Synthesis of bithiophenesilane dendrimer of the first generation

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The synthesis of tris{5´-[methylbis(2-thienyl)silyl]-2,2´-bithienyl-5-yl}methylsilane, a first-generation bithiophenesilane dendrimer, is described. The conditions of effective formation of methyltrithienylsilane were found; methyltris(5-bromo-2-thienyl)silane and a number of other monofunctional derivatives of methyltrithienylsilane were synthesized for the first time. The advantages and drawbacks of the Suzuki and Kumada reactions for the formation of bithienyl fragments in the synthesis of oligothienylsilane dendrimers are discussed.

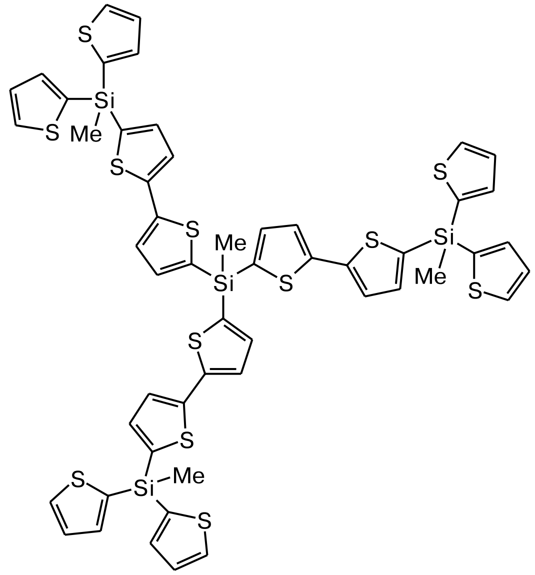
Key words: thiophenesilane dendrimers, organosilicon compounds, oligothiophenes, Kumada reaction, Suzuki reaction.

The advent of new classes of polymeric compounds such as hyperbranched polymers and dendrimers consisting of monodisperse synthetic hyperbranched macromolecules[1] brought about the question of the influence of the topology of polymeric molecules on the set of properties of these substances, in particular, the electric and optical properties. Among numerous objects diverse in chemical nature, thiophene-containing systems attract attention due to their specific optical characteristics. Hyperbranched 2,3,5-polythiophene[2] and a dendrimer[3] consisting of thiophene rings connected through positions 2, 3, and 5 have recently been synthesized. Polythiophene exhibited a broad absorption band in the visible range, strong fluorescence, and efficient intramolecular charge transfer.

A number of organoelement dendrimers based on polysiloxanes, polycarbosilanes, polycarbosilanesiloxanes, polyphosphazenes, polygermanes,[4,5] *etc.*, are also known. An attempt to prepare organosilicon dendrimers containing thiophene rings has also been undertaken. Tetrathienylsilane,[6,7] which can be considered as a branching core or a zero-generation dendrimer, and a first-generation organosilicon dendrimer containing 16 thiophene rings[8] have been described. However, dendrimers containing oligothiophene units linked directly to silicon atoms have not been reported as yet. The interest in the synthesis and properties of such systems is based on the recent discovery of strong fluorescence of star-shaped organosilicon molecules containing α,α´-bi- and terthiophene units.[9] On the one hand, this effect is due to σ-π-conjugation between the silicon atoms and the aromatic π-system of oligothiophenes, and, on the other hand, it is enhanced by the star-shaped structure of the molecule. These compounds were shown[9] to possess higher fluorescence quantum yields than the corresponding oligothiophenes or their linear analogs.

Recently, hyperbranched organosilicon polymers with a similar structure containing in particular thiophene units have been prepared. These include hyperbranched poly(2,5-silylthiophens),[10] polycarbosilanes from silyl-substituted thiophenes,[11] polycarbosilarenes,[12] and polysilylenevinylenes.[13] However, the effect of three-dimensional polymeric architecture is weakly pronounced in hyperbranched polymers,[10] evidently due to structure irregularity and the presence of substantial amounts of linear fragments in the molecules.

