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Bithiophenesilane-Based Dendronized Polymers: Facile Synthesis and Properties of Novel Highly Branched Organosilicon Macromolecular Structures

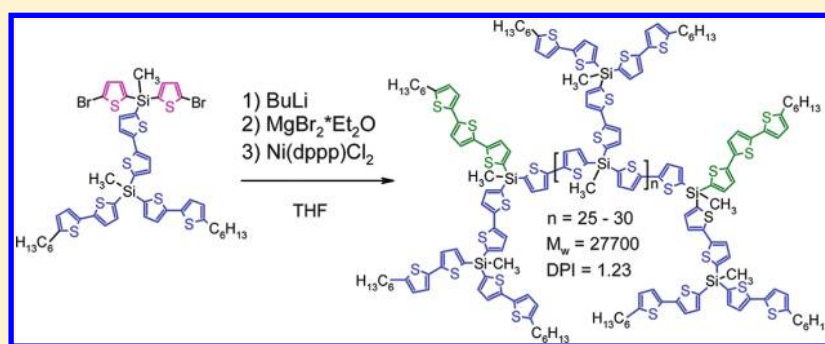
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S Supporting Information



ABSTRACT: The synthesis of two novel bithiophenesilane-based dendronized polymers by a chain growth Kumada polymerization, their molecular properties in dilute solutions and thermal properties in the bulk are described and compared with those of bithiophenesilane dendrimers. GPC equipped with a dual light scattering detector has shown that the polymers exhibit narrow polydispersity indices (PDI = 1.22–1.23) and have a weight-average polymerization degree of 44 for **P1** and 30 for **P2**, which correspond to 88 and 120 bithiophenesilane fragments, respectively. Spectral-luminescent investigations showed that both polymers among with the bithiophenesilanes contain from 1 to 4 terthiophenesilane fragments in every macromolecule, which leads to the so-called “dendritic molecular antenna” effect. The intramolecular energy transfer efficiency was measured to be 50 and 70% for polymers **P1** and **P2** respectively, which, alongside with the results of viscometric studies, points out to the compact conformation of these macromolecules in solution, which is close to those of bithiophenesilane dendrimers.

