Bithiophenesilane Dendrimers: Synthesis and Thermal and Optical Properties

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For the first time the synthesis and thermal and optical properties of a number of first-generation bithiophenesilane dendrimers with alkyl end groups, namely, tris{5′-[methylbis(5′-hexyl-2,2′-bithienyl-5-yl)silyl]-2,2′-bithienyl-5-yl}methylsilane (**1**), tris{5′-[methylbis(5-hexyl-2-thienyl)silyl]-2,2′-bithienyl-5-yl}methylsilane (**2**), and tris{5′-[methylbis(5-ethyl-2-thienyl)silyl]-2,2′-bithienyl-5-yl}methylsilane (**3**), are described. The influence of the dendritic architecture on the thermal and optical properties was investigated and compared to those of the linear and branched bithiophenesilanes. The results obtained showed a significant increase of the fluorescence quantum yield Q with an increasing number of bithiophenesilane fragments being a constituent part of the dendritic molecule. It reaches 30% for dendrimer 1 with nine such fragments as compared to $Q = 6\%$ for 5,5′-bis(trimethylsilyl)-2,2′-bithiophene and $Q = 1.8\%$ for 5-hexyl-2,2′-bithiophene. This effect was explained by the impact of the specific dendritic molecular structure on the fluorescence efficiency. It is noteworthy that the emission wavelength was maintained at the same violet-blue region (380−385 nm) for all the compounds under consideration. Tuning the terminal alkyl chains of the dendrimers allowed creating stable amorphous materials, in contrast to the dendrimer without alkyl chains, tris{5′-[methylbis(2-thienyl)silyl]-2,2′-bithienyl-5-yl}methylsilane (**4**), or model bithiophenesilanes, all of which tend to crystallize under different conditions. Bearing in mind the high thermal stability and excellent solubility of the bithiophenesilane dendrimers, these materials present a new promising class of violet-blue emitters for photonics, organic electronics, and other applications.

Introduction

Thiophene and its derivatives have been extensively investigated and used as building blocks for creation of various semiconducting polymers and oligomers over the past decade.[1] Branched structures among them attract much attention among researchers.[2] Many of these materials have been utilized in organic light-emitting diodes (OLEDs),[3] field-effect transistors (OFETs),[4] and photovoltaic (PV) applications.[5] Hyperbranched 2,3,5-polythiophene[6] and dendrimers consisting of thiophene rings connected through positions 2, 3, and 5 have been synthesized.[7] Phenyl-cored thiophene dendrimers,[8] conjugated oligothiophene-dendron-capped CdSe nanoparticles,[9] and thiophene-dendron-jacketed poly(amidoamine) dendrimers[10] have also been reported. Due to multifunctionality and good solubility, dendrimers can be processed from their solutions to create active layers in organic electronic devices. Different dendrimers were applied either as light-emitting materials[11] or as an electron-transporting layer[12] in OLEDs. Dendrimer-encapsulated chromophores were also utilized in multichro-

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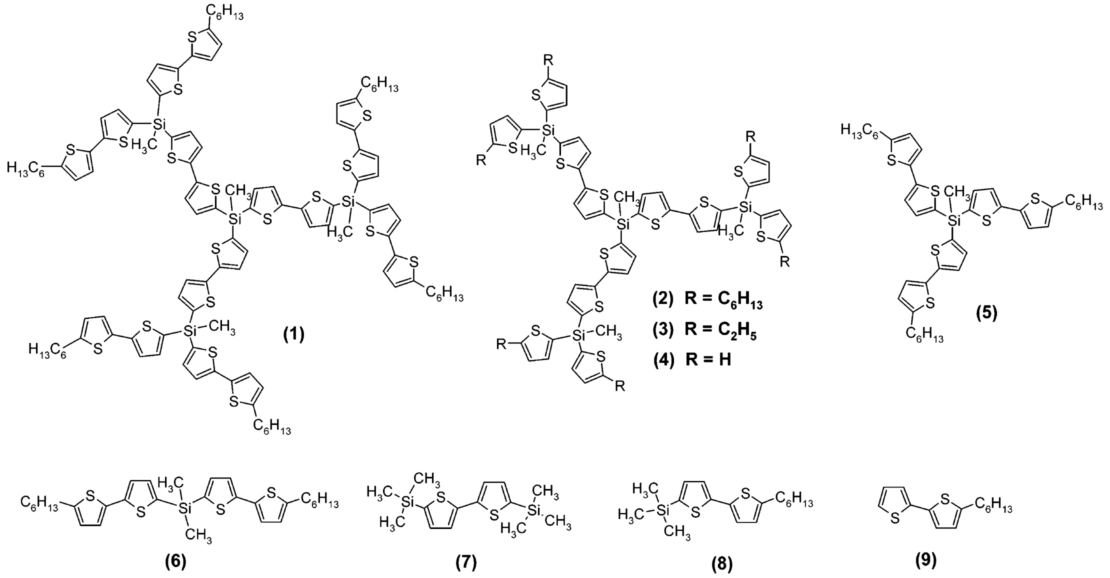
Scheme 1. Structural Formulas of Bithiophenesilane Dendrimers and Their Linear and Branched Low Molar Weight Analogues



mophoric OLEDs.[13] Tetrathienylsilane,[14] which can be considered as a branching core or a zero-generation dendrimer, and a first-generation organosilicon dendrimer containing 16 thiophene rings have also been described.[15] Hyperbranched poly(2,5-silylthiophenes) containing alternating silylene and thiophene groups along the branches were reported in 1999.[16] The first dendrimer containing bithiophene units linked directly to silicon atoms have recently been synthesized by our group.[17] Interest in the synthesis and properties of such systems was stimulated by the discovery of the strong fluorescence of star-shaped organosilicon molecules containing α,α'-bi- and terthiophene units.[18] These compounds, however, contain a silicon−silicon bond, which is photochemically reactive.[19] Linear organosilanylene−oligothienylene copolymers are also known for their optical, hole-transporting, and conducting properties.[20] This work reports on the synthesis of a new series of bithiophenesilane dendrimers with alkyl end groups (**1**−**3**) via Suzuki and Kumada coupling reactions, as well as on advantages of the thermal and optical properties of these dendrimers as compared to the dendrimer without alkyl end groups (**4**) and their linear and branched low molar weight analogues (**5**−**9**) (Scheme 1).

Results and Discussion

Synthesis. In this work the synthesis of first-generation bithiophenesilane dendrimers with alkyl end groups was elaborated. As opposed to dendrimer **4** without terminal alkyl groups, which was obtained from symmetrical methyltrithienylsiane,[17] new unsymmetrical methyltrithienylsilanes with one 2-thienyl and two 5-alkylthienyl groups (named below also as dendrons) were obtained and used as building blocks for the synthesis of new dendrimers. These were prepared for the first time starting from commercially available methyltrichlorosilane and methyltriethoxysilane (Scheme 2a).