The present study considers synthetic routes to a new class of compounds, oligothiophenesilane dendrimers exemplified in newly synthesized tris{5´-[methylbis(2-thienyl)silyl]-2,2´-bithienyl-5-yl}methylsilane **1**, a first-generation bithiophenesilane dendrimer ($Si_42T_3T_6$):



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Results and Discussion

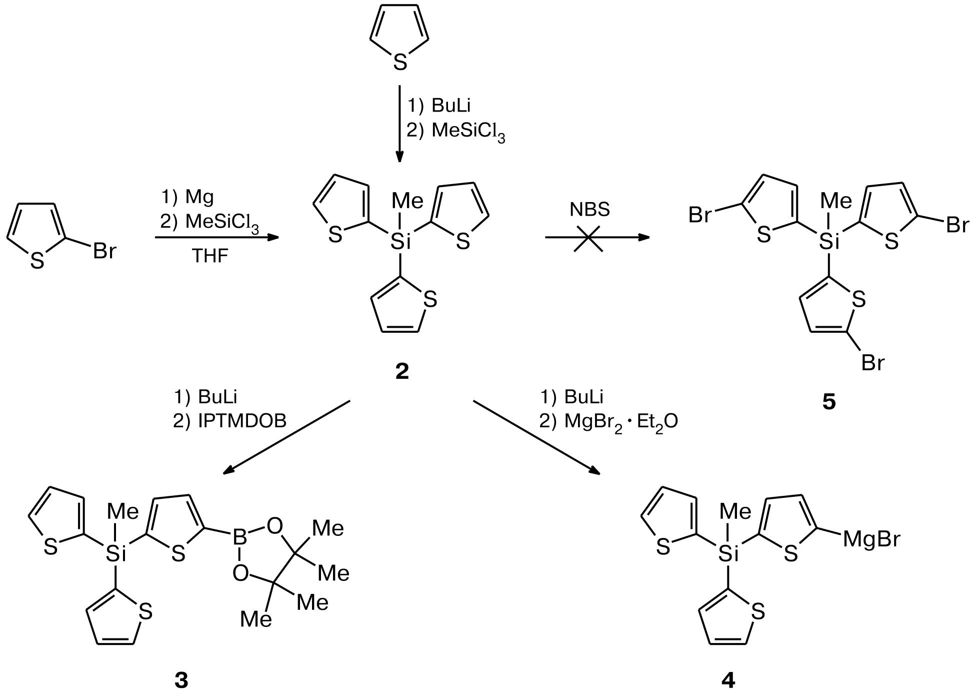
The catalytic coupling of thiophene residues, which had proved useful in the synthesis of oligothiophenes,[14,15] was proposed for the dendrimer preparation. Methyltrithienylsilane (**2**) was chosen as the starting reagent (Scheme 1).

The synthesis of this compound from $MeSiCl_3$ and 2-thienylmagnesium bromide in 10% yield is published.[6] The reaction was carried out in an ether—hexane mixture for 1 h at room temperature. We suggested that the low yield is due to the short reaction time, the presence of nonpolar hexane in the reaction mixture, and the low reactivity of thienylmagnesium bromide. When the reaction was carried out in boiling ether for 24 h, chloro(methyl)dithienylsilane was the major reaction product (up to 75%), the yield of the target product being no higher than 18%. This conclusion was based on the ^1H NMR spectra in which the signal for the MeSi group in the monosubstituted product occurred at δ 0.34, that in the disubstituted product is at δ 0.68, and the signal for the trisubstituted product was found at δ 0.96, which is consistent with published data.[6]

Organolithium derivatives in the thiophene series are known[16a] to be much more reactive than the Grignard reagents. Therefore, the reaction of $MeSiCl_3$ with 2-thienyllithium seemed to be the most facile route to compound **2**. Indeed, this reaction yielded trisubstituted product **2** almost exclusively (^1H NMR). However, analysis by gel permeation chromatography (GPC) showed the presence of substantial amounts of oligomers probably resulting from exchange reactions of the reactive protons in position 5 of the thiophene rings in the target product with thienyllithium or from the formation of the dilithium derivative of thiophene. The yield of compound **2** was 33% with thienyllithium prepared *in situ* by the standard procedure from thiophene and butyllithium, which implied a 20% excess of thiophene.[16b] The use of a twofold excess of thiophene for suppressing the side reactions allowed the content of methyltrithienylsilane (**2**) in the reaction mixture to be increased to 58%. However, the most efficient route to compound **2** involved the reaction of thienylmagnesium bromide with $MeSiCl_3$ in refluxing THF for 20 h (see Scheme 1), the yield of methyltrithienylsilane **2** being 72%.