INTRODUCTION

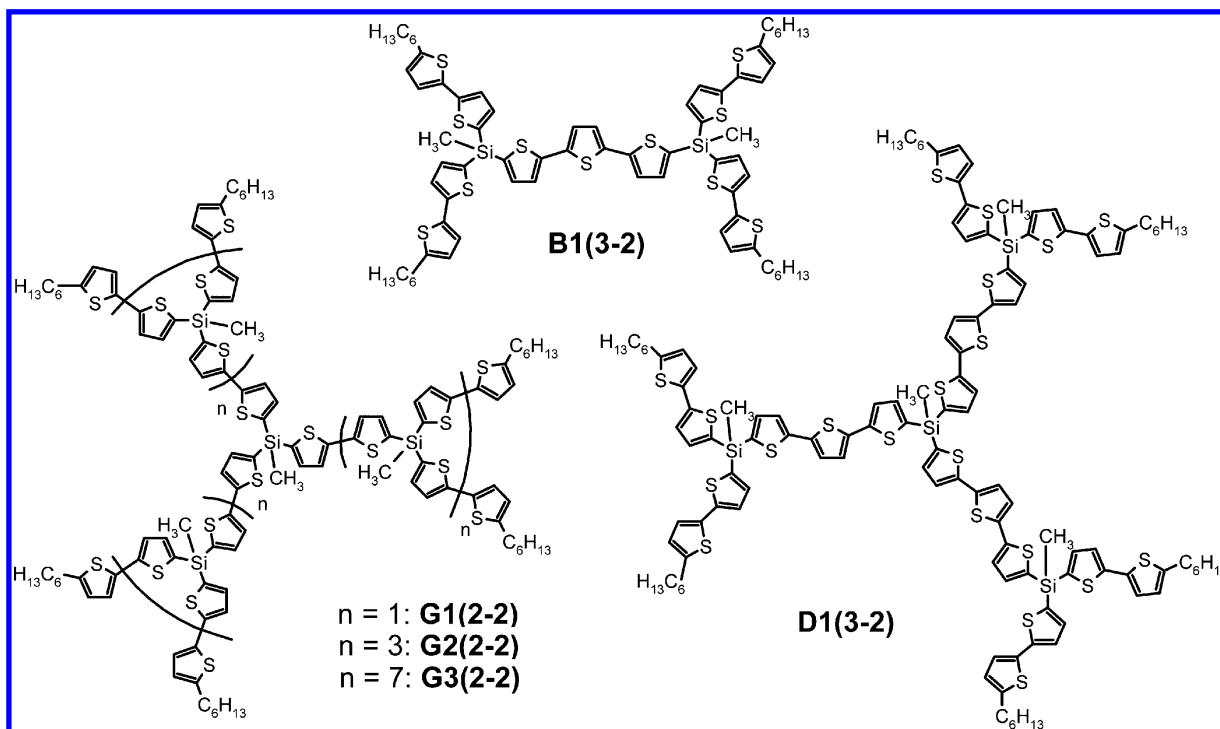
Macromolecules consisting of oligothiophenesilane repeating units are of significant interest to researchers from the point of view of their applications as functional materials in organic electronics and photonics.^{1,2} Exhibiting good luminescent^{3,4} and semiconducting properties,^{5,6} they can be used as precursors in the preparation of conducting polymers,⁷ as functional materials for emitting layer in polymer light emitting diodes⁸ or as perspective donor materials for organic photovoltaic cells (solar cells).^{9–11} Among them, bithiophenesilane systems exhibit a good fluorescence quantum yield Q_F , which is significantly higher than that of the bithiophene luminophore itself¹² and depends on the degree of branching of the molecule.¹³ It was also shown that similar star-like molecules show Q_F significantly higher than that of the corresponding linear polymer, poly[(tetraethyldisilanylene)-bithiophene].¹⁴ Recently, a family of bithiophenesilane dendrimers (**Gn**(2–2) in Scheme 1) with efficient photoluminescence in the violet-blue spectrum range was

reported.^{15–17} In the case of organosilicon dendritic molecules, consisting of bi- and terthiophenesilane fragments (**D1**(3–2) and **B1**(3–2) in Scheme 1), the “molecular antenna” effect was observed.¹⁸ It was shown that this effect results from the existence of the efficient inductive-resonant transfer of the energy of electronic excitation from bithiophenesilane (donor) to terthiophenesilane (acceptor) fragments of the macromolecule.¹⁹ A similar effect was observed also in some other bithiophenesilane-containing dendrimers.^{20,21} Such properties of oligothiophenesilane systems are related, on the one hand, to the presence of σ – π conjugation between an oligothiophene fragment and a silicon atom directly linked to it, and to the absence of conjugation between the neighboring oligothiophene fragments, separated by the silicon atom, on the other hand. It makes them different from fully conjugated hyper-