The different reactivity of magnesium and lithium thiophene derivatives with chloro- and alkoxysilanes was used for this synthesis. First, methyl-2-thienyldichlorosilane (**10**) and methyl-2-thienyldiethoxysilane (**11**) were obtained from 2-thienylmagnesium bromide and methyltrichlorosilane or methyltriethoxysilane, respectively. Then the reaction of compounds **10** and **11** with the corresponding lithium derivatives of 5-alkylthiophenes gave rise to the desired unsymmetrical methyltrithienylsilanes **12a**,**b**. Lithiation of compounds **12a**,**b** with butyllithium gave the corresponding monolithium derivatives, treatment of which with an ether complex of magnesium dibromide, $MgBr_2 \cdot Et_2O$, gave Grignard reagents **13a**,**b**. These were reacted with tris(5-bromo-2-thienyl)methylsilane under Kumada conditions to give dendrimers **2** and **3**, having three internal bithienyl and six external monothienyl functional groups with hexyl or ethyl end groups, respectively (Scheme 2b). It should be noted that in contrast to the Kumada route used for the synthesis of dendrimer **4**, without alkyl end groups,[17] no formation of high molar weight byproducts was observed in this case.

The Kumada reaction, used for the synthesis of dendrimers **2**−**4**, has an advantage of fast velocity (the reactions were complete within 1 h), low reaction temperature (0 to +25 °C), and small amount of catalyst used (usually 0.5−1%). However, yields of the products obtained were moderate, in spite of the usage of 25−40% excess of the dendron's Grignard reagents, and decreased with increasing dendron size, in relation to the length of the alkyl groups (Table 1, Figure 1). That is why the other synthetic route was chosen for the synthesis of the largest dendrimer, **1**, with nine bithienyl fragments, in both the interior and the exterior of the molecule, and hexyl end groups (Scheme 3).

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Scheme 2. Synthesis of Unsymmetrical Thienylsilane Precursors (a) and Dendrimers 2 and 3 by Kumada Coupling (b)

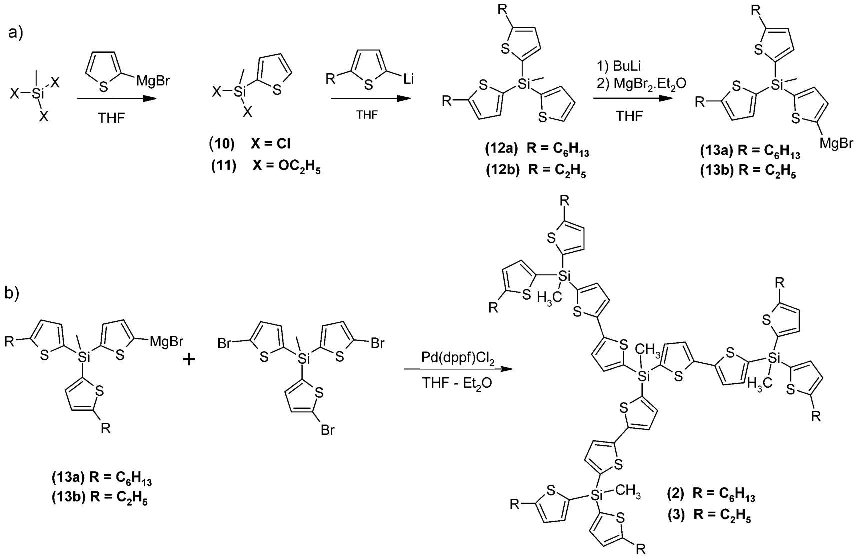

Table 1. Comparison of Efficiency of Suzuki and Kumada Reactions for the Synthesis of Bithiophenesilane Dendrimers

reaction	compound	excess of dendron, %	reaction yield, %	isolated yield, %
Suzuki	**1**	15	80	53
	4[a]	10	65	32
Kumada	**2**	25	29	10
	3	40	53	41
	4[a]	30	55	36

[a] Data from ref 17.

For this purpose a new unsymmetrical bithienylsilane precursor, **15**, with one 2-thienyl and two 5-hexyl-2,2′-bithienyl groups was prepared starting from commercially available methyltrimethoxysilane (Scheme 3a) by the procedure similar to those described for compound **12b**. First, methyl-2-thienyldimethoxysilane, **14**, was obtained from 2-thienylmagnesium bromide and methyltrimethoxysilane. Then it was reacted with the lithium derivative of 5-hexyl-2,2′-bithiopene to yield bis(5′-hexyl-2,2′-bithien-5-yl)(methyl)2-thienylsilane, **15**. Subsequent lithiation followed by the lithium exchange with an organoboron residue, which took place *in situ* on treatment with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (IPTMDOB), gave rise to 2-{5-[methylbis(5′-hexyl-2,2′-bithienyl-5-yl)silyl]-2-thienyl}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, **16**. It was reacted with tris(5-bromo-2-thienyl)methylsilane under Suzuki conditions to give dendrimer **1**, having three internal and six external bithienyl functional groups with hexyl end groups (Scheme 3b).

As a result, dendrimer **1** was obtained in 80% reaction and 53% isolated yield after column chromatography (Figure 1). A similar tendency for higher reaction yield of the Suzuki reaction was observed for the dendrimer **4**, which was synthesized by both techniques (Table 1).[17] These results indicate that the Suzuki reaction is more promising for the synthesis of large oligothiophenesilane compounds as compared to the Kumada reaction in spite of its several disadvantages, namely, long reaction time (usually 40−70 h) under reflux at elevated temperature (ca. 100 °C) and the rather high quantity of catalyst needed (5−10%).

The structure and purity of the dendrimers and intermediate compounds obtained were unambiguously proved by a combination of GPC chromatography, elemental analysis, and ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy methods (see Figure 1, Experimental Section, and Supporting Information).

Table 2. Optical Properties of Dilute Solutions of the Dendrimers and Model Compounds

compound	absorption, λ_{max}, nm	luminescence, λ_{max}, nm	luminescence quantum yield, Q, %
1	333	385	30
2	238, 332	385	20
3	238, 332	385	20
4	238, 332	385	20
5	331	385	19
6	325	382	9.3
7	322	381	6.0
8	321	381	5.8
9	308	374	1.7

As far as preparation of the model low molecular weight bithienylsilanes is concerned, synthesis of compounds **5**, **6**, and **8** is described elsewhere.[21] Tour et al. have reported the synthesis of 5,5′-bis(trimethylsilyl)-2,2′-bithiophene (**7**) from 2-iodo-5-(trimethylsilyl)thiophene in 56% yield.[22] We have chosen a different methodology; namely, compound **7** was obtained by lithiation of 2,2′-bithiophene with 2 equiv of butyllithium, followed by reaction with 2 equiv of Me_3SiCl in 88% yield (Scheme 4).

Optical Properties. Optical properties of dilute solutions of dendrimers **1**−**4** and model compounds **5**−**9** were studied by absorption/fluorescence spectroscopy in the UV/vis region. The results are summarized in Table 2. All measurements were made in spectroscopic-grade *n*-hexane. As can be seen from these data, all dendrimers show significantly higher luminescence quantum yield *Q* as compared to any linear low molar weight analogue.