This compound was used to prepare mono- and trifunctional derivatives needed for the dendrimer synthesis. Monofunctional derivatives were synthesized by monolithiation with butyllithium of one of the three thiophene rings present in methyltrithienylsilane at position 5 (see Scheme 1). Subsequent lithium exchange with an organoboron or a magnesium bromide residue took place *in situ* on treatment with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (IPTMDOB) or the ether complex of magnesium dibromide $MgBr_2 \cdot Et_2O$, to give 2-{5-[methylbis(2-thienyl)silyl]-2-thienyl}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3**) in 89% yield and with 86% purity (the starting methyltrithienylsilane accounted

Scheme 1

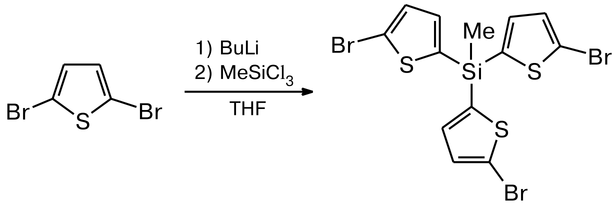


for the rest 14%). 5-[Methylbis(2-thienyl)silyl]-2-thienylmagnesium bromide (**4**) was not isolated in a pure state, the product obtained *in situ* being introduced in the next step of the dendrimer synthesis. Analysis of compound **3** by ^{1}H NMR spectroscopy and GPC showed the absence of by-products, which is indicative of methyltrithienylsilane monolithiation and virtually quantitative subsequent lithium exchange by the organoboron residue.

Bromination of methyltrithienylsilane with NBS, which has proved efficient in the selective bromination of thiophene and oligothiophenes at position 2(5),[17] did not lead to the desired outcome, despite the use of various solvents and solvent mixtures, *e.g.*, DMF, $CHCl_3$, THF, $CHCl_3$—AcOH (1 : 1) often employed in the bromination of (oligo)thiophenes and their derivatives.[18] No changes were observed even after 60 h when the reaction was carried out in chloroform. In all other cases, 2,5-dibromothiophene resulting from cleavage of the $C_{thiophene}$—Si bond was the major bromination product. It should be noted that bromination of *tert*-butyldimethylsilylbi-, -ter-, and -quaterthiophenes on treatment with NBS in chloroform for 15 h in 84 to 96% yields has been reported.[19] Presumably, in the case of methyltrithienylsilane **2**, which contains monothienyl groups, no bromination in chloroform took place due to too low reactivity of the proton in position 5 of the thiophene residue in a low-polarity solvent, while the insufficient stability of the Si—$C_{thiophene}$ bond precluded the use of more polar solvents. It is known[18] that the reactivity of the 2(5)-proton in α,α-oligothiophenes markedly increases with an increase in conjugation (the number of thiophene rings).

The key compound for the dendrimer synthesis, namely, methyltris(5-bromo-2-thienyl)silane (**5**), was obtained through the organolithium derivative prepared from 2,5-dibromothiophene, which was made to react with $MeSiCl_3$ (Scheme 2). The starting 2,5-dibromothiophene was prepared by bromination of thiophene with NBS in anhydrous DMF using the published procedure for selective bromination of thiophene and oligothiophene derivatives.[18]

Scheme 2



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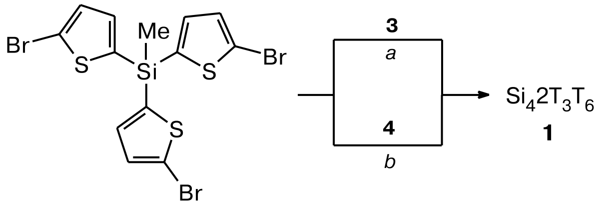
This reaction was found to proceed much more smoothly than that with thiophene to give compound **5** in 72% yield even when only a 10% excess of 2,5-dibromothiophene was used. All three chlorine atoms in $MeSiCl_3$ are substituted almost completely and higher oligomers are formed as the main by-products, as in the case of thienyllithium. Preparative GPC purification resulted in chromatographically pure compound **5** that was used in the subsequent synthesis.

