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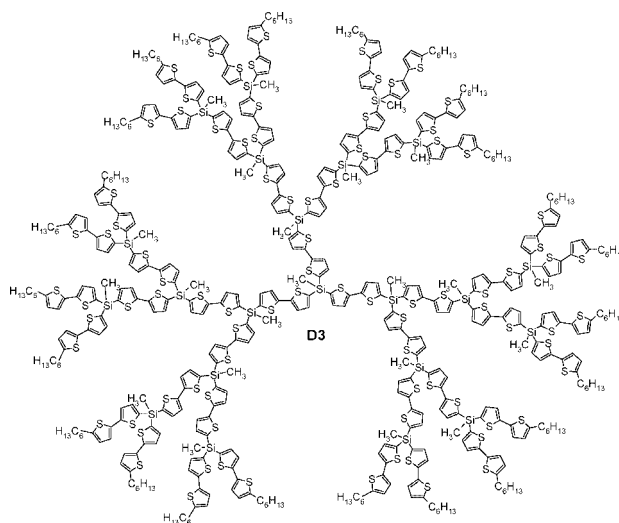
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ABSTRACT



Three generations of bithiophenesilane monodendrons and dendrimers consisting of 3–45 2,2'-bithiene-5,5'-diyl units were synthesized by means of effective coupling reactions between the corresponding bithienyllithium derivatives and chlorosilanes. These compounds show efficient photoluminescence in the violet-blue region, the quantum yield of which is 5–15 times higher than that for the parent bithiophene or bithiophenesilanes.

During the past few years, the number of luminescent dendrimers has increased rapidly.¹ These compounds are currently attracting the interest of researchers because of their unusual chemical and physical properties, as well as the wide range of

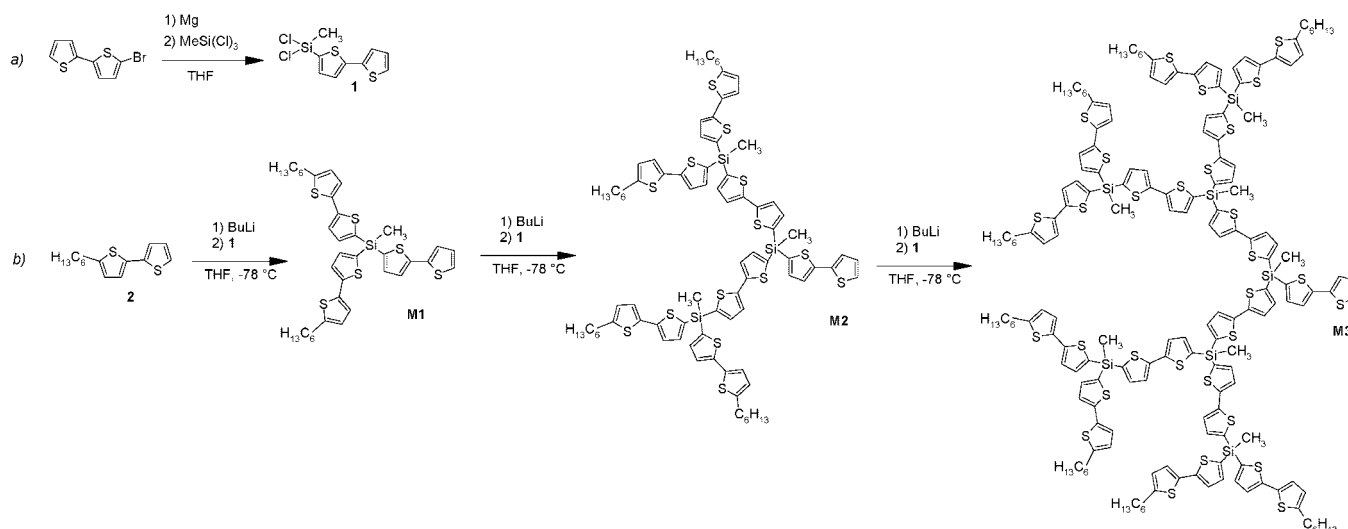
potential applications for a new generation of optical and electrical devices: organic light emitting diodes (OLEDs), solar cells, lasers, sensors, etc.² Among luminescent dendritic macromolecules, the thiophene-containing dendrimers are promising materials, due to the unique properties of oligothiophenes and their derivatives, such as high charge carrier mobility,³ efficient