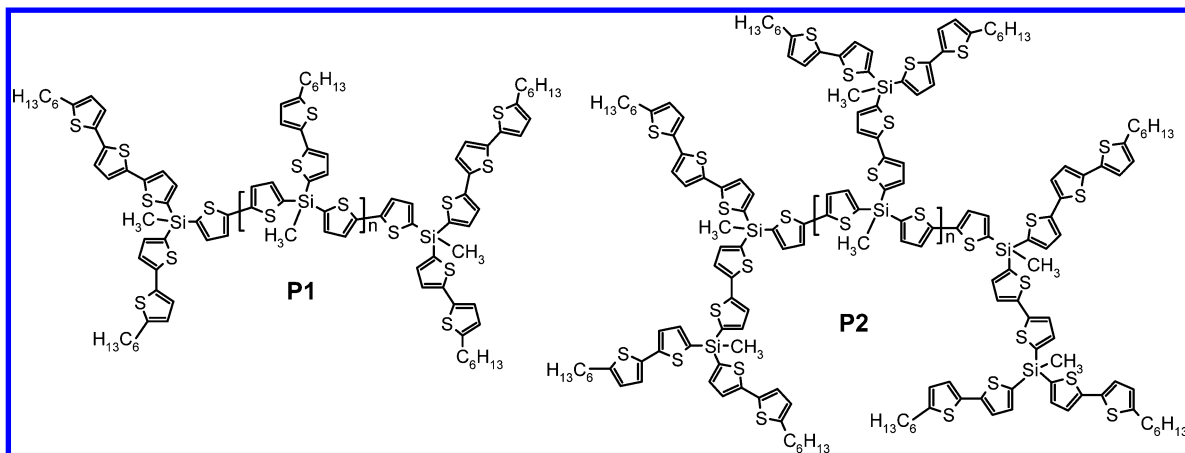
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Scheme 1. Structural Formulas of Bithiophenesilane-Containing Dendrimers.^{17,18}

Scheme 2. General Structural Formulas of Bithiophenesilane-Containing Dendronized Polymers P1 and P2



branched 2,3,5-polythiophenes²² and polythiophene dendrimers^{23,24} consisting of 2-, 3-, and 5-linked thiophene rings. The latter have a wide absorption spectrum in the vis spectrum range, which allows to use them as donor materials in organic solar cell.²⁵

Dendronized polymers feature hybrid structures of both classical polymeric systems and dendrimers.^{26,27} They are promising for applications in various areas, such as biological²⁸ and medical²⁹ sciences, catalysis in polymer chemistry³⁰ and others. An increased interest to such 3D macromolecules based on conjugated structures is governed by the perspectives of their utilization in optoelectronics, where they could serve as efficient light emitting materials.³¹ However, most of the dendronized polymers reported before have a conjugated backbone and isolating dendritic wedges.^{32–35} In this sense, the synthesis of dendronized polymers containing oligothiophene fragments linked to each other via silicon atoms both in the backbone and in the wedges (Scheme 2) looks intriguing. That

is why the purpose of the present work was the elaboration of an efficient scheme of the synthesis of such systems and studying the influence of their specific molecular structure on the physical properties in comparison to bithiophenesilane-containing dendrimers obtained before.^{17,18}

EXPERIMENTAL PART

Materials. *n*-Butyl lithium (1.6 M solution in hexane), 1,2-dibromoethane, magnesium, 1,3-bis(diphenylphosphino)propanenickel(II) chloride Ni(dppp)Cl₂ (Acros Organics), were used as received without additional purification. THF, diethyl ether, toluene, and hexane were dried and purified according to the known techniques and then used as solvents. 5-hexyl-2,2'-bithiophene was prepared according to the technique described earlier.³⁶ The first generation of bithiophenesilane monodendron 2,2'-bithiophen-5-yl-[bis(5'-hexyl-2,2'-bithiophen-5-yl)]methylsilane (**6**) was synthesized according the method described before.¹⁷ The solvents were evaporated in vacuum under a pressure of up to 1 Torr at 40 °C.

GPC analysis was performed by means of a Shimadzu LC10A^{VP} series chromatograph (Japan) equipped with an RID-10A^{VP} refractometer and SPD-M10A^{VP} diode matrix as detectors and a Phenomenex column (USA) with a size of $7.8 \times 300 \text{ mm}^2$ filled with the Phenogel sorbent with a pour size of 500 Å; THF was used as the eluent.

