

## An Electroluminescent Polysilole and Some Dichlorooligosiloles

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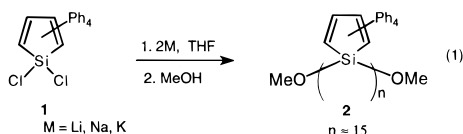
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Siloles are of considerable current interest, both because of their unusual electronic properties<sup>1</sup> and because of their possible application as electron-transporting materials in devices such as light-emitting diodes (LED's).<sup>2</sup> Siloles exhibit a low reduction potential and a low-lying LUMO energy level, attributed to  $\sigma^*$ - $p^*$  conjugation arising from the interaction between the  $\sigma^*$  orbital of the  $\sigma$ -bonded silicon atom and the  $p^*$  orbital of the butadiene moiety of the ring.<sup>3,4</sup>

In contrast to siloles, polysilanes display low oxidation potentials and a high-lying HOMO, resulting from  $\sigma$ -delocalization along the Si–Si chain.<sup>5</sup> A combined polysilane–polysilole might then be of special interest, since it could provide both electron-donating and electron-accepting properties within the same molecule. In fact, silole–polysilane copolymers have been synthesized, both in our laboratories<sup>6</sup> and by Sakurai and co-workers,<sup>7</sup> and shown to be electroluminescent.

We report here what is apparently the first example of a polysilole homopolymer, in which every silicon atom in the polymer chain is also part of a silole ring. This polymer (**2**) was easily obtained from the readily available compound, 1,1-dichlorotetraphenylsilole (**1**),<sup>8</sup> by reduction with lithium, sodium or potassium, in >30% yield (eq 1).<sup>9</sup> The molecular weight and



yield of polysilole **2** depended only slightly on the nature of the alkali metal. From its molecular weight ( $M_n \approx 5500$ ,  $M_w/M_n = 1.1$  determined by SEC, confirmed by end-group analysis) **2** is actually an extended oligomer with a degree of polymerization of about 15, rather than a high polymer. Nevertheless it shows polymer-like properties, and in particular, it can be cast into a thin film from solution.

Reaction of **1** with 1.2 equiv of lithium produced a mixture of **3**, **4**, and **5** (eq 2), which were separated by preparative size exclusion chromatography and characterized by <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectroscopy.<sup>10</sup> **3** and **4** were identified as the dichlorooligosiloles Cl(C<sub>4</sub>Ph<sub>4</sub>Si)<sub>2</sub>Cl and Cl(C<sub>4</sub>Ph<sub>4</sub>Si)<sub>3</sub>Cl, respectively.

(1) Tamao, K.; Kawachi, A. *Adv. Organomet. Chem.* **1995**, 38, 1–58; Tamao, K.; Yamaguchi, S. *Pure Appl. Chem.* **1996**, 68, 139.

(2) Tamao, K.; Uchida, M.; Izumizawa, T.; Furukawa, K.; Yamaguchi, S. *J. Am. Chem. Soc.* **1996**, 118, 11974.

(3) Khabashesku, V. N.; Balaji, V.; Boganov, S. E.; Nefedov, O. M.; Michl, J. *J. Am. Chem. Soc.* **1994**, 116, 320.

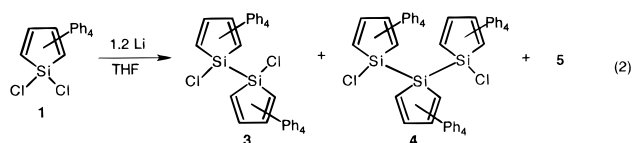
(4) Yamaguchi, S.; Tamao, K. *Bull. Chem. Soc. Jpn.* **1996**, 69, 2327; Yamaguchi, Y. *Synth. Met.* **1996**, 82, 149.

(5) West, R. In *Comprehensive Organometallic Chemistry II*; Davies, A. G., Ed.; Pergamon: Oxford, 1995; pp 77–110.

(6) Sohn, H.; Liu, Y.; West, R., unpublished studies.

(7) Sanji, T.; Sakai, T.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1998**, 120, 4552.