As noted above, catalytic reactions resulting in the coupling of the thiophene residues, which have proved efficient in the synthesis of oligothiophenes,[14,15] have been chosen for dendrimer **1** synthesis. These include the Suzuki reaction of aryl halides with arylboronic acid or its derivatives carried out in an alkaline medium in the presence of palladium catalysts,[20] and the Kumada reaction whose essence is the formation of biaryls from aryl halides and their magnesium or zinc derivatives in the presence of palladium or nickel catalysts.[21] An advantage of the latter reaction is that it is almost complete in several tens of minutes at room or even at a reduced temperature, unlike the Suzuki reaction, which requires refluxing at 100 °C for several tens of hours. In addition, the Kumada reaction requires an order of magnitude less catalyst than the Suzuki reaction (0.5—1% *vs.* 5—10%). However, the Suzuki reaction has an obvious advantage, which completely overrides its drawbacks, in particular, the lack of exchange of the boronic acid residue with halogen, which allows one to avoid side reactions in the synthesis of nonsymmetrical oligothiophenes[22] and the formation of by-products with higher molecular masses in the synthesis of dendrimers.

Scheme 3



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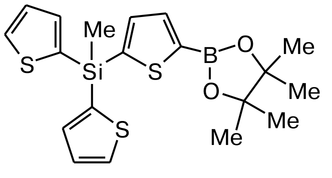
a. $Pd(PPh_3)_4$, PhMe, 2 *M* Na_2CO_3; *b*. $Pd(dppf)Cl_2$, THF—Et_2O



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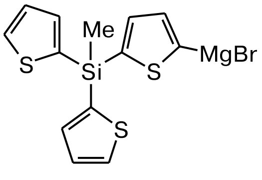

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The synthesis of dendrimer **1** by the Suzuki reaction (Scheme 3, pathway *a*) was carried out in the presence of a 30% excess of compound **3**. The reaction was moni-