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Scheme 1. Synthesis of Methyl(2,2'-bithien-5-yl)dichlorosilane **1** (a) and Bithiophenesilane Monodendrons of Generations 1–3 (b)



fluorescence,⁴ excellent stability in ambient conditions (even at elevated temperatures),⁵ and easy functionalization.⁶ Thiophene-containing 2D and 3D star-shaped⁷ and dendritic macromolecules have been utilized as functional materials in organic photovoltaics (OPVs),⁸ organic thin film transistors (OTFTs),⁹ and organic light-emitting diodes (OLEDs).¹⁰ Recently, a number of dendrimers of the first generation containing bithiophene units linked directly to silicon atoms have been reported.¹¹ They showed efficient photoluminescence in the violet-blue region and quantum yields of which are significantly higher than those measured for linear or branched bithiophenesilanes. We report herein the synthesis of a number of bithiophenesilane monodendrons and dendrimers from the first to the third generations by means of effective coupling between the bithienyllithium derivatives and chlorosilanes (Schemes 1 and 2). A similar approach to Si–thiophene bond formation was reported by Lucevic (et al.) in 1981. Namely, tetrathienyllsilane, which can be considered as a branching core or a zero generation dendrimer, was prepared by reactions of 2-thienyllithium or 2-thienylmagnesium bromide with tetrachlorosilane or tetraethoxysilane.¹² Later, Nakayama et al. reported the synthesis of the first generation of the organosilicon dendrimer, containing 16 thiophene rings, starting from a polythium

precursor.¹³ However, these synthetic techniques have led to low yields of the products and did not allow obtaining higher generations of the dendrimers because of nonoptimal reaction conditions or insolubility of polythienyllithium derivatives used.

Our strategy for the preparation of functional bithienyllsilane precursors and monodendrons is outlined in Scheme 1. The key compound for the monodendrion synthesis, namely, methyl-2,2'-bithien-5-yl-dichlorosilane (**1**), was obtained by the dropwise addition of 2,2'-bithien-5-yl-magnesium bromide to a 10-fold excess of methyltrichlorosilane in THF, with the isolated yield of 70%. The coupling reaction of the lithium derivative of 5-hexyl-2,2'-bithiophene with compound **1** generated monodendrion **M1** in 98% reaction yield (according to GPC) after stirring at –78 °C for 30 min. The second and third generations of the monodendrons were obtained by a similar reiterative procedure of the monolithiation of corresponding monodendrons **M1** and **M2**, followed by coupling with compound **1**. The reaction yields for **M2** and **M3** were also very good (90% and 70%, respectively). It is noteworthy that each of the monodendrons obtained has an active 5-thienyl proton, which allows their further modifications.

Dendrimers **D1–D3** (see Scheme 2) were prepared by a similar technique using lithiation of the corresponding monodendrons followed by their coupling with methyltrichlorosilane at –78 °C. The reaction yields for **D1**, **D2**, and **D3** decreased with increasing generation number and were found to be 87, 67, and 25%, respectively. It is interesting to note that all the coupling reactions between the bithienyllithium derivatives and the chlorosilanes were carried out without any excess of the