(8) Joo, W. -C.; Hong, J. -H.; Choi, S. -B.; Son, H.-E.; Kim, C. H. *J. Organomet. Chem.* **1990**, 391, 27.



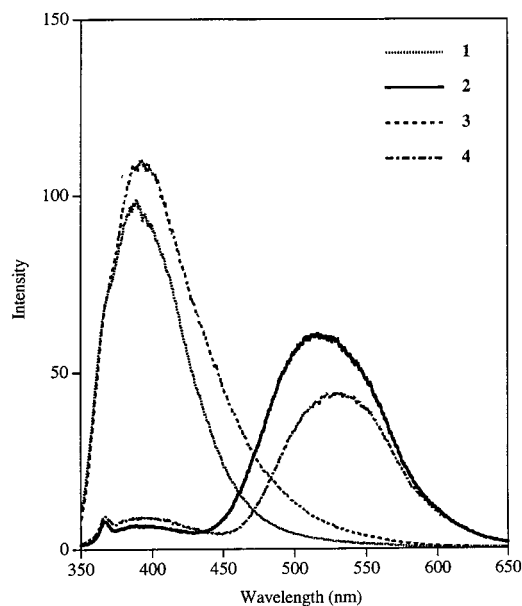
Compound **5**, which shows only a single <sup>29</sup>Si resonance, is tentatively identified as a cyclooligosilane. The X-ray crystal structures for **3** and **4** were determined and are shown in Figure 4<sup>11</sup> and Figure 5.<sup>12</sup> The silole rings in both **3** and **4** are arranged in an all-gauche conformation along the Si–Si bond skeleton. The dihedral angles,  $\angle C4-Si1-Si2-C32$  of  $58.36^\circ$  and  $\angle C32-Si2-Si3-C60$  of  $61.08^\circ$ , in **4** show that the silole rings are strongly rotated relative to one another.<sup>13</sup>

(9) Preparation of polysilole **2**: **1** (3.0 g, 6.6 mmol) in THF (130 mL) was treated with 2 equiv of either Li, Na, or K. After the mixture was refluxed for 3 days, 4 mL of methanol was added to the reaction mixture. After removal of the solvent, the residual solid was dissolved in 5 mL of THF and then poured into 1.2 L of methanol. Polysilole **2** was obtained as pale yellow powder after the third cycle of dissolution–precipitation followed by freeze-drying. **2**: (Li 0.93 g, 37%,  $M_w = 5200$ ,  $M_w/M_n = 1.11$ , determined by SEC with polystyrene standards; Na 0.75 g, 30%,  $M_w = 5300$ ,  $M_w/M_n = 1.16$ ; K 0.91 g, 36%,  $M_w = 5700$ ,  $M_w/M_n = 1.15$ ); <sup>1</sup>H NMR (300.133 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta = 6.30-7.40$  (br, m, Ph), 3.56 (br, OMe); <sup>13</sup>C NMR (75.403 MHz, CDCl<sub>3</sub>) ( $\delta = 77.00$ )  $\delta = 53.6$  (s, OMe); 125–131 (m, silole carbons); 137–147 (br, m, Ph); <sup>29</sup>Si NMR (71.548 MHz, CDCl<sub>3</sub>)  $\delta = 6.72, -40.79$ . Endgroup analysis was employed to determine the chain length by integrating the area for the phenyl protons and methoxy protons. A ratio of about 15 siloles to 2 methoxy groups was observed. The chain length from the endgroup analysis is consistent with the molecular weight determined by GPC.

