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An Electroluminescent Polysilole and Some Dichlorooligosiloles

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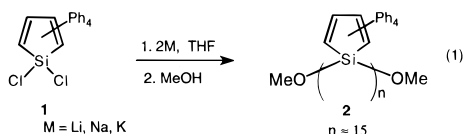
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Siloles are of considerable current interest, both because of their unusual electronic properties¹ and because of their possible application as electron-transporting materials in devices such as light-emitting diodes (LED's).² Siloles exhibit a low reduction potential and a low-lying LUMO energy level, attributed to σ^* – p^* conjugation arising from the interaction between the σ^* orbital of the σ -bonded silicon atom and the p^* orbital of the butadiene moiety of the ring.^{3,4}

In contrast to siloles, polysilanes display low oxidation potentials and a high-lying HOMO, resulting from σ -delocalization along the Si–Si chain.⁵ 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 laboratories⁶ and by Sakurai and co-workers,⁷ 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**),⁸ by reduction with lithium, sodium or potassium, in >30% yield (eq 1).⁹ 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 ¹H, ¹³C, and ²⁹Si NMR spectroscopy.¹⁰ **3** and **4** were identified as the dichlorooligosiloles Cl(C₄Ph₄Si)₂Cl and Cl(C₄Ph₄Si)₃Cl, respectively.

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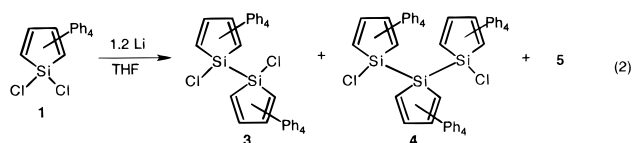
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Compound **5**, which shows only a single ²⁹Si resonance, is tentatively identified as a cyclooligosilane. The X-ray crystal structures for **3** and **4** were determined and are shown in Figure 4¹¹ and Figure 5.¹² The silole rings in both **3** and **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° and $\angle C32-Si2-Si3-C60$ of 61.08°, in **4** show that the silole rings are strongly rotated relative to one another.¹³

(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%, $M_w = 5700$, $M_w/M_n = 1.15$); ¹H NMR (300.133 MHz, CDCl₃) $\delta = 6.30$ –7.40 (br, m, Ph), 3.56 (br, OMe); ¹³C NMR (75.403 MHz, CDCl₃) $\delta = 77.00$); $\delta = 53.6$ (s, OMe); 125–131 (m, silole carbons); 137–147 (br, m, Ph); ²⁹Si NMR (71.548 MHz, CDCl₃) $\delta = 6.72$, –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 °C. **3**: yellow crystals (2.0 g, 47%); mp 300–304 °C; ¹H NMR (300.133 MHz, CDCl₃) $\delta = 6.55$ –6.58 and 6.92–7.18 (m, 40H, Ph); ¹³C{H} NMR (75.403 MHz, CDCl₃) $\delta = 77.00$); $\delta = 137.35$, 137.04, 129.86, 129.81, 129.31, 127.99, 127.92, 127.45, 126.90, 126.61; ²⁹Si NMR (71.548 MHz, CDCl₃) $\delta = 0.24$; MS(EI) m/z (%) 840 (2) [M⁺], 804 (2) [M⁺ – Cl], High-resolution MS calcd for C₅₆H₄₀Cl₂Si₂ 840.2045, found 840.2038. **4**: yellow crystals (1.1 g, 25%); mp 329 °C dec; ¹H NMR (300.133 MHz, CDCl₃) $\delta = 6.25$ –6.43 and 6.83–7.14 (m, 60H, Ph); ¹³C{H} NMR (75.403 MHz, CDCl₃) $\delta = 77.00$); $\delta = 158.11$, 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; ²⁹Si NMR (71.548 MHz, CDCl₃) $\delta = 7.00$, –40.73; MS(FAB) m/z (%) 1224.5 (7) [M⁺]. **5**: yellow crystals (0.8 g, 19%); mp 309 °C dec; ¹H NMR (300.133 MHz, CDCl₃) $\delta = 6.25$ –6.55 and 6.75–7.30 (m, 60H, Ph); ¹³C{H} NMR (75.403 MHz, CDCl₃) $\delta = 77.00$); $\delta = 156.77$, 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; ²⁹Si NMR (71.548 MHz, CDCl₃) $\delta = 6.80$. In the preparative GPC 5% of higher molecular weight products were also obtained.

(11) X-ray structure analysis of **3**·2(CDCl₃), $M_r = 1080.71$, triclinic, $P\bar{1}$, $a = 10.3966$ (4) Å, $b = 13.5722$ (5) Å, $c = 19.5007$ (7) Å, $\alpha = 86.870$ (2)°, $\beta = 89.759$ (2)°, $\gamma = 74.235$ (2)°, $V = 2644.02$ (17) Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.357$ Mg m^{–3}, $F(000) = 1108$, $\lambda = 0.71073$ Å, $\theta = 153$ (2) K. A yellow transparent crystal (crystal size 0.35 × 0.35 × 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 α radiation (2.41° < θ < 25.00°). 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**: C₈₄H₆₀Cl₂Si₃, $M_r = 1224.49$, monoclinic, $P2_1/c$, $a = 17.227$ (2) Å, $b = 13.636$ (2) Å, $c = 27.757$ (2) Å, $\alpha = 90$ °, $\beta = 97.495$ (6)°, $\gamma = 90$ °, $V = 1301.2$ (2) Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.258$ Mg m^{–3}, $F(000) = 2560$, $\lambda = 1.54178$ Å, $\theta = 113$ (2) K. A yellow transparent crystal (crystal size 0.40 × 0.20 × 0.10 mm) was mounted under a coating of paratone-N. Intensity data were collected by the ω scan method (2.59° < θ < 57.01°) 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.