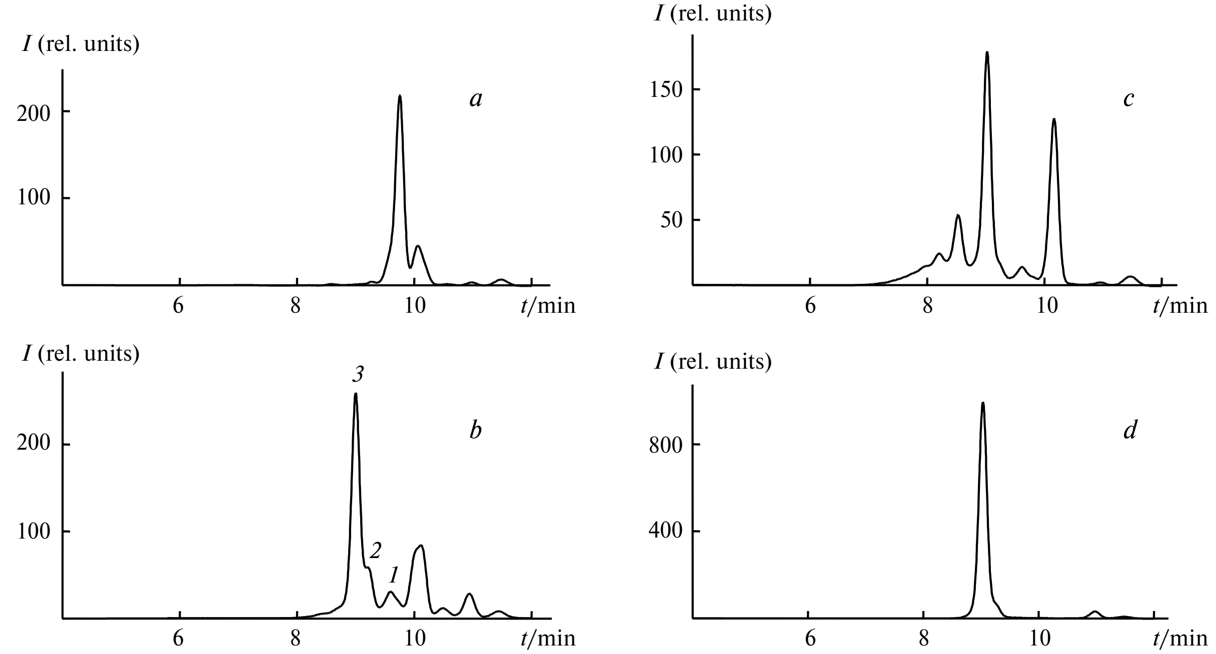

Fig. 1. GPC curves: (*a*) mixture of compounds **3** and **5** at the beginning of the Suzuki reaction, (*b*) after completion of the Suzuki reaction: (*1*) mono- (*2*) di, and trisubstituted product; (*c*) after completion of the Kumada reaction; (*d*) dendrimer **1** after purification (Phenogel column, 10^3 Å, diode matrix as the detector, λ = 254 nm).

tored by GPC using an instrument equipped with a diode matrix detector, which allowed recording three-dimensional chromatograms in the retention time—wavelength—signal intensity coordinates. Thus, not only new peaks could be detected in the chromatograms during the reaction but also each peak could be identified based on the absorption spectrum in the 190—800 nm wavelength range. This method is especially efficient for the formation of (poly)conjugated systems or for reactions accompanied by a change in the conjugation length, because this allows recording the individual spectra for components of the mixture provided that they are resolved into individual peaks during chromatographic analysis. Since the reaction proceeds rather slowly (the completion required refluxing for 120 h), we were able to follow the kinetics of this process by withdrawing samples for analysis every 8—10 h. The reaction was found to be stepwise to give first one bithienyl fragment, then two fragments, and finally three fragments. Both the final dendrimer **1** and the two intermediates differed from the starting reactants in not only the retention time (Fig. 1) but also in the spectra (Fig. 2). The formation of the second and third bithienyl groups shifted the retention time to higher molecular massess but did not produce any new absorption bands, only the ratio between the peaks at 239 and 334 nm being changed (Fig. 2, curves *4*, *5*). Presumably, the absorption at 239 nm corresponds to the Si—T terminal groups (see Fig. 2, spectrum *1*, T is the thiophene ring), while the absorption peak at 334 nm is due to the Si—T—T—Si fragments. The fact that the formation of two successive bithienyl fragments at the same central silicon atom in the dendrimer molecule did not shift the absorption peak indicates that these fragments are not conjugated. A similar phenomenon has also been observed[23] in the addition of oligothiophene fragments to benzene in positions 1, 3, and 5. This unusual structure of the dendrimer **1** molecule is of interest from both the fundamental standpoint to study absorption, intramolecular energy transfer, and the subsequent photo- and electroluminescence and the practical standpoint for the possible preparation of light-emitting diodes.

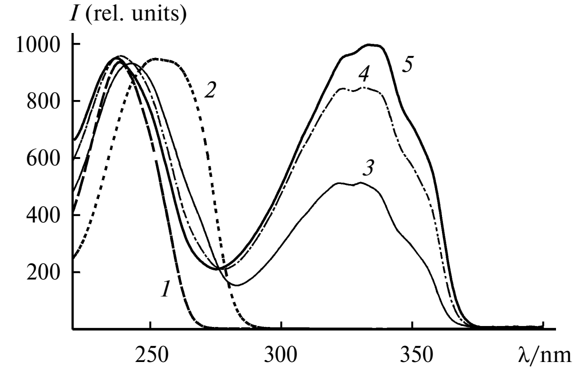

Fig. 2. Absorption spectra of compound **2** (*1*), compound **5** (*2*), intermediate compounds formed in the synthesis of dendrimer **1** with one (*3*) or two (*4*) bithienyl groups, and dendrimer **1** (*5*).

The reaction was carried out until the reaction mixture no longer changed according to GPC. The final mixture (see Fig. 1, *b*) contained 57% the target compound **1**, 8% the intermediate with two bithienyl groups, and 6% the intermediate with one bithienyl group; taking into account the 30% excess of compound **3**, this corresponds to 81% yield in the reaction. Pure dendrimer **1** (Fig. 1, *d*) was isolated by preparative GPC. Attention is attracted by the virtual absence of reaction by-products with higher molecular masses compared to the target product, which makes the Suzuki reaction promising for the preparation of higher-generation dendrimers. The presence of mono- and disubstituted products is apparently related to deboration of the organoboron derivative **3**, which resulted in a deficiency of this reagent by the end of the reaction.