The lowest *Q* (1.8%) belongs to 5-hexyl-2,2′-bithiophene, **9**, which has no silicon atom chemically linked to a bithiophene moiety. Attaching one or two trimethylsilyl groups to the bithiophene leads to an increase of *Q* to ca. 6% (compounds **7** and **8**), which is practically independent of the number of trimethylsilyl groups attached to the bithiophene. In compound **6**, which is actually a linear analogue of the dendrimers under consideration, two bithiophene units attached to one silicon atom increase *Q* to 9.3%. However all bithiophenesilane dendrimers

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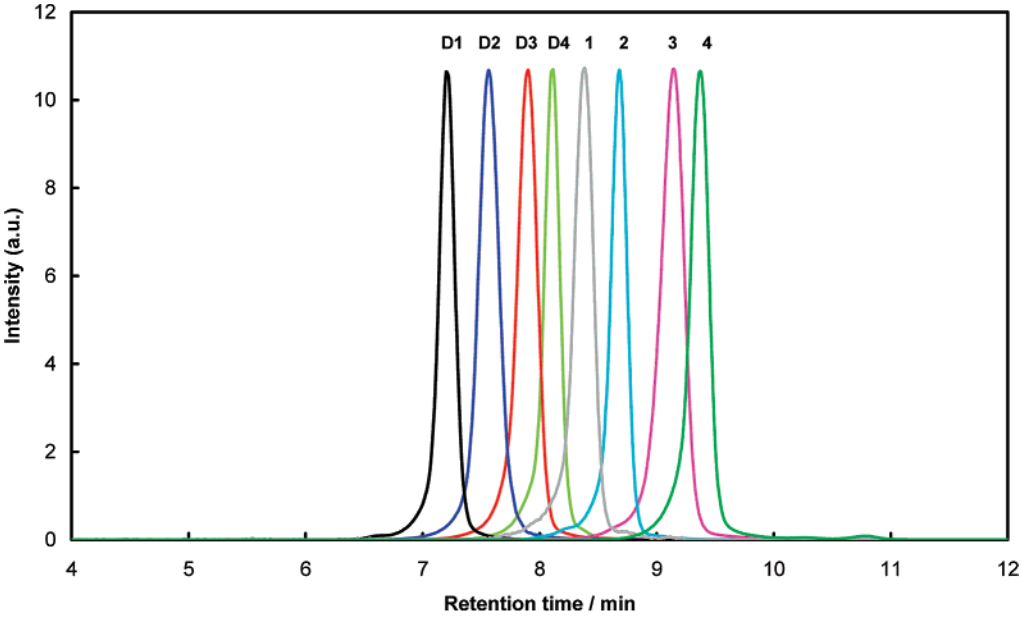
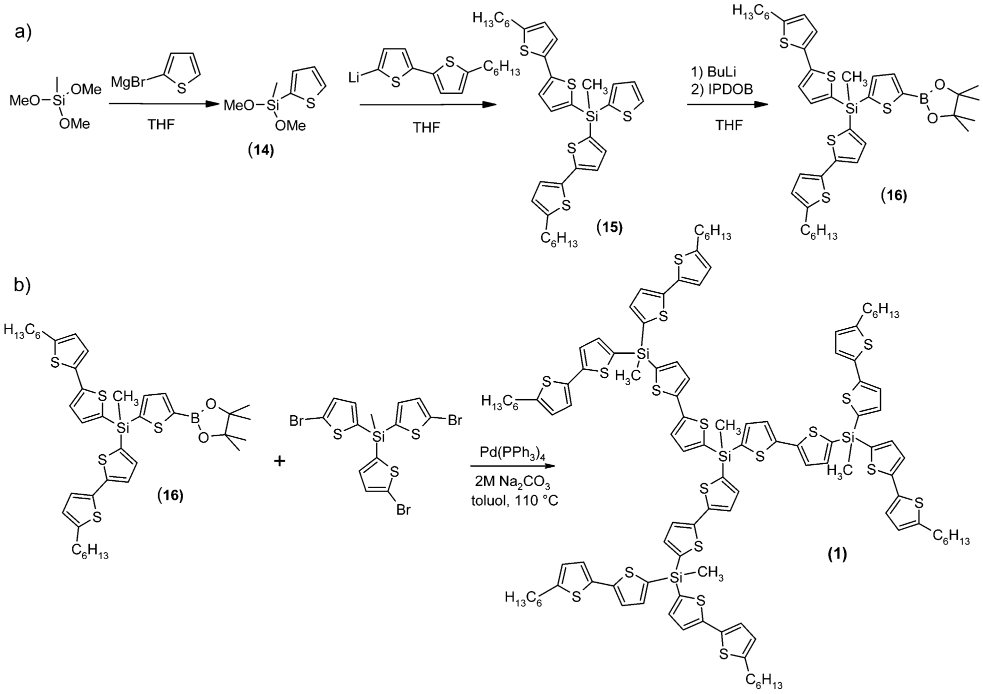
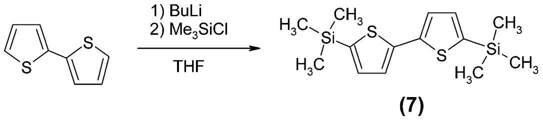


Figure 1. GPC curves of bithiophenesilane dendrimers and corresponding dendrons obtained: D1, dendrimer **1** (black curve); D2, dendrimer **2** (blue curve); D3, dendrimer **3** (red curve); D4, dendrimer **4** (green curve); 1, compound **15** (gray curve); 2, compound **12a** (light blue curve); 3, compound **12b** (pink curve); 4, methyltrithienylsilane (light green curve).

Scheme 3. Synthesis of Unsymmetrical Bithienylsilane Precursors (a) and Bithiophenesilane Dendrimer 1 by Suzuki Reaction (b)



Scheme 4. Synthesis of 5,5 Bis(trimethylsilyl)-2,2-bithiophene 7



have *Q* values not less than 20%, which indicates the influence of the 3-D architecture of the dendrimers on their luminescence efficiency.

The optical properties of dendrimers **2**−**4** were identical, which is not surprising, since they differ only by the presence of alkyl end groups, which are transparent in the UV−vis region. Optical properties of dendrimer **4** were investigated in detail. Its absorption, excitation, and luminescent spectra as well as an energy-level diagram are shown in Figure 2. The absorption spectrum consists of two intensive peaks with $\lambda_{\max}$ at 238 and 332 nm, corresponding mainly to the absorption coming from the thiophene and bithiophene units of the dendrimer molecule. Interestingly, these maxima and the spectral shape of the peaks do not depend on the solvent used (hexane, THF, ethanol), in contrast to any of their low molar weight analogues. However, its luminescence spectrum consists of only one intensive peak with $\lambda_{\max}$ at 385 nm, and it is the same for the excitation at 332 or 238 nm. At first glance, this should indicate an efficient energy transfer from the outer thiophene to the inner bithiophene

