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[7] Single crystals of **1a**·**2a** were grown by slow evaporation over about one week of a CH$_2$Cl$_2$/toluene/hexane solution containing an approximately 1:1 molar ratio of **1a** and **2a**. A dark brown crystal was selected under oil under ambient conditions, attached to the tip of a glass fiber, and transferred to a Bruker AXS SMART diffractometer/CCD area detector operating with ω scans. Crystal data: $C_{74}H_{100}N_{10}O_{10}Os$ · hexane, crystal dimensions 0.36 × 0.21 × 0.14 mm, monoclinic, $P2_1/n$, $a = 21.7391(4)$, $b = 16.9339(2)$, $c = 22.4259(2)$ Å, $\beta = 95.5360(10)^\circ$, $V = 8217.09(19)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.266$ g cm^{-3}, $F(000) = 3280$, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $T = 193(2)$ K, $2\theta = 46.5$, reflections collected/unique 48602/11617 (R(int) = 0.2205). The structure was solved by direct methods (SHELXL-97) and refined by full-matrix least-squares methods on F^2 with 891 parameters. All non-hydrogen atoms except for those of the disordered solvent molecules (hexane) were refined anisotropically. Hydrogen atoms were assigned to idealized positions. $R_1 = 0.1089$ ($I > 2\sigma(I)$), $wR_2 = 0.2122$ (all data), GOF 1.015; max./min. residual density 0.805/−0.479 e Å^{-3}. The high R value is partly due to the disorder of the solvent molecules, and poor quality of the crystal resulted from unavoidable loss of solvent during data acquisition. Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-137734. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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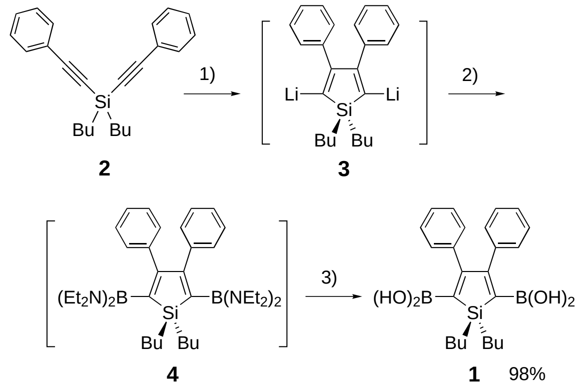
Silole–Thiophene Alternating Copolymers with Narrow Band Gaps[**]

Shigehiro Yamaguchi, Tomoyuki Goto, and Kohei Tamao[*]

In the chemistry of π-conjugated polymers, the control of the band gap, which is necessary to obtain specific electrical and photophysical properties, is a fundamental goal.[1] Successful stratergies for creating a narrow band gap involve the construction of donor–acceptor type polymers,[2] planar ladder-type conjugated systems,[3] polymers based on fused-ring systems,[4] and copolymers with a specific combination of monomer units such as poly(thienylene–vinylene)s.[5] A new alternative to these approaches would be the modification of carbon π-conjugated systems with main group elements such as boron, silicon, and phosphorus.[6]

In this context, the silole–thiophene 1/1 alternating copolymer is an interesting target compound,[7] in which the ring silicon atoms fix the labile *s*-cis butadiene skeleton of the poly(thienylene–butadienylene) chain. In addition, the silicon atoms in the ring are expected to affect the electronic structure through unique orbital interactions such as σ*–π* conjugation.[8] Although its narrow band gap has been predicted theoretically[9, 10] and experimentally,[7c] its synthesis has been hampered by the limited availability of suitable 2,5-difunctionalized silole precursors.[11] These precursors should be isolable but sufficiently reactive towards coupling reactions for high molecular weight polymers to be obtained. We now report the preparation of silole-2,5-diboronic acid **1**, a suitable monomer,[12] and its use in a Suzuki–Miyaura coupling[13] for the first synthesis of silole–thiophene alternating copolymers.