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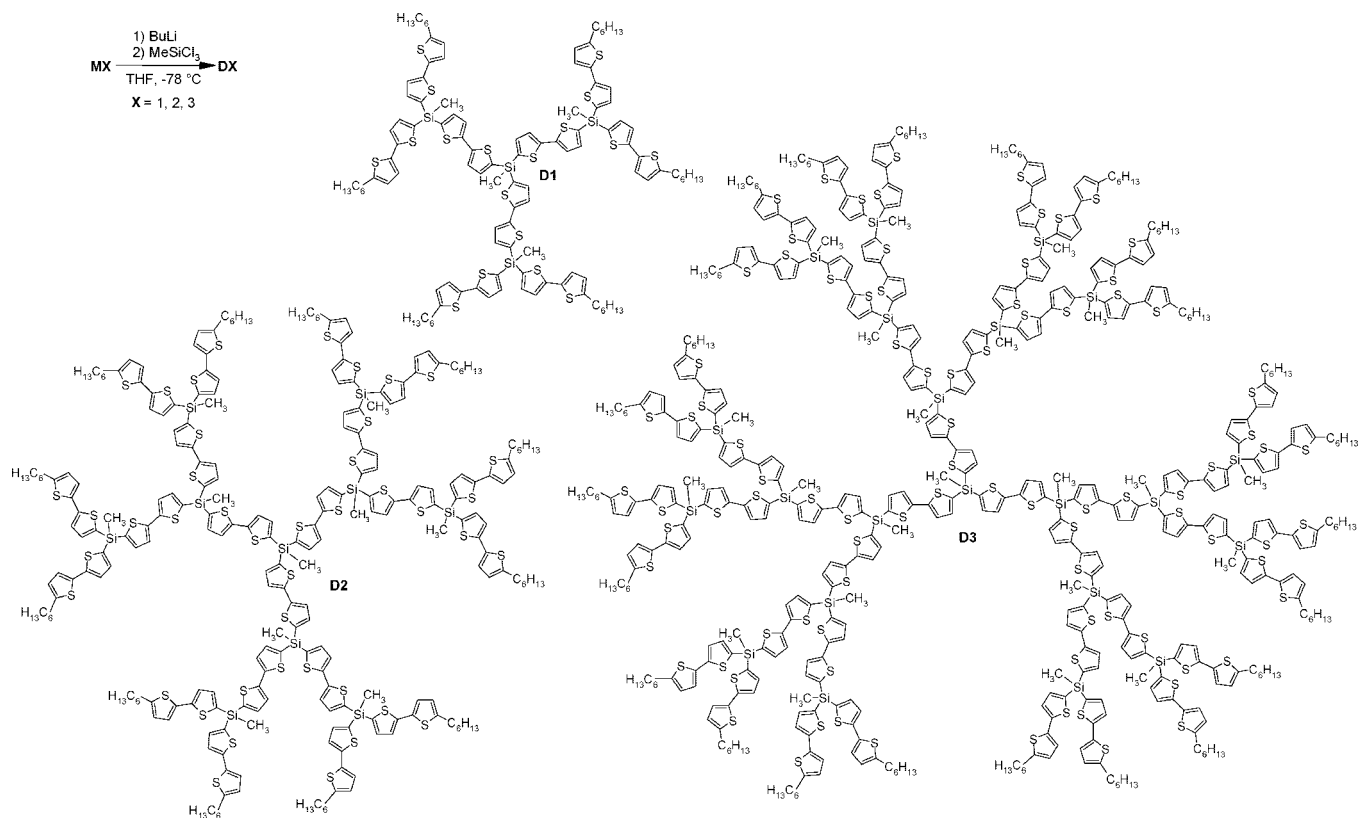
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Scheme 2. Synthesis and Structural Formulas of Bithiophenesilane Dendrimers of Generations 1–3



corresponding lithiated monodendron, with good yields and high rates even at low temperatures. The low reaction yield in the case of **D3** can be explained by both steric difficulties and low concentration of the focal functionality in monodendron **M3**. All bithiophenesilane monodendrons and dendrimers obtained were easily separated from the main byproducts (undersubstituted compounds) by classical column chromatography. All these macromolecules are highly soluble at room temperature in common organic solvents such as chloroform, THF, toluene, chlorobenzene, etc., and display good film forming properties. All new compounds synthesized were characterized by ^1H , ^{13}C , and ^{29}Si NMR spectra, elemental analysis, MALDI-TOF mass spectroscopy, and GPC, equipped with RI, RALS, and LALS detectors (see Supporting Information). However, it should be noted that MALDI-TOF analysis failed for **M3**, **G2**, and **G3**, due to the easy fragmentation of silicon-containing dendrimers at high generations.¹⁴ To our knowledge, there is no literature data of successful MALDI-TOF analysis for silicon-containing molecules with high molecular weights. The molecular weights measured by the light scattering technique are in good agreement with the calculated values (Table 1).

Thus, there are several advantages of this new approach of the synthesis of bithiophenesilane dendrimers as compared to the methodology based on Suzuki or Kumada reactions,¹¹ such as the absence of expensive Pd catalysts, faster reaction rates and higher yields of the product, and their easy purification and

possibility to obtain higher generations of dendrimers. It is noteworthy that this approach is quite universal and can be used for the synthesis of different soluble arylsilane dendrimers.

The optical properties of the model compounds,¹⁵ monodendrons, and dendrimers obtained were investigated by UV–vis spectroscopy in their dilute solutions. The results are summarized in Table 1. The absorption spectra of the monodendrons and dendrimers of all three generations are quite similar: all of them are slightly broadened and red-shifted with respect to the model 5-hexyl-2,2'-bithiophene due to the influence of the silicon atom to a π system of the bithiophenes. It is noteworthy that attachment of the methylsilyl group to 5-hexyl-2,2'-bithiophene leads to an increase of the molar extinction coefficient (ϵ) from 13 000 to 19 000 $\text{M}^{-1}\text{cm}^{-1}$. A monotonic increase in the ϵ of the monodendrons and the dendrimers was observed as the number of bithiophene units in the macromolecule was increased. The highest value of $\epsilon = 870\,000\, \text{M}^{-1}\text{cm}^{-1}$ was obtained for dendrimer **D3** having 45 bithiophene units and a molecular weight of 10 383. This value is more than twice as high as compared to ϵ obtained for the fourth generation of the oligothiophene dendrimer having comparable molecular weight of 8239.^{8b}