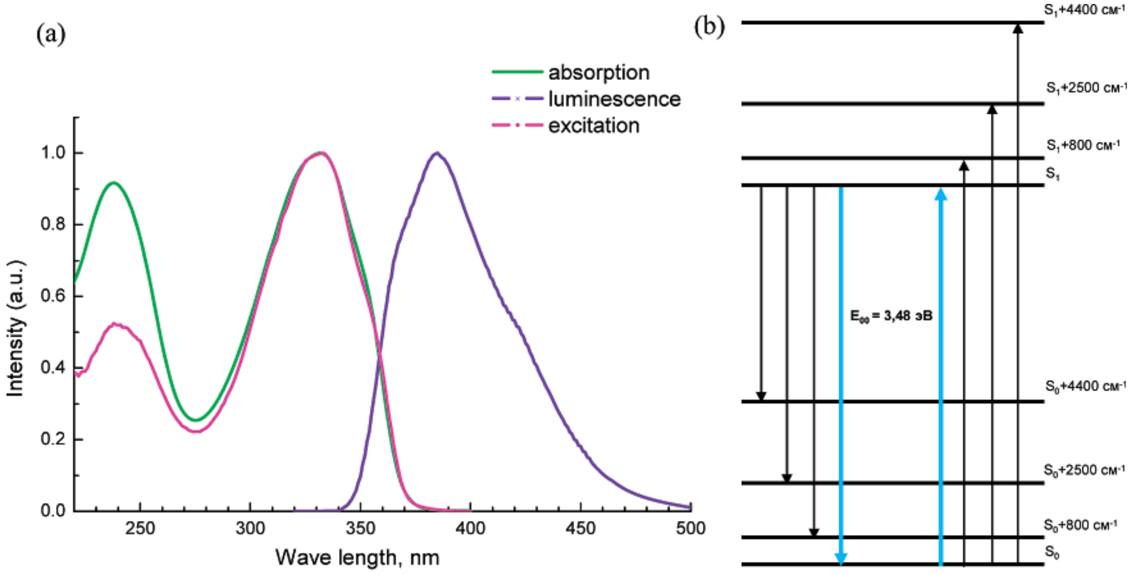


Figure 2. Absorption, excitation, and luminescence spectra (a) and an energy-level diagram (b) of bithiophenesilane dendrimer **4** (measured as dilute solutions in THF).

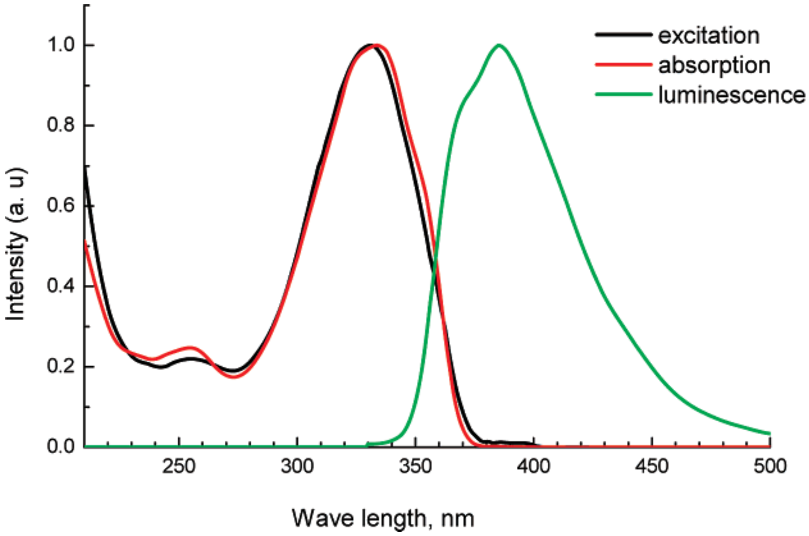


Figure 3. Absorption, excitation, and luminescence spectra of bithiophenesilane dendrimer **1** (measured as dilute solutions in THF).

units within the dendrimer molecule. However, a detailed investigation of the luminescence efficiency showed that the quantum yield, which was 20% under excitation at 332 nm, drops to 8% when exited at 238 nm. Comparison of the absorption and the excitation spectra of this dendrimer and model compounds **6**−**9** led us to conclude that only a part of the absorbance at 238 nm (ca. 75 ± 5%) comes from the thiophene units, while the other part (ca. 25 ± 5%) is a constituent part of the absorbance of the bithiophene fragments, which is mostly responsible for the luminescence coming from the excitation at 238 nm. A rough estimation based on the absorption and luminescence data indicates that the efficiency of the energy transfer from thiophenesilane to the bithiophenesilane units within the dendrimer molecule does not exceed 20%. These observations indicate that the impact of thienylsilyl groups on the luminescence of dendrimers **2**−**4** small, and mostly their internal core, consisting of three bithienylsilyl groups, linked to the same silicon atom, gives a luminescence efficiency equal to 20%. This conclusion supports the data for branched model compound **5**, having only three bithiophene units linked to the same silicon atom and having $Q = 19\%$ (Table 2).

The optical properties of dendrimer **1**, having nine bithienyl units, are illustrated in Figure 3. It can be seen that its absorbance and excitation spectra coincide in all spectral regions. The luminescence quantum yield is further increased up to 30%, which could be explained only by the fact that bithiophenesilane units are structurally organized in the 3-D dendritic architecture of the dendrimer. It has the same luminescence $\lambda_{\max}$ at 385 nm as all other bithiophenesilane dendrimers described, and it is very close to the luminescence spectra of low molar weight bithiophenesilances **5**−**8**. The data obtained showed that there is $\sigma-\pi$ conjugation between a bithiophene fragment and a silicon atom, leading to a red shift of approximately 13 nm for compound **8** as compared to initial bithiophene **6**. However, addition of further bithiophene units to the same silicon atom has a negligible influence on the energy gap (compare data for compounds **5**, **6**, and **8** in Table 1). Moreover, the presence of nine bithiophene units in the molecule of dendrimer **1** does not change its absorption or luminescence spectra as compared to compound **5**, having only three such units, indicating that delocalization of the π electrons is limited to a bithiophenesilane fragment in such molecules. These observations lead to the conclusion that in spite of $\sigma-\pi$ conjugation between a silicon

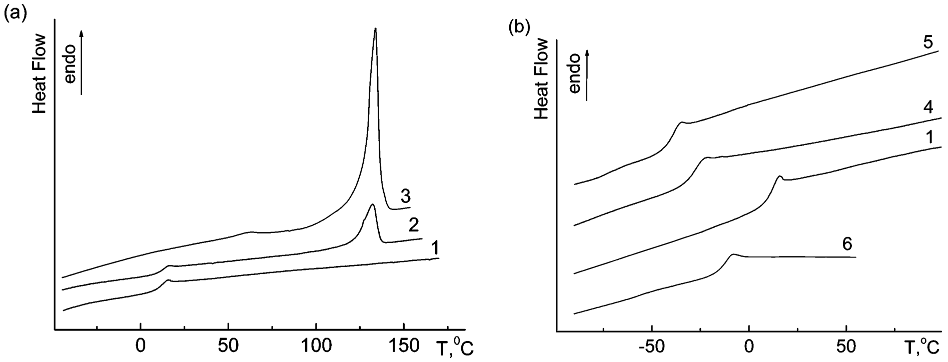


Figure 4. DSC heating curves of bithiophenesilane dendrimer **4** (a) and dendrimers **2**−**4** (b): curve 1, for dendrimer **4** as received; 2, for dendrimer **4** after annealing at 4 °C during 2 months; 3, for dendrimer **4** after annealing at 4 °C during 2 months followed by annealing at 65 °C during 30 min; 4, for dendrimer **3**; 5, for dendrimer **2**; and 6, for dendrimer **1**.