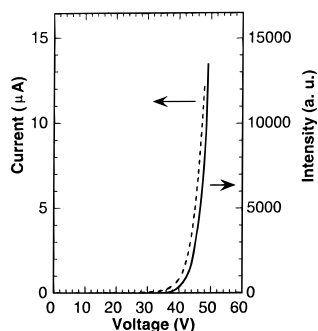
(10) Preparation of dichlorooligosiloles **3** and **4**: 1,1-dichloro-2,3,4,5-tetraphenylsilole (5.0 g, 11 mmol) and lithium (91 mg, 13 mmol) were stirred in THF (120 mL) at room temperature for 24 h. The reaction gave initially a red color and finally a yellow solution. The solvent was removed under reduced pressure. Toluene (50 mL) was added to the yellow solid, and the solution was filtered to remove LiCl salt. The products, **3**, **4**, and **5**, were separated by preparative GPC. Crystals of bisilole **3** were obtained from dichloromethane and of tersilole **4** from diethyl ether, at  $-20^\circ\text{C}$ . **3**: yellow crystals (2.0 g, 47%); mp  $300-304^\circ\text{C}$ ; <sup>1</sup>H NMR (300.133 MHz, CDCl<sub>3</sub>)  $\delta = 6.55-6.58$  and  $6.92-7.18$  (m, 40H, Ph); <sup>13</sup>C {<sup>1</sup>H} NMR (75.403 MHz, CDCl<sub>3</sub>) ( $\delta = 77.00$ )  $\delta = 137.35, 137.04, 129.86, 129.81, 129.31, 127.99, 127.92, 127.45, 126.90, 126.61$ ; <sup>29</sup>Si NMR (71.548 MHz, CDCl<sub>3</sub>)  $\delta = 0.24$ ; MS(ED)  $m/z$  (%) 840 (2) [ $M^+$ ], 804 (2) [ $M^+ - Cl$ ], High-resolution MS calcd for C<sub>56</sub>H<sub>40</sub>Cl<sub>2</sub>Si<sub>2</sub> 840.2045, found 840.2038. **4**: yellow crystals (1.1 g, 25%); mp  $329^\circ\text{C}$  dec; <sup>1</sup>H NMR (300.133 MHz, CDCl<sub>3</sub>)  $\delta = 6.25-6.43$  and  $6.83-7.14$  (m, 60H, Ph); <sup>13</sup>C {<sup>1</sup>H} NMR (75.403 MHz, CDCl<sub>3</sub>) ( $\delta = 77.00$ )  $\delta = 158.11, 155.84, 139.21, 138.69, 138.29, 137.47, 137.42, 137.32, 130.66, 130.57, 130.39, 129.98, 129.79, 127.81, 127.04, 126.98, 126.49, 126.31, 126.26, 126.17$ ; <sup>29</sup>Si NMR (71.548 MHz, CDCl<sub>3</sub>)  $\delta = 7.00, -40.73$ ; MS(FAB)  $m/z$  (%) 1224.5 (7) [ $M^+$ ]. **5**: yellow crystals (0.8 g, 19%); mp  $309^\circ\text{C}$  dec; <sup>1</sup>H NMR (300.133 MHz, CDCl<sub>3</sub>)  $\delta = 6.25-6.55$  and  $6.75-7.30$  (m, 60H, Ph); <sup>13</sup>C {<sup>1</sup>H} NMR (75.403 MHz, CDCl<sub>3</sub>) ( $\delta = 77.00$ )  $\delta = 156.77, 138.54, 138.02, 131.22, 129.86, 129.05, 128.24, 127.59, 127.51, 126.82, 126.76, 126.22, 126.14, 125.31$ ; <sup>29</sup>Si NMR (71.548 MHz, CDCl<sub>3</sub>)  $\delta = 6.80$ . In the preparative GPC 5% of higher molecular weight products were also obtained.

(11) X-ray structure analysis of **3**·2(CDCl<sub>3</sub>),  $M_r = 1080.71$ , triclinic,  $P\bar{1}$ ,  $a = 10.3966$  (4) Å,  $b = 13.5722$  (5) Å,  $c = 19.5007$  (7) Å,  $\alpha = 86.870$  (2) $^\circ$ ,  $\beta = 89.759$  (2) $^\circ$ ,  $\gamma = 74.235$  (2) $^\circ$ ,  $V = 2644.02$  (17) Å<sup>3</sup>,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.357$  Mg m<sup>-3</sup>,  $F(000) = 1108$ ,  $\lambda = 0.71073$  Å,  $\theta = 153$  (2) K. A yellow transparent crystal (crystal size  $0.35 \times 0.35 \times 0.04$  mm) was mounted under a coating of paratone-N. Intensity data were collected using a Siemens SMART ccd area detector mounted on a Siemens P4 diffractometer equipped with graphite-monochromated Mo K $\alpha$  radiation ( $2.41^\circ < \theta < 25.00^\circ$ ). From a total of 23 252 measured data, 9072 were independent ( $R_{\text{int}} = 0.0360$ ). The structure was solved by direct methods and refined by the full-matrix least-squares method on  $F^2$ . A total of 621 parameters were refined against 58 restraints and 9072 data to give  $wR(F^2\text{-all}) = 0.1817$  and  $S = 1.078$ . The final  $R(F\text{-obs})$  was 0.0653 for the 6798 observed data. The thermal ellipsoids were drawn at the 50% probability level.