In view of emission spectra, all of the monodendrons **M1–M3** and dendrimers **D1–D3** exhibit apparently identical violet-blue light emissions with two maxima at 373 and 390

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Table 1. Optical Properties of Dilute Solutions of the Monodendrons, Dendrimers, and Model Compounds

compound	Mw ^c	M _{LS} ^d	number of 2T units	absorption λ_{\max}^b [nm]	molar extinction coefficient ϵ [M ⁻¹ cm ⁻¹]	luminescence $\lambda_{\max}^{b,e}$ [nm]	luminescence quantum yield, ^{b,e,f} Q [%]
Hex-2T	250	—	1	308	13000	374	1.8
Hex-2T-Si(CH ₃) ₃ ^a	323	—	1	320	19000	380	5.8
(CH ₃) ₃ Si-2T-Si(CH ₃) ₃ ^b	327	—	1	322	20000	381	6.0
M1	707	830	3	333	58100	372/386	19
M2	1621	1800	7	333	142800	373/390	27
M3	3448	3700	15	333	354000	373/390	29
D1	2162	2250	9	333	174000	374/388	30
D2	4902	5150	21	334	420000	375/390	31
D3	10383	11800	45	336	870000	376/390	30

^a Data from ref. ^b Measured in THF. ^c Calculated from the molecular formula. ^d Measured by GPC using a dual light scattering detector. ^e Excited at the absorption maxima. ^f Using POPOP ($\Phi = 0.98$) as a standard.

nm. This is 15 nm red-shifted compared to the emission of the parent 5-hexyl-2,2'-bithiophene. The luminescence quantum yield Q reaches 30% for all the generations of the dendrimers under consideration, which is 5–15 times higher than that for the parent bithiophene or bithiophenesilanes. To the best of our knowledge, it is unique that the luminescence efficiency of the dendrimers significantly exceeds Q of its constituent chromophores and does not depend on the generation number. The reasons for this behavior can be explained by favorable changes of the energy levels of the chromophores caused by both the inductive effect of Si and the influence of a local field of the adjacent 2T units, arranged into star-shaped structures within the dendritic molecule. As a result, probability of a nonradiative conversion ($S_1 \rightarrow S_0$ and $S_1 \rightarrow T_1 \rightarrow S_0$) is decreased. After reaching the size of **D1** (that is about 2 nm), the structure of the local environment of the internal 2T units does not change (see Supporting Information for more details). Similar effects of leveling off the enhancements of the optical properties (in this case, two-photon absorption) on the first generation were found for triarylamine dendrimers.¹⁶ It was explained by the fact that the size of the spectroscopic unit (coherent domain) is comparable with the size of G1.

In summary, the syntheses of the bithiophenesilane monodendrons and dendrimers through effective coupling between bithienyllithium derivatives and chlorosilanes were designed and successfully carried out. In comparison to the known synthetic routes through Suzuki or Kumada reactions, significantly faster rates and higher yields of the reactions were achieved. Furthermore, the new synthetic route allows higher generations of dendrimers to be obtained and does not require the use of the expensive palladium catalyst. Dilute solutions of the compounds obtained show the efficient photoluminescence in the violet-blue region with quantum yields around 30%. That is 15 times higher as compared to the parent 2,2'-bithiophene and does not depend on the generation number or molecular symmetry. Apart

from the luminescent properties, these monodendrons and dendrimers are interesting molecular objects being carbosilane dendrimers with rigid aromatic spacers between the branching points. Comparison of their thermal, hydrodynamic, and other molecular properties with those of “flexible” polyallylcarbosi-lane dendrimers as well as characteristics of organic photonic and electronic devices made from these bithiophenesilane dendrimers will be the focus of our further publications.

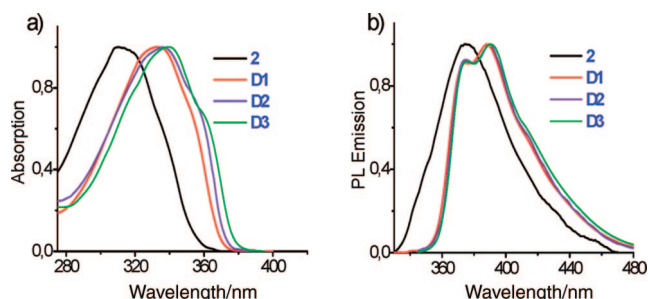


Figure 1. Normalized absorption (a) and luminescence spectra (b) of bithiophenesilane dendrimers **D1**–**D3** and parent compound **2** (measured as dilute solutions in THF).

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Supporting Information Available: Experimental details, synthetic procedures, GPC, ¹H, ¹³C, and ²⁹Si NMR spectra of all the new compounds obtained, and discussion of the optical data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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