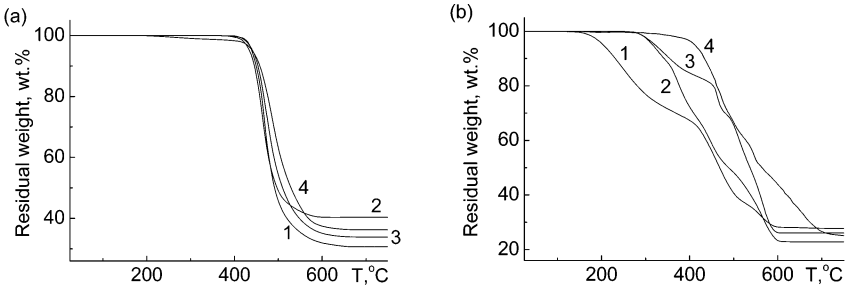


Figure 5. TGA curves for dendrimers **1** (1), **2** (2), **3** (3), and **4** (4) in argon (a) and in air (b) at a heating rate of 5 K/min.

atom and a bithiophene unit, a conjugation of several bithiophenes through the silicon atom does not happen, like it was observed, for instance, for oligothiophenes linked to 1,3,5-positions of a benzene ring.[4a] However, silicon significantly increases the luminescence efficiency of the bithiophenes units attached, especially if they are organized in a 3-D dendritic architecture. The mechanism of increasing the efficiency of luminescence in the dendritic structure is not clear yet and deserves special investigations.

Thermal Behavior. Phase behavior of the dendrimers was investigated by the DSC method and is summarized in Figure 4. The most complex thermal behavior is seen for dendrimer **4**, which as received showed only a glass transition at 11 °C (Figure 4a, curve 1) and was soluble in hexane. However, after annealing at +4 °C during 2 months it lost its solubility in hexane, which proved to be due to its partial crystallization. On the DSC curve for this sample (Figure 4a, curve 2) besides the glass transition there is a small endothermic peak with a maximum at 133 °C (ΔH = 9.5 J/g). Heating the hexane solution did not increase the dendrimer's solubility, but instead led to its complete crystallization, and only an endotherm, corresponding to the melting of the crystalline phase at 133 °C with ΔH = 38 J/g, is observed on the DSC curve (Figure 4, curve 3). Melting of the crystal structure during the first heating scan gives again only the glass transition on cooling and second heating scans. Moreover, its solubility in hexane resumes.

Dendrimers **2** and **3**, with the alkyl end groups, have excellent solubility and have no tendency to crystallize. Their DSC curves show only glass transitions at −29 and −41 °C for **3** and **2**, respectively. The glass transition temperature decreases with increasing the length of the alkyl groups (Figure 4b). This observation could be explained by a plasticizing effect of the alkyl end groups, which increases from ethyl to hexyl groups. Dendrimer **1** has a glass transition temperature at −14 °C, which is somewhat higher than the value obtained for dendrimer **2**, also having hexyl end groups.

The thermal stability of the dendrimers was checked by the TGA method, which showed that they are thermostable up to 400 °C in argon (Figure 5a). In the presence of oxygen their stability decreases in the order **4** > **3** > **2** > **1**. The destruction onset (5% weight loss) is 408, 318, 312, and 203 °C for dendrimers **4**, **3**, **2**, and **1**, respectively (Figure 5b). These data indicate that the thermal stability of the dendrimers under consideration is mainly determined by the properties of its thiophenesilane core, whereas the thermo-oxidative stability depends more on the structure of its external layer (end groups).

It is noteworthy that 2,2′-bithiophene-5-hexyl-2,2′-bithiophene (**9**) and all low molar weight linear and branched bithiophenesilanes (**5**−**8**) under study are crystalline materials.[21] In contrast, all alkyl-terminated bithiophenesilane dendrimers are amorphous and have no tendency to crystallize. Since crystallization usually disturbs the optical properties, especially the luminescence, these bithiophenesilane dendrimers are a new promising class of materials for various photonic and optoelectronic applications. Preliminary investigations showed that the optical properties of dendrimer **1** in the bulk are very similar to those in dilute solutions, showing high photoluminescence efficiency in the violet-blue region. These results as well as characteristics of the electroluminescent devices made from oligothiophenesilane dendrimers will be the focus of our further publications.

Conclusions

To sum up, in this work a number of bithiophenesilane dendrimers were synthesized and characterized for the first time. We have shown that these dendrimers have better photoluminescence properties than the corresponding low molar weight and linear analogues. The multifunctional nature of the bithiophenesilane dendrimers allows tuning their solubility and thermal properties. All these new compounds are thermostable up to 400 °C and possess effective luminescence in the violet-blue region. This approach could be important for the creation of new materials with controllable solubility and phase behavior and useful optical properties for various photonic and optoelectronic applications.

Experimental Section

Materials. Hexane solutions of butyllithium (1.6 and 2.5 M), thiophene, 2-bromothiophene, 2-ethylthiophene, and *N*-bromosuccinimide (Acros Organics), 1,1′-bis(diphenylphosphino)ferrocenepalladium(II) chloride [Pd(dppf)Cl_2], tetrakis(triphenylphosphine)palladium(0) [Pd(PPh_3)$_4$], and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dixaborolane (Aldrich) were used as received; trimethylchlorosilane, methyltrichlorosilane, methyltrimethoxysilane, and methyltriethoxysilane were distilled before use; THF and diethyl ether were dried over CaH_2 and distilled from $LiAlH_4$ under argon. For investigation of optical properties spectrophotometric-grade THF and hexane (Acros Organics) were used as received. 2,2′-Bithiophene was synthesized according to a literature procedure.[23] 2-Hexylthiophene and 5-hexyl-2,2′-bithiophene were obtained using the procedure described elsewhere.[24] Methyltris(5-bromo-2-thienyl)silane was prepared by the technique described previously.[17]

Methods. ^{1}H NMR spectra were recorded on a Bruker WP-250 SY spectrometer at 250.13 MHz using tetramethylsilane as the internal standard. ^{13}C NMR spectra were recorded on a Bruker DRX500 spectrometer at 125.76 MHz, while ^{29}Si NMR spectra were recorded on a Bruker DRX500 spectrometer at 99.36 MHz. GPC analysis was performed on a Shimadzu instrument with a RID-10A refractometer and a SPD-M10AVP diode matrix as detector using 7.8 × 300 mm Phenomenex columns (USA) filled with a Phenogel sorbent with pore sizes of 500 and 10^3 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 under vacuum below 1 Torr at 40 °C. Thermogravimetric analysis (TGA) was carried out by “Derivatograph-C” (MOM, Hungary) at a heating rate of 5 K/min in air and in argon atmosphere on samples weighing from 3 to 10 mg. The relaxation and phase transitions were studied by differential scanning calorimetry (DSC) using a Mettler DSC-822e thermosystem at a scanning rate of 10 K/min in argon. Sample weights were typically chosen to be between 5 and 10 mg. A multifunctional absorption−luminescence spectrometer ALS01M was used for the measurements of absorption and luminescence spectra, which were recorded in the region 200−600 nm in dilute UV-grade THF or hexane solutions at the concentration range $10^{-5}-10^{-8}$ mol/L to avoid self-absorption. In all cases the optical density of the solutions used for the measurements of quantum yield did not exceed 0.05 in a 10 mm thick quartz cuvette. Mass spectra (MALDI-MS) were recorded on a Bruker Daltonics Reflex-III mass spectroscope in the positive ion regime using the reflect mode with a target voltage of 20mV. 2,4,9-Antracenetriol was used as a matrix. The samples were prepared by dissolution of the compounds under investigation in chloroform ($c = 10^{-4}-10^{-6}$ M) and mixed with a solution of the matrix (20 mg/mL) in chloroform in the ratio 1:1.