(12) X-ray structure analysis of **4**: C<sub>84</sub>H<sub>60</sub>Cl<sub>2</sub>Si<sub>3</sub>,  $M_r = 1224.49$ , monoclinic,  $P2_1/c$ ,  $a = 17.227$  (2) Å,  $b = 13.636$  (2) Å,  $c = 27.757$  (2) Å,  $\alpha = 90^\circ$ ,  $\beta = 97.495$  (6) $^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 1301.2$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.258$  Mg m<sup>-3</sup>,  $F(000) = 2560$ ,  $\lambda = 1.54178$  Å,  $\theta = 113$  (2) K. A yellow transparent crystal (crystal size  $0.40 \times 0.20 \times 0.10$  mm) was mounted under a coating of paratone-N. Intensity data were collected by the  $\omega$  scan method ( $2.59^\circ < \theta < 57.01^\circ$ ) on a Siemens P4 diffractometer. From a total of 9024 measured data, 8698 were independent ( $R_{\text{int}} = 0.1177$ ). The structure was solved by direct methods with the SHELXS-86 program and refined by the full-matrix least-squares method on using the SHELXL-93 program.  $R(F\text{-obs}) = 0.1008$ ,  $wR(F^2\text{-all}) = 0.3063$ ,  $S = 1.046$  for 8688 data and 803 variables. The thermal ellipsoids were drawn at the 50% probability level.



**Figure 1.** Fluorescence spectra of **1–4** at  $10^{-5}$  M for **1, 3,** and **4** and  $10$  mg/L for **2**, in THF. Excitation was at 330 nm.



**Figure 2.** Current–voltage–intensity characteristics for single-layer LED containing **2**. The turn-on voltage was 26 V.

Compounds **1, 2, 3,** and **4** all exhibit bands near 300 and 370 nm in their electronic absorption spectra. The fluorescence of these compounds, however, differs drastically. As shown in Figure 1, compounds **1** and **3** emit near 380 nm; however, **4**, with two Si–Si bonds, and polymer **2** show anomalous, strongly Stokes-shifted emission near 520 nm. Moreover **2** is intensely electroluminescent, with similar 520-nm emission.<sup>16</sup> The current–voltage curve for **2** is shown in Figure 2, and the electroluminescence spectrum for **2** acting as a single-component LED is given in Figure 3. The external quantum efficiency is  $3 \times 10^{-2}$  % at a current density of  $0.3 \text{ mA/cm}^2$ .<sup>17</sup>

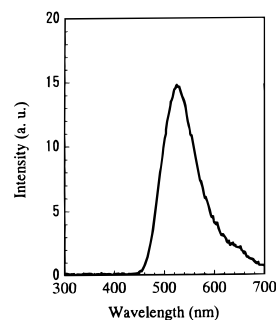
(13) The structure of **4** differs from that of the related but less hindered tersilole and quatersilole reported by Tamao and co-workers,<sup>14</sup> which have gauche–trans and gauche–trans–gauche arrangements of the silole rings, as well as the permethyl-tersilole reported by Kira and co-workers,<sup>15</sup> which has a trans–trans relationship between the silole rings.

(14) Yamaguchi, S.; Jin, R.-Z.; Tamao, K. *Organometallics* **1997**, *16*, 2486.

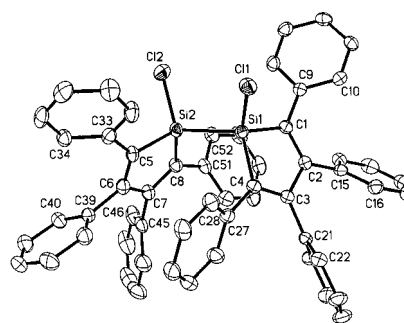
(15) Kanno, K.; Ichinohe, M.; Kabuto, C.; Kira, M. *Chem. Lett.* **1998**, 99.