Light scattering experiments were performed on Shimadzu HPLC System, equipped with DGU14U degasser unit, LC-10AD pump, CTO-10A column oven with a Phenomenex column (USA) with a size of $7.8 \times 300 \text{ mm}^2$ filled with the Phenogel sorbent with a pour size of 10^3 Å , RID-10A refractometer, Viscotek 270 Dual detector (RALS and LALS) and Omniscan 4.5 Software. The sample loop was 100 μL , angle RALS 90° , angle LALS 7° . The system was calibrated using polystyrene standard with $M_w = 10050$, $dn/dc = 0.185$ (Polymer Laboratories). The molar weight of the standard was chosen in the range of M_w of the samples under investigation for better accuracy of the measurements. Using the exact concentrations of the samples, close to 5.00 mg/mL, the values of dn/dc were determined from RI data, which were found to be 0.24 for both polymer samples investigated. Then this value was used by Omniscan 4.5 software to calculate the real M_w from the light scattering (RALS and LALS) data.

For thin layer chromatography, "Sorbfil" (Russia) plates were used. In the case of column chromatography, silica gel 60 ("Meck") was taken.

^1H NMR spectra were recorded at a "Bruker WP-250 SY" spectrometer, working at a frequency of 250.13 MHz and utilising the DMSO- d_6 signal (2.45 ppm) as the internal standard. ^{13}C and ^{29}Si NMR spectra were recorded using a "Bruker Avance II 300" spectrometer at 75 and 60 MHz, respectively. In the case of ^1H NMR spectroscopy, the compounds to be analyzed were taken in the form of 1% solutions in CCl_4 -DMSO- d_6 mixture. In the case of ^{13}C and ^{29}Si NMR spectroscopy, the compounds to be analyzed were taken in the form of 5% solutions in CDCl_3 . The spectra were then processed on the computer using the ACD Laboratories software.

Mass-spectrometry measurements were performed on the Micro-mass M@ldi MALDI-TOF MS instrument operating in the reflection mode. To prepare the samples separate solutions of the starting material and matrix in THF with concentrations of 1 mg/mL and a solution of salt (silver triflate) in deionized water at a concentration of 1 mg/mL were mixed and applied to a steel target (at $\sim 2 \text{ uL}$) to dry, volume ratio of 1:1:1. 2,5-dihydrobenzoic acid, 2-(4-hydroxyphenylazo)benzoic acid, and 3-indolacrylic acid were used as the matrix substance. The standard laser operating frequency was 10 Hz. Standard spectra were regularly obtained by combining approximately 100 single laser shot spectra.

Elemental analysis of C, H elements was carried out using CHN automatic analyzer CE1106 (Italy). Experimental error is 0.30–0.50%. Analysis of Br element was carried by visual titration technique using $\text{Hg}(\text{NO}_3)_2$ and diphenylcarbazone as indicator. The burning was done in the Sheninger flask using alkaline solution of hydrogen peroxide as an absorbent. Experimental error is 0.30–0.50%. Spectrophotometry technique was used for the Si analysis as described in ref 37.

The absorption and luminescence spectra were recorded over a range of 250–600 nm in dilute solutions in THF (UV-grade) with a concentration of 10^{-5} – 10^{-6} M in order to avoid self-absorption. The luminescence measurements were performed on an ALS01 M multifunctional absorption-luminescence spectrometer, the detailed description of which can be found elsewhere.¹³ The absorption spectra were recorded on a Shimadzu UV-2501PC spectrophotometer (Japan). Unless stated otherwise, all reactions were carried out under argon atmosphere using water-free solvents. The intrinsic viscosity of solutions was measured in THF at $25.0 \pm 0.1^\circ\text{C}$ on an Ubbelohde viscometer with a capillary diameter of 0.3 mm using Schott AVS 370 System having a laser automatic level detection.

For the DSC measurements, the glass transition temperatures were obtained at a heating rate of 10°C in argon atmosphere in a Mettler DSC-822e differential scanning calorimeter. TGA was performed on the "Derivatograph-C" (MOM, Hungary) in air and argon at a heating rate of $5^\circ\text{C}/\text{min}$ on samples of about 10 mg by weight.