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

Synthesis. Methyl(thien-2-yl)dichlorosilane (10). A solution of 27.25 g (0.167 mol) of 2-bromothiophene in 250 mL of diethyl ether was added dropwise to a suspension of 6.09 g (0.25 mol) of magnesium in 15 mL of diethyl ether. The Grignard reagent was refluxed for 1 h and cooled to 0 °C, and 17.82 mL (0.152 mol) of methyltrichlorosilane was added dropwise. The reaction mixture was refluxed for 3 h, washed with anhydrous hexane, and filtered off on a G4 glass filter under argon. The product was purified by distillation in vacuum (15 mBar, 73 °C) (lit.: 11 mbar, 68−69 °C)[25] to give 93.9% pure (GC) thienylsilane **10** (16.7 g, 57%) as a colorless liquid. ^{1}H NMR (δ in $CDCl_3$, TMS/ppm): 1.09 (s, 3H), 7.25 (dd, 1H, $J_1 = 3.1$ Hz, $J_2 = 4.9$ Hz), 7.57 (d, 1H, $J = 3.1$ Hz), 7.77 (d, 1H, $J = 4.9$ Hz).

Methyl(thien-2-yl)diethoxysilane (11). A solution of 8.25 g (50 mmol) of 2-bromothiophene in 80 mL of diethyl ether was added dropwise to a suspension of 1.82 g (75 mmol) of magnesium in 10 mL of diethyl ether. The Grignard reagent was refluxed for 1 h and cooled to room temperature, and 9.16 mL (46 mmol) of methyltriethoxysilane was added dropwise. The reaction mixture was refluxed for 3 h, washed with anhydrous hexane, and filtered off on a G4 glass filter under argon. The product was purified by distillation under vacuum (15 mbar, 97 °C) to give 99.0% pure (GC) thienylsilane **11** (5.41 g, 54%) as a colorless liquid. ^{1}H NMR (δ in $CDCl_3$, TMS/ppm): 0.41 (s, 3H), 1.25 (t, 6H, $J = 7.3$ Hz), 3.85 (q, 4H, $J = 7.3$ Hz), 7.21 (dd, 1H, $J_1 = 3.7$ Hz, $J_2 = 4.9$ Hz), 7.42 (d, 1H, $J = 3.7$ Hz), 7.64 (d, 1H, $J = 4.9$ Hz). ^{13}C NMR (δ in $CDCl_3$): −3.03, 18.26, 58.75, 128.07, 131.42, 133.66, 135.77. ^{29}Si NMR (δ in $CDCl_3$): −21.43. Anal. Calcd for $C_9H_{16}O_2SSi$: C, 49.96; H, 7.45; S, 14.82; Si, 12.98. Found: C, 50.09; H, 7.56; S, 14.80; Si, 12.83.

Bis(5-hexyl-2-thienyl)(methyl)2-thienylsilane (12a). A solution of 10.75 mmol of buthyllithium in 4.3 mL of hexane (2.5 M solution) was added dropwise to a solution of 2-hexylthiophene (1.84 g, 10.94 mmol) in 20 mL of THF, while the temperature was kept between −75 and −70 °C. The cooling bath was then removed, and the temperature was allowed to rise to 0 °C. The reaction mixture was cooled again to −75 °C, and 1.4 mL (10.75 mmol) of compound **10** in 5 mL of THF was added. The solution was stirred at room temperature for 8 h. It was then poured into 50 mL of water and 100 mL of diethyl ether. The organic layer was washed with water and dried over sodium sulfate. The solvent was evaporated under vacuum, and the residue was dried at 1 Torr to give 2.07 g of crude product, containing 45% of compound **12a** (GPC). This product was purified by column chromatography on silica gel (eluent toluene−hexane, 1:20) to give pure compound **12a** (0.72 g, 34%). ^{1}H NMR (δ in $CDCl_3$, TMS/ppm): 0.87 (s, 3H), 0.87(t, 6H, $J = 6.7$ Hz), 1.20−1.43 (overlapped peaks, 12 H), 1.67 (m, 4H, $J = 7.3$ Hz), 2.83 (t, 4H, $J = 7.3$ Hz), 6.86 (d, 2H, $J = 3.1$ Hz), 7.19 (d, 2H, $J = 3.1$ Hz), 7.21 (d, 1H, $J = 3.7$), 7.39 (d, 1H, $J = 3.7$ Hz), 7.66 (d, 1H, $J = 3.7$ Hz). ^{13}C NMR (δ in $CDCl_3$): 0.16, 14.06, 22.55, 28.88, 30.06, 31.55, 31.64, 125.65, 128.20, 131.95, 132.60, 135.76, 136.71, 136.92, 153.46. Anal. Calcd for $C_{25}H_{36}S_3Si_1$: C, 65.16; H, 7.87; S, 20.87; Si, 6.09. Found: C, 65.24; H, 7.88; S, 20.85; Si, 6.17.

Bis(5-ethyl-2-thienyl)(methyl)2-thienylsilane (12b) was synthesized according to the procedure described for compound **12a** from 2.0 g (17.83 mmol) of 2-ethylthiophene, 11.00 mL of 1.6 M butyllthium solution in hexane (17.83 mmol), and 1.6 g (8.47 mmol) of methylthienyldiethoxysilane (**11**) to give 2.42 g of crude product, containing 72% of compound **12b** (GPC). It was purified by column chromatography on silica gel (eluent toluene−hexane, 1:5) to give pure compound **12b** (1.55 g, 53%). ^{1}H NMR (δ in $CDCl_3$, TMS/ppm): 0.88 (s, 3H), 1.31(t, 6H, $J = 7.3$ Hz), 2.89 (q, 4H, $J = 7.3$ Hz), 6.88 (d, 2H, $J = 3.1$ Hz), 7.18−7.23 (overlapped peaks, 3H), 7.40 (d, 1H, $J = 3.7$), 7.66 (d, 1H, $J = 3.7$ Hz). ^{13}C NMR (δ in $CDCl_3$): 0.15, 15.86, 23.37, 29.71, 125.09, 128.22, 131.98, 132.53, 135.68, 136.74, 136.98, 154.94.