The drawbacks of the Suzuki reaction have been avoided in the synthesis of dendrimer **1** by the Kumada reaction (Scheme 3, pathway *b*) in the presence of Pd(dppf)Cl_2 as the catalyst. In this case, after 2.5 h at room temperature, dendrimer **1** was the major reaction product, while the mono- and disubstituted intermediates were virtually absent (see Fig. 1, *c*). In view of the 30% excess of compound **4**, which is converted quantitatively, following work-up, into methyltrithienylsilane (**2**), the yield was 55%. The only but a serious drawback of this reaction is the formation of substantial amounts of by-products with molecular masses higher than that of the target dendrimer. The reason is the exchange between the halide and magnesium halide reacting groups known for the Kumada reaction,[22] which can only be somewhat retarded by optimizing the reaction conditions (decreasing the temperature, selecting the optimal catalyst for these reactants) but cannot be avoided completely. In this case, the exchange gives rise to both types of functional groups in polyfunctional molecules, which deteriorates the reaction unambiguity and, finally, affords macromolecules with different molecular masses. Nevertheless, preparative GPC of the crude product resulted in isolation of dendrimer **1** fully identical to the product obtained by the Suzuki reaction.

Thus, we studied various synthetic routes to a new class of compound, oligothiophenesilane dendrimers. Tris{5´-[methylbis(2-thienyl)silyl]-2,2´-bithienyl-5-yl}methylsilane (**1**), a first-generation bithiophenesilane dendrimer, was synthesized for the first time starting from trichloromethylsilane, thiophene, and 2-bromothiophene.

Experimental

Hexane solutions of butyllthium (1.6 and 2.5 *M*), thiophene, 2-bromothiophene, and *N*-bromosuccinimide (Acros organics), 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, tetrakis(triphenylphosphine)palladium(0) Pd$(PPh_3)_4$, and 1,1´-bis(diphenylphosphino)ferrocenepalladium(II) Pd(dppf)Cl_2 chloride (Aldrich) were used; $MeSiCl_3$ was distilled directly prior to use; THF and diethyl ether were dried over CaH_2 and distilled from $LiAlH_4$.

^{1}H NMR spectra were recorded on a Bruker WP-250 SY spectrometer (250.13 MHz) using tetramethylsilane as the internal standard. GPC analysis was performed on a Shimadzu instrument with a RID-10A refractometer and a SPD-M10AVP diode matrix as detectors using 7.8×300 mm Phenomenex columns (USA) filled with the Phenogel sorbent with pore sizes of 10^3 and 10^4 Å and THF as the eluent. The preparative chromatographic system consisted of an Akvilon high-pressure isocratic pump, a RIDK-102 refractometric detector (Czech Republic), and Phenomenex preparative columns (300×21.2 mm) (USA) filled with a Phenogel sorbent with a pore size of 10^3 Å; THF was used as the eluent. The solvents were removed *in vacuo* (1 Torr) at 40 °C.

All reactions, unless stated otherwise, were carried out in an inert atmosphere using anhydrous solvents.

2,5-Dibromothiophene. A solution of NBS (44.00 g) in anhydrous DMF (200 mL) was slowly added dropwise in the dark to a solution of thiophene (10.00 g) in anhydrous DMF (100 mL) at −15 °C. Then cooling was removed and the mixture was stirred for 6 h at room temperature. After completion of the reaction, the reaction mixture was poured into 500 mL of ice water and 600 mL of dichloromethane. The organic layer was separated, washed several times with water to a neutral pH, and dried with anhydrous Na_2SO_4. The solvent was evaporated to give 29.91 g of an oily liquid. Vacuum distillation gave 20.76 g (72%) of the title compound with b.p. 53 °C (1 Torr), 98.6% purity (according to GLC). ^{1}H NMR ($CDCl_3$), δ: 6.83 (s, 2 H).