The preparation of **1** is based on the intramolecular reductive cyclization of bis(phenylethynyl)silane **2**,[14] (Scheme 1). Reaction of the diyne **2** with four equivalents of



Scheme 1. Synthesis of **1**: 1) LiNaph (4 equiv), THF, room temperature (RT); 2) (Et$_2$N)$_2$BCl (4 equiv), −78 °C ~ RT; 3) 1N HCl.

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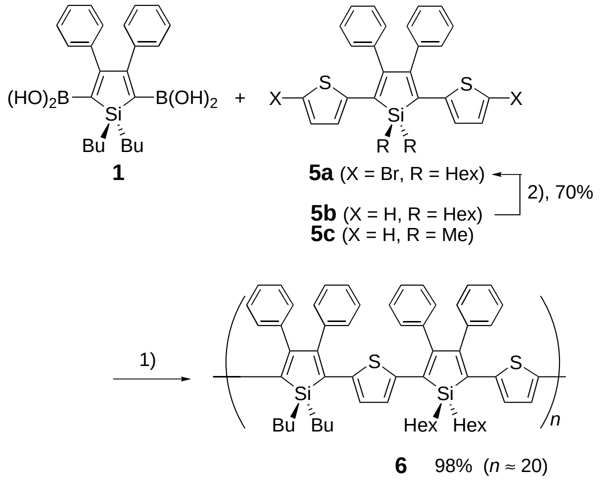
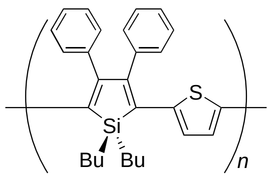
lithium naphthalenide yielded 2,5-dilithiosilole **3** quantitatively. Treatment of **3** with four equivalents of $(Et_2N)_2BCl$ gave 2,5-diborylsilole **4** (not isolated), which was hydrolyzed to afford **1** in 98 % yield. The use of $(Et_2N)_2BCl$ was essential because the typical procedure to obtain boronic acids, the direct reaction of the dilithiosilole with $B(O\mathit{i}Pr)_3$ followed by hydrolysis,[15] did not produce the desired product.

As the counterpart for the Suzuki–Miyaura coupling, we chose 2,5-bis(5-bromo-2-thienyl)silole **5a**, readily obtained by the bromination of 2,5-dithienylsilole **5b**[16] (Scheme 2). The Suzuki–Miyaura coupling of the **1** with the dibromide **5a** was carried out under basic conditions with the catalyst system $[Pd_2(dba)_3]\cdot CHCl_3/4\,PPh_3$ (Scheme 2) and afforded the alternating copolymer **6** in 98 % yield; molecular weights of **6** were determined by GPC analysis with polystyrene standards $M_w = 48700$ and $M_n = 18400$ ($n \approx 20$ (≈ 80 five-membered rings in total)). The use of the tri-ring dibromide **5a** was important in obtaining high molecular weight polymer, for example, the coupling of **1** with 2,5-dibromothiophene yielded a lower molecular weight polymer **6′** ($M_w = 9000$, $M_n = 4600$, $n \approx 11$ (≈ 22 five-membered rings in total)) in 52 % yield. The structure of **6** was verified by ^1H and ^{13}C NMR spectroscopy. The ^1H NMR spectrum shows only one singlet at $\delta = 6.19$, assignable to the thienylene protons, demonstrating the highly ordered structure of **6**. The polymer is remarkably stable and no decomposition was observed even after one year in air.

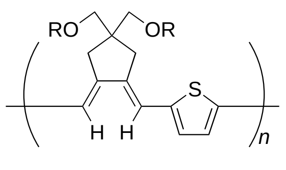


Scheme 2. Synthesis of **6**: 1) $[Pd_2(dba)_3]\cdot CHCl_3$ (0.025 equiv), PPh_3 (0.1 equiv), Na_2CO_3 (2 equiv), $THF/H_2O = 4/1$, reflux, 72 h. 2) *N*-bromosuccinimide (NBS)(2.1 equiv), DMF, RT. Hex = *n*-hexyl.