Synthesis. (5-Bromothiophene-2-yl)lithium (2). A solution of 3.09 g (12.8 mmol) 2,5-dibromothiophene (1) in 20 mL THF was cooled down to -78°C , after which 8.0 mL (12.8 mol) of a solution of 1.6 M *n*-butyllithium in hexane was added slowly dropwise to it followed by stirring during 1 h at that temperature. The obtained solution of compound 2 was used immediately in the following stage of synthesis without isolation or purification of the product.

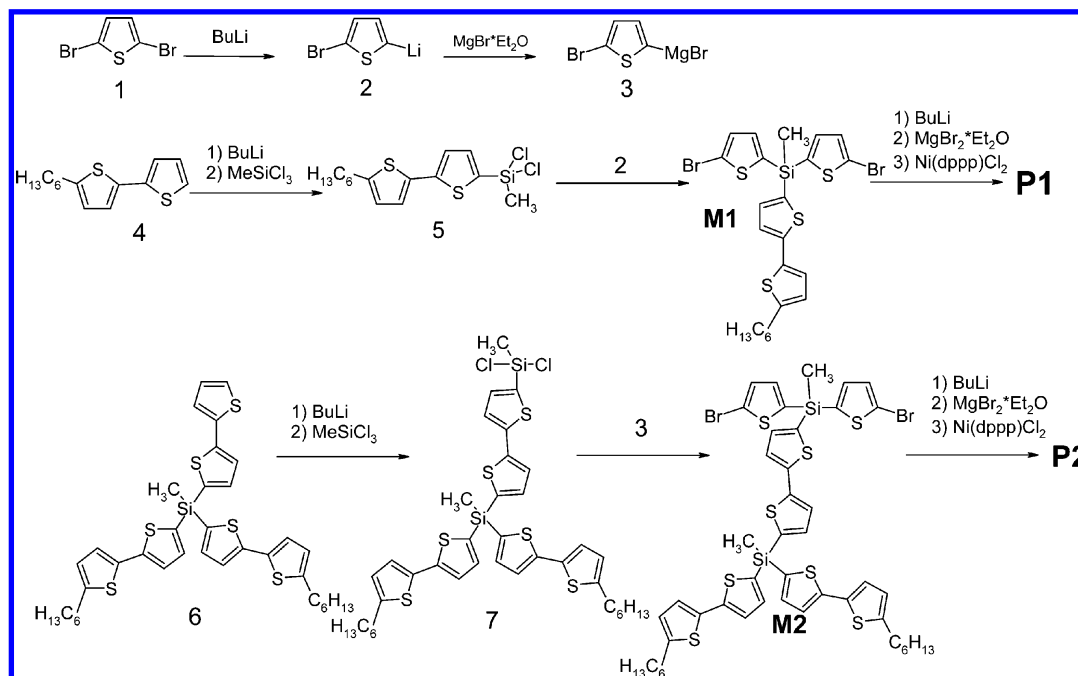
(5-Bromothiophene-2-yl)magnesium Bromide (3). 4.7 mL (8 mmol) of a solution of 1.6 M *n*-butyllithium in hexane was added slowly dropwise to a solution of 1.81 g (8 mmol) of 2,5-dibromothiophene in 50 mL of THF previously cooled down to -78°C . The reaction mixture was then stirred for 1 h at that temperature. After that 0.01 mol of an ether complex of magnesium bromide (prepared *in situ* by the Grignard reaction from 1,2-dibromoethane and magnesium in ether) was added and the reaction mixture was stirred for additional 2 h. The obtained solution of compound 3 was used in the following stage of synthesis without isolation or purification of the product.

Dichloro(5'-hexyl-2,2'-bithiophene-5-yl)methylsilane (5). A solution of 1.6 g (6.4 mmol) of 5-hexyl-2,2'-bithiophene (4) in 45 mL of THF was cooled down to -78°C followed by the slow dropwise addition to it of 4.0 mL (6.4 mmol) of a solution of 1.6 M *n*-butyllithium in hexane. The reaction mixture was stirred for 1 h at -78°C . In a separate flask a solution of 11.2 mL (96 mmol) of methyltrichlorosilane in 15 mL of THF was cooled down to -78°C , after which the previously obtained lithium derivative of compound 4 was added to it slowly dropwise. When the whole amount of it was added, the cooling bath was removed and the temperature of the reaction mixture was allowed to rise to 20°C . An excess of methyltrichlorosilane was then distilled with toluene, and the solution of freshly synthesized compound 5 in toluene was used in the following stage of synthesis without isolation or purification of the product.