Tris{5′-[methylbis(5-hexyl-2-thienyl)silyl]-2,2′-bithienyl-5-yl}-methylsilane (2). A 1.6 M solution of butyllthium in hexane (1.95 mL) was added dropwise to a solution of compound **12a** (1.44 g,

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3.12 mmol) in 30 mL of THF, while the temperature was kept between −70 and −75 °C. The reaction mixture was stirred for 30 min at −75 °C, the cooling bath was then removed, and the temperature was allowed to rise to 0 °C. An ether complex of $MgBr_2$ (freshly prepared from Mg (0.13 g, 5.3 mmol) and dibromoethane (0.77 g, 4.06 mmol) in 12 mL of anhydrous ether) was added dropwise to the reaction mixture, which was then stirred for 30 min at 0 °C and for 1 h without cooling. The solution of compound **13a** obtained was placed into a dropping funnel of the second reaction glass and was added dropwise to a suspension of $Pd(dppf)Cl_2$ (20 mg, 0.025 mmol) in a solution of methyltris(5-bromo-2-thienyl)silane (0.44 g, 0.83 mmol) in 10 mL of diethyl ether, while the temperature was kept between 0 and +10 °C. Then cooling was removed and stirring was continued for 8 h at 23 °C. Afterward it was poured into 50 mL of ice water and extracted twice with freshly distilled diethyl ether. The combined organic phase was washed with water and dried over sodium sulfate. Evaporation of the solvent and drying at 1 Torr gave 2.49 g of crude product, containing 19% of compound **2** (GPC). Preparative GPC gave pure dendrimer **2** (139.6 mg, 10%). MALDI-MS: *m/z* 1668.99 (M^+, requires 1669.00). ^{1}H NMR (δ in DMSO−CCl_4, TMS/ppm): 0.83 (s, 9H), 0.87 (t, 18H, J = 7.3 Hz), 0.93 (s, 3H), 1.23−1.42 (overlapped peaks, 36H), 1.66 (m, 12H, J = 7.3 Hz), 2.82 (t, 12H, J = 7.3 Hz), 6.84 (d, 6H, J = 3.1 Hz), 7.14 (d, 6H, J = 3.7 Hz), 7.21 (d, 3H, J = 3.7 Hz), 7.28−7.34 (overlapped peaks, 9H). ^{13}C NMR (δ in $CDCl_3$): −0.20, 0.01, 14.04, 22.54, 28.88, 30.07, 31.54, 31.62, 125.51, 125.61, 125.72, 132.19, 134.11, 136.04, 137.04, 137.45, 137.88, 143.51, 144.36, 153.62. ^{29}Si NMR (δ in $CDCl_3$): −25.69, −25.10. Anal. Calcd for $C_{88}H_{114}S_{12}Si_4$: C, 63.33; H, 6.88; S, 23.05; Si, 6.73. Found: C, 63.00; H, 6.67; S, 23.16; Si, 6.70.

Tris{5′-[methylbis(5-ethyl-2-thienyl)silyl]-2,2′-bithienyl-5-yl}methylsilane (3) was obtained as described for compound **2** using 1.55 g (4.45 mmol) of compound **12b**, 2.22 mL of 1.6 M butyllthium solution in hexane (3.56 mmol), 0.141 g (5.8 mmol) of Mg, 0.92 g (5.41 mmol) of dibromoethane, 24 mg (0.033 mmol) of $Pd(dppf)Cl_2$, and 0.47 g (0.87 mmol) of methyltris(5-bromo-2-thienyl)silane to give the product **3** (0.49 g, 41%). MALDI-MS: *m/z* 1332.34 (M^+, requires 1332.35). ^{1}H NMR (δ in DMSO−CCl_4,-TMS/ppm): 0.83 (s, 9H), 0.93 (s, 3H), 1.31 (t, 18H, J = 7.3 Hz), 2.88 (q, 12H, J = 7.3 Hz), 6.88 (d, 6H, J = 3.7 Hz), 7.16 (d, 6H, J = 3.7 Hz), 7.23 (d, 3H, J = 3.7 Hz); 7.28−7.34 (overlapped peaks, 9H). ^{13}C NMR (δ in $CDCl_3$): −0.23, −0.00, 15.84, 23.38, 125.15, 125.53, 125.62, 132.11, 134.13, 135.96, 137.10, 137.48, 137.88, 143.53, 144.34, 155.08. ^{29}Si NMR (δ in $CDCl_3$): −25.62, −25.09. Anal. Calcd for $C_{64}H_{66}S_{12}Si_4$: C, 57.70; H, 4.99; S, 28.88; Si, 8.43. Found: C, 58.22; H, 4.95; S, 28.70; Si, 8.07.

Methyl(thien-2-yl)dimethoxysilane (14). A solution of 28.56 g (0.175 mol) of 2-bromothiophene in 200 mL of THF was added dropwise to a suspension of 4.63 g (0.19 mol) of magnesium in 30 mL of THF. The Grignard reagent was refluxed for 1 h and cooled to −78 °C, and 21.7 g (0.16 mol) of methyltrimethoxysilane was added dropwise. The reaction mixture was refluxed for 10 h, washed with anhydrous hexane, and filtered off on a G4 glass filter under argon. The product was purified by distillation (198 °C) to give of 98.9% pure (GC) thienylsilane **14** (9.85, 33%) as a colorless liquid. ^{1}H NMR (δ in $CDCl_3$, TMS/ppm): 0.40 (s, 3H), 3.58 (s, 6H), 7.22 (dd, 1H, J_1 = 3.7 Hz, J_2 = 4.9 Hz), 7.41 (d, 1H, J = 3.7 Hz), 7.66 (d, 1H, J = 4.9 Hz). ^{13}C NMR (δ in $CDCl_3$): −4.10, 50.60, 128.12, 131.61, 132.48, 135.92. ^{29}Si NMR (δ in $CDCl_3$): −17.93. Anal. Calcd for $C_7H_{12}O_2SSi$: C, 44.65; H, 6.42; S, 17.03; Si, 14.91. Found: C, 44.66; H, 6.45; S, 17.10; Si, 14.77.

Bis(5′-hexyl-2,2′-bithien-5-yl)(methyl)2-thienylsilane (15) was obtained as described for compound **12b** using 4.4 g (17.6 mmol) of 5-hexyl-2,2′-bithiophene, 10.00 mL of 1.6 M butyllithium solution in hexane (16.00 mmol), and 1.48 g (8.8 mmol) of methylthienyldimethoxysilane (**14**) to give 5.80 g of crude product, containing 71% of compound **15** (GPC). It was purified by a column chromatography on silica gel (eluent toluene−hexane, 1:5) to give pure compound **15** (3.25 g, 65%). ^{1}H NMR (δ in $CDCl_3$, TMS/ppm): 0.89 (t, 6H, J = 6.7 Hz), 0.93 (s, 3H), 1.23−1.45 (overlapped peaks, 12 H), 1.67 (m, 4H, J = 7.3 Hz), 2.78 (t, 4H, J = 7.3 Hz), 6.66 (d, 2H, J = 3.7 Hz), 7.00 (d, 2H, J = 3.7 Hz), 7.17 (d, 2H, J = 3.7 Hz), 7.22 (d, 1H, J = 3.7 Hz), 7.26 (d, 2H, J = 3.7 Hz), 7.44 (d, 1H, J = 3.7 Hz), 7.70 (d, 1H, J = 3.7 Hz). ^{13}C NMR (δ in $CDCl_3$): −0.03, 14.07, 22.56, 28.72, 30.16, 31.52, 31.55, 123.92, 124.32, 124.81, 128.38, 132.39, 133.36, 134.35, 134.65, 137.08, 137.72, 145.05, 145.89. Anal. Calcd for $C_{33}H_{40}S_5Si_1$: C, 63.41; H, 6.45; S, 25.65; Si, 4.49. Found: C, 63.21; H, 6.63; S, 25.34; Si, 4.23.