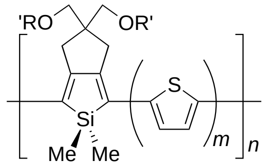
Polymer **6** is a bronze powder, but affords an ink-blue solution in THF or chloroform. The UV/Vis absorption spectrum of **6** in chloroform has λ_{max} at 648 nm, 230 nm longer than that of the methyl derivative 2,5-dithienylsilole **5c** (λ_{max} 418 nm)[16a] and, moreover, 8 nm longer than that of **6′** ($\lambda_{max} = 640$ nm). This suggests that the π-conjugation is effectively extended over more than 22 rings, this being the average number of silole and thiophene rings in **6′**. The λ_{max} value of **6** is also 110 nm longer than that of the poly(thienylene–butadienylene) **7** ($\lambda_{max} = 538$ nm), recently prepared by Tilley and Lucht.[17] The large difference between **6** and **7** clearly demonstrates the significant structural and electronic effects the ring silicon atoms have on the electronic structure of the π-conjugated main chain.



6′ ($n \approx 11$)



7 (R = *n*-hexyl)



8a ($m = 2$)
8b ($m = 3$)
8c ($m = 4$)

(R′ = *t*BuMe$_2$Si)

The absorption spectrum of polymer **6** is highly temperature dependent (Figure 1). As the temperature decreases, the vibronic fine structure of the absorption band of **6** becomes obvious, and at 183 K, the $\lambda_{0\text{-}0}$ band shifts to 727 nm. The band gap, determined from the $\lambda_{0\text{-}0}$ band edge, is 1.55 eV, is small for linear π-conjugated polymers consisting of five-membered heteroaryls,[1] but coincides well with the theoretical value predicted by Hong et al. ($E_{g,calc} = 1.55$ eV).[9] A comparison of this value with those of the silole–thiophene copolymers **8a–c** previously prepared by us[7c] shows a good linear correlation between the silole/thiophene ratio and the band gap ($E_g = 1.97 - 0.419$(silole/thiophene), $r = 0.995$), (Figure 2). The different substitution modes of the silole rings[18] mean that some caution is required interpreting this comparison but the linear correlation suggests that narrower band gaps may be achieved by increasing the silole content.

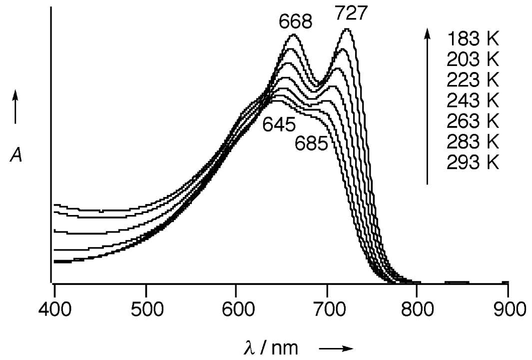


Figure 1. Variable temperature UV/Vis absorption spectra of **6** in 2-MeTHF in the range 293–183 K.

The successful preparation of silole-2,5-diboronic acids has opened the door to a new chemistry of alternating silole–arene copolymers. This has been demonstrated by the present synthesis of silole–thiophene alternating copolymers and by the unique properties that these polymers display.

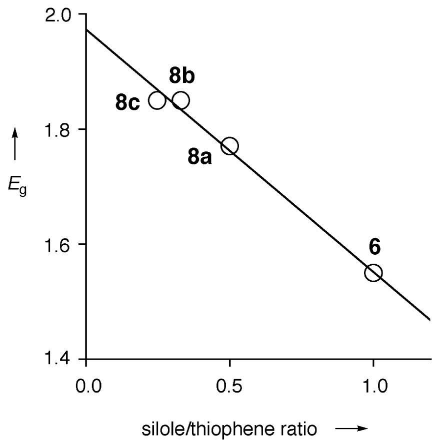


Figure 2. Plot of the band gaps (E_g) determined from absorption edge versus silole/thiophene ratios for a series of silole – thiophene copolymers.

