed to warm to room temperature. The resulting white suspension was passed through a pad of Celite, and the filtrate was concentrated in vacuo to give a pale orange solid. The solid was suspended in hexane (400 mL × 1, 250 mL × 1), and the resulting suspension was filtered to afford a colorless solution. Evaporation of the solvent gave a pale yellow powder (5.77 g), which contains the title compound as the main component. The crude product was used for the next step without further purification: ^{1}H NMR (300 MHz, C_6D_6) δ 1.20 (d, $J = 6.0$ Hz, 36H), 4,36 (d, $J = 6.0$ Hz, 6H), 5.71 (s, 2H), 7.61 (s, 6H); ^{13}C{^{1}H} NMR (68 MHz, C_6D_6) δ 22.60, 71.77, 123.20, 138.02, 149.18; ^{29}Si NMR (53 MHz, INEPT, C_6D_6) δ −36.34; HRMS-EI (*m/z*) M$^+$ calcd for $C_{36}H_{50}O_6Si_2$, 634.3146; found, 634.3130.

9,10-Dibromo-2,3,6,7,14,15-hexa(isopropoxy)-9,10-disilatriptycene (1). Under an argon atmosphere, a mixture of the crude product of the dihydrodisilatriptycene (5.67 g, 8.93 mmol if pure), $PdCl_2$ (296 mg, 0.893 mmol), and carbon tetrabromide (4.78 g, 27.0 mmol) in hexane (40 mL) was allowed to heat at 60 °C for 16 h to give a black suspension. After evaporation, the residue was suspended in hexane (50 mL × 2), and the resulting suspension was passed through a pad of Celite to give a yellow solution. The solution was concentrated in vacuo to give a yellow oil. Recrystallization from toluene (15 mL) afforded **1** as white solids (1.57 g, 1.98 mmol, 21% yield based on the triarylsilane). The obtained white solid had mp 218−221 °C, not pure enough, but used in the next step without further purification: ^{1}H NMR (300 MHz, C_6D_6) δ 1.15 (d, $J = 6.0$ Hz, 36H), 4.39 (sept, $J = 6.0$ Hz, 6H), 7.80 (s, 6H); ^{13}C{^{1}H} NMR (68 MHz, C_6D_6) δ 22.40, 71.82, 121.32, 136.03, 149.80; ^{29}Si NMR (53 MHz, INEPT, C_6D_6) δ −13.44; HRMS-EI (*m/z*) M$^+$ calcd for $C_{36}H_{48}O_6{}^{79}Br_2Si_2$, 790.1356; found, 790.1343; [M + 2]$^+$ calcd for $C_{36}H_{48}O_6{}^{79}Br{}^{81}BrSi_2$, 792.1336; found, 792.1371; [M + 4]$^+$ calcd for $C_{36}H_{48}O_6{}^{81}Br_2Si_2$, 794.1315; found, 794.1334.

Syntheses of DSiT[*n*]. (a) Addition of a THF Solution of 1 to LiNaph (see eq 1). Under an argon atmosphere, to LiNaph (0.52 M in THF, 0.76 mL, 0.40 mmol) was added dropwise a solution of **1** in THF (2 mL). After being stirred at −78 °C for 1 h, chlorotrimethylsilane (80 μL, 0.63 mmol) was added to the resulting dark green solution. The reaction mixture was stirred for 10 min at −78 °C and was allowed to warm to room temperature. After evaporation of the solvent, the resulting yellow solid was subjected to vacuum sublimation to remove naphthalene, and toluene was added to the residue. Filtration of the resulting white suspension through a pad of Celite and the subsequent evaporation of the solvent gave white solids. The crude mixture was separated by recycling GPC (toluene) to give **DSiT[1]** (37.1 mg, 49% yield) and **DSiT[2]** (9.8 mg, 14% yield).

(b) Addition of LiNaph to a THF Solution of 1 (see eq 1). Under an argon atmosphere, to a solution of **1** (78.0 mg, 0.098 mmol) in THF (1 mL) was added dropwise LiNaph (0.56 M in THF, 0.70 mL, 0.39 mmol) at −78 °C. After being stirred at −78 °C for 2 h, chlorotrimethylsilane (80 μL, 0.63 mmol) was added to the resulting dark green solution. The reaction mixture was stirred for 10 min at −78 °C and was allowed to warm to room temperature. After evaporation of the solvent, the resulting yellow solid was subjected to vacuum sublimation to remove naphthalene, and toluene was added to the residue. Filtration of the resulting white suspension through a pad of Celite and the subsequent evaporation of the solvent gave white solids. The crude mixture was separated by recycling GPC (toluene) to give **DSiT[1]** (8.7 mg, 11% yield, $t_R = 78$ min), **DSiT[2]** (37.4 mg, 53% yield, $t_R = 73.5$ min), and **DSiT[3]** (20.8 mg, 30% yield, $t_R = 70$ min).