Methyltris(2-thienyl)silane (2) A solution of 2-bromothiophene (24 mL, 0.247 mol) in anhydrous THF (300 mL) was added dropwise to a suspension of Mg (7.04 g, 0.289 mol) in THF (20 mL) and 2-bromothiophene (2 mL). The reaction mixture was refluxed for 1 h and trichloromethylsilane (8 mL, 0.067 mol) was slowly added to the hot mixture. The mixture was refluxed for 20 h and cooled by ice water, and 1 *M* HCl was slowly added dropwise (until the medium was slightly acidic and excess magnesium completely dissappeared). Ether (400 mL) was added to the resulting mixture, the organic layer was separated, washed several times with water to neutrality, and dried with anhydrous Na_2SO_4. Evaporation of solvents gave 20.55 g of a yellowish oily liquid containing 72% of the title product **2** (GPC data). Vacuum distillation followed by purification by column chromatography on silica gel (elution with hexane) gave 15.12 g (61%) of compound **2** with b.p. 152—154 °C (1 Torr), purity 99.8% (according to GLC). ^{1}H NMR ($CDCl_3$), δ: 0.96 (s, 3 H, SiMe); 7.22 (dd, 3 H, J_1 = 3.7 Hz, J_2 = 4.9 Hz); 7.40 (dd, 3 H, J_1= 3.7 Hz, J_2= 1.2 Hz); 7.69 (dd, 3 H, J_1 = 4.9 Hz, J_2= 1.2 Hz).

2-{5-[Methylbis(2-thienyl)silyl]-2-thienyl}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3). A 1.6 *M* solution of BuLi (3.20 mL, 5.1 mmol) in hexane was added dropwise to a solution of compound **2** (1.50 g, 5.1 mmol) in anhydrous THF (40 mL), the temperature being maintained in the range of −70 to −75 °C. The reaction mixture was stirred for 30 min at −75 °C, cooling was discontinued, and the temperature was brought to 0 °C. Then the mixture was cooled again to −75 °C and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.05 mL, 5.1 mmol) was added in one portion. The reaction mixture was stirred for 30 min at −78 °C, cooling was discontinued, and the mixture was stirred for 3 h. After completion of the reaction, ether (100 mL) and ice water (50 mL) containing 5 g of NaCl were added. The organic layer was separated, washed several times with water to a neutral pH, and dried over Na_2SO_4 and the solvent was evaporated to give 1.91 g (89%) of yellow crystals containing 86% of the product **3** and 14% of the starting compound **2** (GPC data). The product was used in the subsequent synthesis without further purification. ^{1}H NMR ($CDCl_3$), δ: 0.94 (s, 3 H, SiMe); 1.33 (s, 12 H, 4 MeC); 7.20 (dd, 2 H, J_1 = 3.7 Hz, J_2 = 4.9 Hz); 7.40 (dd, 2 H, J_1 = 3.7 Hz, J_2 = 1.2 Hz); 7.45 (d, 1 H, J = 3.1 Hz); 7.67 (dd, 2 H, J_1 = 4.9, J_2 = 1.2 Hz); 7.69 (d, 1 H, J = 3.1 Hz).

Methyltris(5-bromo-2-thienyl)silane (5). Anhydrous THF (30 mL) was slowly added dropwise to a 1.6 *M* solution of BuLi (10.35 mL) in hexane, the temperature being maintained in the range of −10 to −20 °C. The reaction mixture was cooled to −60 °C, and a solution of 2,5-dibromothiophene (4.01 g, 17 mmol) in anhydrous THF (10 mL) was slowly added dropwise, the temperature being maintained in the range of −50 to −60 °C. Then the reaction mixture was warmed up to −20 °C and stirred at this temperature for 15 min. The reaction mixture was cooled to −78 °C and trichloromethylsilane (0.6 mL) was added. The mixture turned slightly yellow and the temperature rose to −60 °C. When the temperature of the reaction mixture had dropped again to −78 °C, the cooling bath was removed and the temperature was brought to ~20 °C. After completion of the reaction, the mixture was poured into a mixture of ice water (100 mL) containing 1.5 mL 1 *M* HCl and freshly distilled ether (200 mL). The organic layer was washed with water and dried with Na_2SO_4. The solvent was evaporated to give 3.08 g of a crude product. According to GPC, the yield was 72%. Preparative GPC gave 0.88 g (33%) of pure compound **5**. ^{1}H NMR ($CDCl_3$, 250 MHz), δ: 0.85 (s, 3 H, SiMe); 7.10 (d, 3 H, J = 3.7 Hz); 7.13 (d, 3 H, J = 3.7 Hz). Found (%): C, 29.74; H, 1.81; Br, 45.45; S, 18.12; Si, 5.19. Calculated (%): C, 29.51; H, 1.71; Br, 45.30; S, 18.18; Si, 5.31.