Experimental Section

1: A mixture of granular lithium (139 mg, 20 mmol) and naphthalene (2.56 g, 20 mmol) in THF (12 mL) was stirred at room temperature under argon for 4 h before a solution of **2** (1.72 g, 5 mmol) in THF (11 mL) was added. The mixture was cooled to −78 °C and a solution of $(Et_2N)_2BCl$ (3.81 g, 20 mmol) in THF (10 mL) was added dropwise over 25 min. The resulting mixture was allowed to warm to room temperature over 6 h. After removal of solvents, Et_2O was added to the residue, and the insoluble materials were removed by filtration. 1N hydrochloric acid (60 mL) was added to the filtrate and the mixture was extracted several times with Et_2O. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was dissolved in a small amount of Et_2O and reprecipitated with hexane (ca. 200 mL) to give **1** (2.13 g, 4.9 mmol) in 98 % yield as a white, spectroscopically pure solid: m.p. 82 °C (decomp.); ^1H NMR (270 MHz, $CDCl_3$): $\delta = 0.99$ (t, $J = 7.0$ Hz, 6H), 0.96 – 1.06 (m, 4H), 1.28 – 1.47 (m, 8H), 3.94 (s, 4H), 6.86 – 6.97 (m, 4H), 7.10 – 7.20 (m, 6H); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = 11.50$, 13.80, 26.42, 26.45, 127.46, 127.98, 128.21, 140.95, 169.61. A satisfactory elemental analysis was not obtained probably due to contamination by a trace amount of water.

6: A mixture of **1** (868.5 mg, 2.0 mmol), **5a** (1.450 g, 2.0 mmol), $[Pd_2(dba)_3]\cdot CHCl_3$ (104 mg, 0.10 mmol), PPh_3 (105 mg, 0.40 mmol), and Na_2CO_3 (424 mg, 4.0 mmol) in a THF/H_2O (4/1, 20 mL) mixture was refluxed for 72 h. The reaction mixture was poured into vigorously stirred hexane (400 mL) and the insoluble material collected by filtration. The residue was suspended in methanol/H_2O (1/1; 120 mL) and sonicated for 10 min. The mixture was then filtered, and the insoluble part collected and washed with methanol (80 mL) then hexane (80 mL). Soxhlet extraction from the residue with THF gave the soluble polymer **6** (1.78 g) in 98 % yield as a bronze solid: ^1H NMR (270 MHz, $CDCl_3$): $\delta = 0.70 – 0.90$ (brm, 20H), 1.05 – 1.43 (brm, 24H), 6.19 (brs, 4H), 6.70 – 6.93 (brm, 8H), 6.98 – 7.19 (brm, 12H); ^{13}C NMR (67.8 MHz, $CDCl_3$): $\delta = 13.66$, 14.11, 22.59, 23.34, 25.54, 25.93, 31.36, 32.44, 126.40, 126.81, 128.19, 129.33, 130.26, 139.80, 142.84, 153.55; UV/Vis ($CHCl_3$, 293 K): λ_{max} (lg ε per recurring unit) = 648 (4.73), 685 (sh, 4.70); elemental analysis, calcd (%) for $(C_{60}H_{68}S_2Si_2)_n$: C 79.24, H 7.54; found: C 77.13, H 7.33.

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[18] We have confirmed that the 3,4-substituents of silole rings have only a slight effect on the absorption maximum wavelengths of the siloléthiophene copolymers. Thus, silole – thiophene 1/2 copolymer, prepared by the coupling of **1** with 5,5′-dibromo-2,2′-bithiophene, has its absorption maximum at 584 nm, which is comparable to that of **8a** (576 nm).[7c]