2-{5-[Methylbis(5′-hexyl-2,2′-bithienyl-5-yl)silyl]-2-thienyl}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (16). A 1.6 M solution of butyllithium (2.53 mL, 4.0 mmol) in hexane was added dropwise to a solution of compound **15** (2.53 g, 4.0 mmol) in 50 mL of THF, while the temperature was kept between −70 and −75 °C. The reaction mixture was stirred for 30 min at −75 °C, the cooling bath was then removed, and the temperature was allowed to rise to 0 °C. Then it was cooled again to −75 °C, and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.83 mL, 4.0 mmol) was added in one portion. The reaction mixture was stirred for 1 h at −78 °C, the cooling bath was removed, and stirring was continued for 3 h. After completion of the reaction, 300 mL of freshly distilled diethyl ether and 200 mL of degassed ice water containing 4 mL of 1 N HCl were added. The organic phase was separated, washed with water, and dried over sodium sulfate. The solvent was evaporated to give 2.86 g (94%) of white crystals, containing 95% of compound **16** and 5% of the initial compound **15** (GPC). The product was used in the subsequent synthesis without further purification. MALDI-MS: *m/z* 751.05 (M^+, requires 751.06). ^{1}H NMR (δ in $CDCl_3$, TMS/ppm): 0.88 (t, 6H, J = 6.7 Hz), 0.93 (s, 3H), 1.23−1.45 (overlapped peaks, 24H), 1.66 (m, 4H, J = 7.3 Hz), 2.77 (t, 4H, J = 7.3 Hz), 6.66 (d, 2H, J = 3.7 Hz), 6.99 (d, 2H, J = 3.7 Hz), 7.16 (d, 2H, J = 3.7 Hz), 7.25 (d, 2H, J = 3.7 Hz), 7.49 (d, 1H, J = 3.7 Hz), 7.72 (d, 1H, J = 3.7 Hz). ^{13}C NMR (δ in $CDCl_3$): −0.11, 14.07, 22.56, 24.76, 28.72, 30.16, 31.52, 31.55, 84.18, 123.94, 124.33, 124.80, 133.04, 134.34, 137.79, 137.95, 142.76, 145.08, 145.89.

Tris{5′-[methylbis(5′-hexyl-2,2′-bithienyl-5-yl)silyl]-2,2′-bithienyl-5-yl}methylsilane (1). Degassed solutions of compound **16** (1.08 g, 1.43 mmol) and methyltris(5-bromo-2-thienyl)silane (0.22 g, 0.42 mmol) in 20 mL of toluene and a 2 M solution of Na_2CO_3 (2.2 mL) were added to $Pd(PPh_3)_4$ (125 mg, 0.11 mmol), and the mixture was refluxed for 73 h. After completion of the reaction it was cooled to 23 °C, and 50 mL of anhydrous toluene was added. The azeotropic toluene−water mixture was distilled and the product was purified by a column chromatography on silica gel (eluent toluene−hexane, 1:3) to give pure dendrimer **1** (0.53 g, 53%). MALDI-MS: *m/z* 2161.74 (M^+, requires 2161.75). ^{1}H NMR (δ in DMSO−CCl_4, TMS/ppm): 0.86 (t, 18H, J = 7.3 Hz), 0.91 (s, 9H), 0.93 (s, 3H), 1.23−1.40 (overlapped peaks, 36 H), 1.61 (m, 12H, J = 7.3 Hz), 2.74 (t, 12H, J = 7.3 Hz), 6.68 (d, 6H, J = 3.7 Hz), 7.02 (d, 6H, J = 3.1 Hz), 7.21 (d, 6H, J = 3.7 Hz), 7.28(d, 6H, J = 3.1 Hz), 7.31(d, 3H, J = 3.1 Hz), 7.33 (d, 3H, J = 3.7 Hz), 7.38 (d, 6H, J = 3.1 Hz). ^{13}C NMR (δ in $CDCl_3$): −0.23, −0.16, 14.05, 22.55, 28.72, 30.16, 31.51, 31.54, 123.99, 124.37, 124.81, 125.72, 132.94, 134.26, 134.32, 134.77, 137.82, 137.94, 143.94, 144.16, 145.20, 145.93. ^{29}Si NMR (δ in $CDCl_3$): −25.24, −25.05. Anal. Calcd for $C_{112}H_{126}S_{18}Si_4$: C, 62.23; H, 5.88; S, 26.70; Si, 5.20. Found: C, 62.37; H, 5.85; S, 26.18; Si, 5.32.

5,5′-Bis(trimethylsilyl)-2,2′-bithiophene (7). A solution of 3.06 mmol of butyllithium in 1.9 mL of hexane (1.6 M solution) was added to a solution of 2,2′-bithiophene (0.5 g, 3.06 mmol) in 20 mL of THF, and the temperature was kept between −15 and −5 °C. The cooling bath was then removed, and the temperature was allowed to rise to 0 °C. Then it was cooled again to −17 °C, 0.4 mL (3.1 mmol) of trimethylchlorosilane was added. Then again a solution of 3.06 mmol of butyllithium in 1.9 mL of hexane (1.6 M solution) was added to the reaction mixture, the cooling bath was removed, and the temperature was allowed to rise to +15 °C. Then it was cooled again to −17 °C, and 0.4 mL (3.1 mmol) of trimethylchlorosilane was added. The cooling bath was then removed, and the solution was stirred at room temperature for 1 h. The reaction mixture was poured into 50 mL of water and 100 mL of diethyl ether. The organic layer was washed with water and dried with sodium sulfate. The solvent was evaporated under vacuum and the residue was dried at 1 Torr to give 0.96 g of crude product, containing 88% of compound **7** (GPC). It was purified by column chromatography on silica gel (eluent toluene−hexane, 1:7) to give pure compound **7** (0.62 g, 62%). ^{1}H NMR (δ in $CDCl_3$, TMS/ppm): 0.32 (s, 18H), 7.11 (d, 2H, J = 3.7 Hz), 7.21 (d, 2H, J = 3.7). Anal. Calcd for $C_{14}H_{22}S_2Si_2$: C, 54.13; H, 7.14; S, 20.64; Si, 18.08. Found: C, 54.85; H, 7.86; S, 20.07; Si, 17.44.

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Supporting Information Available: ^{13}C and ^{29}Si NMR spectra of dendrimers **1**−**3** (Figures S1-S6). This material is available free of charge via the Internet at http://pubs.acs.org.

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