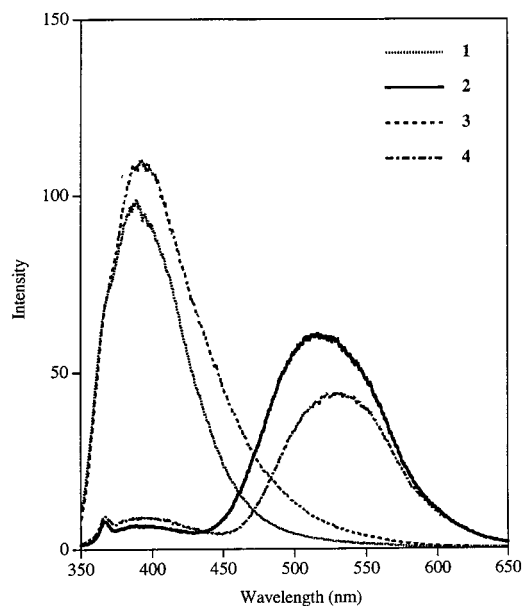


Figure 1. Fluorescence spectra of **1–4** at 10^{-5} M for **1**, **3**, and **4** and 10 mg/L for **2**, in THF. Excitation was at 330 nm.

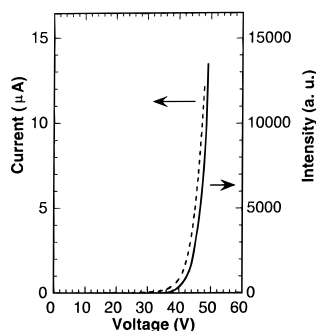


Figure 2. Current–voltage–intensity characteristics for single-layer LED containing **2**. The turn-on voltage was 26 V.

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.¹⁶ The current–voltage curve for **2** is shown in Figure 2, and the electroluminescence spectrum of **2** acting as a single-component LED is given in Figure 3. The external quantum efficiency is 3×10^{-2} % at a current density of 0.3 mA/cm^2 .¹⁷

(13) The structure of **4** differs from that of the related but less hindered tersilole and quatersilole reported by Tamao and co-workers,¹⁴ 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,¹⁵ which has a trans–trans relationship between the silole rings.

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(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 ohm/cm^2 were cleaned by ultrasonic treatment in 2-propanol, treated with Ar plasma, and then stored in an oven at 100°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 2×10^{-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.

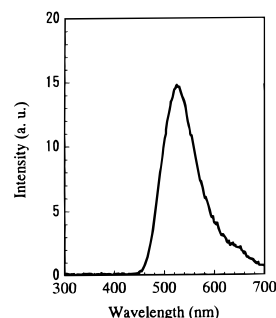


Figure 3. Electroluminescence spectrum of polymer **2** LED at 25°C .

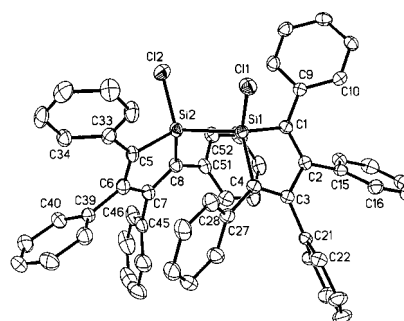


Figure 4. Thermal ellipsoid diagram of structure of **3**. Selected bond lengths (pm): Si1–Si2 236.9 (2), Si1–C11 206.8 (2), Si2–C12 206.9 (2), Si1–C1 186.7 (6), C1–C2 136.8 (8), C2–C3 151.3 (8). Intramolecular angles (deg): C11–Si1–Si2 109.55 (9), Si1–Si2–C12 109.78 (9), C1–Si1–C4 93.5 (2). Selected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

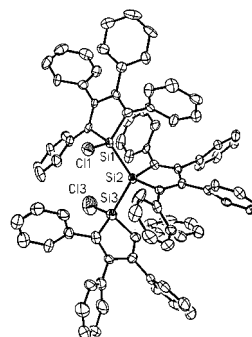


Figure 5. Thermal ellipsoid diagram of structure of **4**. Selected bond lengths (pm): Si1–Si2 237.2 (3), Si2–Si3 235.9 (4), Si1–C11 206.1 (4), Si3–C13 198.3 (5), Si1–C1 186.6 (9), C1–C2 134.8 (12), C2–C3 151.0 (12). Intramolecular angles (deg): Si1–Si2–Si3 120.43 (13), C11–Si1–Si2 113.41 (14), Si2–Si3–C13 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.¹⁸ 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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