(c) Two-Step Procedure for Synthesis of the Longer Oligomers (see eq 2). Under an argon atmosphere, to a solution of **1** (132 mg, 0.167 mmol) in THF (1.5 mL) was added LiNaph (0.70 M in THF, 0.55 mL, 0.39 mmol) at −78 °C. After being stirred for 1 h at −78 °C, to a solution of **1** (66.2 mg, 0.084 mmol) in THF (1 mL) was added the resulting dark red solution. The reaction mixture was stirred for 45 min at −78 °C, and then LiNaph (0.70 M in THF, 0.35 mL, 0.25 mmol) was added at the same temperature. After being stirred for 1 h, chlorotrimethylsilane (0.12 mL, 0.94 mmol) was added at −78 °C. The reaction mixture was stirred for 5 min at −78 °C and was allowed to warm to room temperature to give a yellow solution. After evaporation of the solvent, the resulting white solid was subjected to vacuum sublimation, and toluene was added to the residue. Filtration of the resulting suspension through a pad of Celite and the subsequent evaporation of the solvent gave white solids. The crude mixture was separated by recycling GPC (toluene) to give **DSiT[2]** (17.5 mg, 9.8% yield), **DSiT[3]** (24.2 mg, 14% yield), **DSiT[4]** (48.5 mg, 29% yield, $t_R = 67.5$ min), and **DSiT[5]** (23.3 mg, 14% yield, $t_R = 65$ min).

DSiT[1]: White solid (MeOH); mp >300 °C; ^{1}H NMR (300 MHz, C_6D_6) δ 0.73 (s, 18H), 1.26 (d, $J = 6.0$ Hz, 36H), 4.51 (sept, $J = 6.0$ Hz, 6H), 7.66 (s, 6H); ^{13}C{^{1}H} NMR (68 MHz, C_6D_6) δ 0.24, 22.64, 72.04, 124.56, 141.26, 148.55; ^{29}Si NMR (53 MHz, INEPT, C_6D_6) δ −21.17, −41.63; HRMS-EI (*m/z*) M$^+$ calcd for $C_{42}H_{66}O_6Si_4$, 778.3937; found 778.3936. Anal. Calcd for $C_{78}H_{114}O_{12}Si_6$: C, 64.73; H, 8.54. Found: C, 64.82; H, 8.49.

DSiT[2]: White solid (MeOH); mp >300 °C; ^{1}H NMR (300 MHz, C_6D_6) δ 0.63 (s, 18 H), 0.97 (d, $J = 6.0$ Hz, 36H), 1.30 (d, $J = 6.0$ Hz, 36H), 4.28 (sept, $J = 6.0$ Hz, 6H), 4.53 (sept, $J = 6.0$ Hz, 6H), 7.72 (s, 6H), 8.07 (s, 6H); ^{13}C{^{1}H} NMR (68 MHz, C_6D_6) δ 0.26, 22.05, 22.77, 70.92, 72.05, 123.99, 124.22, 140.36, 140.39, 148.65 (overlapped); ^{29}Si NMR (53 MHz, INEPT, C_6D_6) δ −21.19, −40.93, −41.00; LRMS-FAB $m/z = 1411$ [M + H]$^+$. Anal. Calcd for $C_{78}H_{114}O_{12}Si_6$: C, 66.34; H, 8.14. Found: C, 66.13; H, 7.90.

DSiT[3]: White solid (MeOH); mp >300 °C; ^{1}H NMR (300 MHz, C_6D_6) δ 0.67 (s, 18H), 0.95 (d, $J = 6.0$ Hz, 36H), 1.13 (d, $J = 6.0$ Hz, 36H), 1.31 (d, $J = 6.0$ Hz, 36H), 4.15−4.37 (m, 12H), 4.54 (sept, $J = 6.0$ Hz, 6H), 7.72 (s, 6H), 8.05 (s, 6H), 8.06 (s, 6H); ^{13}C{^{1}H} NMR (68 MHz, C_6D_6) δ 0.27, 22.13, 22.47, 22.74, 71.36, 72.10 (overlapped), 124.25, 124.40, 124.50, 139.65, 140.34, 140.51, 148.65, 148.80, 148.85; ^{29}Si NMR (53 MHz, INEPT, C_6D_6) δ −21.14, −39.90, −40.75, −40.90; LRMS-FAB $m/z = 2044$ [M + H]$^+$. Anal. Cacld for $C_{114}H_{162}O_{18}Si_8$: C, 66.95; H, 7.98. Found: C, 67.12; H, 7.82.