(16) A thin film of **2** was prepared by spin-casting from a toluene solution after filtration through a PTFE filter, pore size  $0.2 \mu\text{m}$ . Film thickness was  $\sim 275 \text{ nm}$ . The photoluminescence spectrum was measured at room temperature using a Shimadzu RF-5300PC fluorescence spectrometer. To prepare the LEDs, ITO glass plates with a resistance of  $30 \text{ ohm/cm}^2$  were cleaned by ultrasonic treatment in 2-propanol, treated with Ar plasma, and then stored in an oven at  $100^\circ\text{C}$ . until use. After spin-coating with **1**, an Mg:Ag layer as a cathode was vacuum-deposited onto the polymer layer at a pressure less than  $2 \times 10^{-6}$  Torr. All these operations were carried out in a clean room of class 1000. The active area of the device was  $2.5 \times 3 \text{ mm}^2$ . Current–voltage characteristics were measured using a Keithley-type 2400 digital sourcemeter. The LEDs were operated at a pulse current of  $100 \mu\text{A}$ .

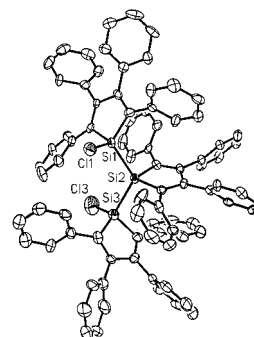
(17) This is the same order of efficiency as reported for other single layer organic ELDs, for example poly(*p*-phenylenevinylene). See: Burroughs, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Burns, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.



**Figure 3.** Electroluminescence spectrum of polymer **2** LED at  $25^\circ\text{C}$ .



**Figure 4.** Thermal ellipsoid diagram of structure of **3**. Selected bond lengths (pm): Si1–Si2 236.9 (2), Si1–C11 206.8 (2), Si2–C12 206.9 (2), Si1–C1 186.7 (6), C1–C2 136.8 (8), C2–C3 151.3 (8). Intramolecular angles (deg): C11–Si1–Si2 109.55 (9), Si1–Si2–C12 109.78 (9), C1–Si1–C4 93.5 (2). Selected torsion angles (deg): C11–Si1–Si2–C12 51.15 (12), C1–Si1–Si2–C8 51.5(3), C5–Si1–Si2–C11 77.4 (2).



**Figure 5.** Thermal ellipsoid diagram of structure of **4**. Selected bond lengths (pm): Si1–Si2 237.2 (3), Si2–Si3 235.9 (4), Si1–C11 206.1 (4), Si3–C13 198.3 (5), Si1–C1 186.6 (9), C1–C2 134.8 (12), C2–C3 151.0 (12). Intramolecular angles (deg): Si1–Si2–Si3 120.43 (13), C11–Si1–Si2 113.41 (14), Si2–Si3–C13 112.4 (2), C1–Si1–C4 93.2 (4). Selected torsion angles (deg): C11–Si1–Si2–Si3 67.16 (20), Si1–Si2–Si3–C13 57.81 (23), C1–Si1–Si2–C29 67.46(43), C29–Si2–Si3–C57 58.20 (46).

The anomalous emission observed for **2** and **4** could result from (a) excimer formation in solution, or (b) formation of a twisted intramolecular charge-transfer (TICT) state.<sup>18</sup> The latter explanation is possible for **2** and **4**, but not for **3**, since twisting of the main chain into a trans-conformation brings silole rings into a face-to-face relationship. Experiments to determine the underlying reasons for the unusual emission are under way.

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**Supporting Information Available:** Tables giving details of the X-ray structure determinations, atomic coordinates and isotropic thermal parameters, bond lengths and bond angles, anisotropic displacement parameters, and hydrogen atom coordinates, for **3** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(18) Bajorek, A.; Paczkowski, J. *Macromolecules* **1998**, *31*, 86; Rettig, W. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 695; Rettig, W. *Top. Curr. Chem.* **1994**, *169*, 253.