Tris{5´-[methylbis(2-thienyl)silyl]-2,2´-bithienyl-5-yl}methylsilane (1). ***A. Suzuki reaction.*** In an inert atmosphere, a degassed solution of compound **3** (1.72 g, 4.1 mmol) and compound **5** (660 mg, 1.24 mmol) in toluene (30 mL), and a 2 *M* solution of Na_2CO_3 (6 mL) were added to $Pd(PPh_3)_4$ (300 mg, 0.26 mmol), and the mixture was heated to reflux. The reaction mixture was stirred under reflux for 120 h, cooled to ~20 °C, and poured into 50 mL of water and 50 mL of toluene. The organic layer was washed with water to a neutral pH and dried with Na_2SO_4. The solvent was evaporated *in vacuo* and the residue was dried at 1 Torr to give 2.21 g of a crude product, containing 57% compound **1** (GPC data). This product was passed through a column with silica gel (using toluene as the eluent) and further purified by preparative GPC (with THF as the eluent) to give 465 mg (32%) of pure dendrimer **1**.

B. Kumada reaction. A 2.5 *M* solution of BuLi in hexane (1.90 mL) was added dropwise to a solution of compound **2** (1.40 g, 1.8 mmol) in anhydrous THF (20 mL), the temperature being maintained between −70 and −75 °C. The reaction mixture was stirred for 30 min at −75 °C, the cooling bath was removed, and the temperature was brought to 0 °C. An ethereal solution of $MgBr_2$ (freshly prepared from Mg (0.23 g, 9.5 mmol) and dibromoethane (1.17 g, 6.2 mmol) in 12 mL of anhydrous ether) was added dropwise to the resulting solution of 5-[methylbis(2-thienyl)silyl]-2-thienyllithium. The reaction mixture was stirred for 30 min at 0 °C and for 1 h without cooling. The solution of 5-[methylbis(2-thienyl)silyl]-2-thienylmagnesium bromide (**4**) thus formed was added dropwise to $Pd(dppf)Cl_2$ (42.5 mg, 0.06 mmol) and a solution of compound **5** (0.65 g, 1.23 mmol) in anhydrous ether (10 mL), the temperature being maintained between 0 and +10 °C. Then cooling was discontinued and the mixture was stirred for 2.5 h at ~20 °C. The reaction mixture was poured into ice water (50 mL) and extracted twice with freshly distilled ether. The combined organic layers were washed with water to a neutral pH and dried with Na_2SO_4. Evaporation of the solvent and drying at 1 Torr gave 1.52 g of a crude product containing 41% of compound **1** (GPC data). Preparative GPC gave 515 mg (36%) of pure dendrimer **1**.

In both cases, preparative GPC gave identical compounds. ^{1}H NMR (DMSO—CCl_4), δ: 0.93 (s, 9 H); 0.94 (s, 3 H); 7.23 (dd, 6 H, J_1 = 3.7 Hz, J_2 = 4.9 Hz); 7.27 (d, 3 H, J = 3.7 Hz); 7.33 (d, 3 H, J = 3.1 Hz); 7.34 (d, 3 H, J = 3.7 Hz); 7.35 (d, 3 H, J = 3.1 Hz); 7.40 (dd, 6 H, J_1 = 3.7 Hz, J_2 = 1.2 Hz); 7.81 (dd, 6 H, J_1 = 4.9 Hz, J_2 = 1.2 Hz). Found (%): C, 53.51; H, 3.53; S, 33.18; Si, 9.50. Calculated (%): C, 53.66; H, 3.64; S, 33.05; Si, 9.65.

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