DSiT[4]: White solid (MeOH); mp >300 °C; ^{1}H NMR (300 MHz, C_6D_6) δ 0.67 (s, 18H), 0.97 (d, $J = 6.0$ Hz, 36H), 1.10 (d, $J = 6.0$ Hz, 36H), 1.11 (d, $J = 6.0$ Hz, 36H), 1.31 (d, $J = 6.0$ Hz, 36H), 4.16−4.37 (m, 18H), 4.54 (sept, $J = 6.0$ Hz, 6H), 7.72 (s, 6H), 8.052 (s, 6H), 8.058 (s, 6H), 8.063 (s, 6H); ^{13}C{^{1}H} NMR

(68 MHz, C_6D_6) δ 0.04, 21.95, 22.30 (overlapped), 22.56, 71.24, 71.34, 71.49, 71.97, 124.26, 124.34, 124.69, 124.75, 139.59, 139.75, 140.33, 140.61, 148.79, 148.84, 148.87, 149.00; ^{29}Si NMR (53 MHz, INEPT, C_6D_6) δ −21.36, −39.75, −40.10, −41.06 (overlapped); LRMS-FAB *m*/*z* = 2676 $[M + H]^+$. Anal. Calcd for $C_{186}H_{258}O_{30}Si_{12}$: C, 67.27; H, 7.90. Found: C, 67.35; H, 7.89.

DSiT[5]: White solid (MeOH); mp >300 °C; ^{1}H NMR (300 MHz, C_6D_6) δ 0.68 (s, 18H), 0.97 (d, *J* = 6.3 Hz, 36H), 1.08−1.15 (m, 108H), 1.32 (d, *J* = 6.3 Hz, 36H), 4.14−4.38 (m, 24H), 4.55 (sept, *J* = 6.3 Hz, 6H), 7.73 (s, 6H), 8.05−8.08 (24H); ^{13}C{^{1}H} NMR (68 MHz, C_6D_6) δ 0.04, 21.94, 22.28 (overlapped), 22.56, 71.24, 71.34, 71.50, 71.55, 71.97, 124.23, 124.37, 124.56, 124.75, 124.84, 139.82, 139.66, 139.82, 140.32, 140.64, 148.82 (overlapped), 148.90, 148.97, 149.00; ^{29}Si NMR (53 MHz, INEPT, C_6D_6) δ −21.59, −39.77 (overlapped), −40.08, −41.06 (overlapped); LRMS-FAB *m*/*z* = 3309 $[M + H]^+$. Anal. Calcd for $C_{186}H_{258}O_{30}Si_{12}$: C, 67.47; H, 7.85. Found: C, 67.25; H, 7.75.

UV Absorption Spectra Measurements. The UV absorption spectra were recorded using a Perkin-Elmer Lambda 900 UV/vis/NIR spectrometer at room temperature. Sample solutions (concentration = 10^{-6}−10^{-7} M) in a square 1 cm quartz cell were used for the measurements. Cyclohexane (UV measurement grade) was purchased from Dijindo Laboratories and was used without further purification.

MCD Spectra Measurements. The MCD spectra were recorded using a JASCO J-820 spectropolarimeter fitted with a 1.5 T electromagnet at room temperature. The cyclohexane solutions of **DSiT[*n*]** (concentration = 10^{-6}−10^{-7} M) in a 1 cm Suprasil quartz cell were used in the measurements. Cyclohexane (UV measurement grade) was purchased from Dojindo Laboratories and was used without further purification.

Emission Spectra Measurements. The emission spectra were recorded using a JASCO FP-6500 spectrometer at room temperature. Cyclohexane (emission spectra grade) was purchased from Nacalai Tesque Inc. and was degassed under flowing argon gas before use. The cyclohexane solutions of **DSiT[*n*]** (concentration = 10^{-8}−10^{-9} M) were prepared in a glovebox filled with argon gas and were placed in a 1 cm square quartz cell.

Acknowledgment. This article is dedicated to the late Professor Yoshihiko Ito. Financial support from the Ministry of Education, Culture, Sports, Science, and Technology of Japan for the Grants-in-Aid for COE Research on Elements Science, No. 12CE2005 for K.T., and the “Joint Project of Chemical Synthesis Core Research Institutions” for H.T. is gratefully acknowledged. S.S. thanks the Research Fellowship of the Japan Society for the Promotion of Science (JSPS) for Young Scientists. We also thank Dr. T. Sasamori (ICR, Kyoto University) for the assistance with the X-ray analysis.

Supporting Information Available: Summary of the X-ray crystallography of **DSiT[2]**. ^{1}H and ^{13}C NMR chart for compound **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM701283E