Bis(5-bromo-2-thienyl)(5'-hexyl-2,2'-bithiophen-5-yl)-methylsilane (M1). A solution of freshly prepared compound 5 in toluene was added dropwise to a freshly prepared solution of compound 2 (from 3.09 g (12.8 mmol) of 2,5-dibromothiophene and 8.0 mL (12.8 mmol) of solution of 1.6 M *n*-butyllithium and 20 mL of THF) in a THF-hexane mixture at -78°C . After the completion of the reaction the reacting mixture was poured into 100 mL of water and 300 mL of diethyl ether. The organic layer was then separated, rinsed with water to pH = 7, dried over anhydrous Na_2SO_4 , which was followed by evaporation of the solvent in a vacuum rotary evaporator. The reaction yield of the raw product was found to be 77% (according to GPC). It was purified by column chromatography on silica gel using a mixture of hexane-toluene (v/v 5:1) as the eluent, to yield 2.06 g (52%) of the pure compound M1 as a light-yellow viscous liquid. ^1H NMR (DMSO- d_6 / CCl_4): 0.88 (t, 3H, $\text{CH}_3\text{-CH}_2\text{-}$, $J = 6.7 \text{ Hz}$), 0.89 (s, 3H, $\text{CH}_3\text{-Si}$), 1.25–1.40 (overlapping peaks, 6H, $\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$ and $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-}$), 1.63 (m, 2H, $\text{-CH}_2\text{-CH}_2\text{-T}$, $J = 7.3 \text{ Hz}$), 2.77 (t, 2H, $\text{-CH}_2\text{-T}$, $J = 7.3 \text{ Hz}$), 6.70 (d, 1H, $J = 3.7 \text{ Hz}$), 7.04 (d, 1H, $J = 3.7 \text{ Hz}$), 7.20 (d, 2H, $J = 3.7 \text{ Hz}$), 7.22–7.26 (overlapping peaks, 3H), 7.28 (d, 1H, $J = 3.7 \text{ Hz}$). ^{13}C NMR (75 MHz, CDCl_3 , δ , ppm): -0.47, 14.07, 22.55, 28.71, 30.15, 31.51, 31.54, 119.38, 124.15, 124.38, 124.88, 131.56, 134.02, 137.28, 137.54, 138.07, 145.61, 146.23. ^{29}Si NMR (60 MHz, CDCl_3 , δ , ppm): -25.78. MALDI MS m/z 724.26 ($\text{M} + \text{Ag}^+$), calculated 724.79. Anal. Calcd for $\text{C}_{23}\text{H}_{24}\text{Br}_2\text{S}_4\text{Si}$: C 44.80; H 3.92; Br 25.92; S 20.80; Si 4.55. Found: C, 44.97; H, 3.95; Br, 25.83; S, 20.75; Si, 4.50.

{5'-[bis-(5'-hexyl-2,2'-bithiophene-5-yl)(methyl)silyl]-2,2'-bithiophene-5-yl}(dichloro)methylsilane (7). First, 2.3 g (3.3 mmol) of 2,2'-bithiophen-5-yl-[bis(5'-hexyl-2,2'-bithiophen-5-yl)]methylsilane (6) in 65 mL of THF was cooled down to -78°C followed by the slow addition to it of 2.0 mL (3.3 mmol) of a solution of *n*-butyllithium in hexane, after which the reaction mixture was stirred during 1 h at -78°C . In a separate flask, a solution of 6.5 mL (82 mmol) of methyltrichlorosilane in 20 mL of THF was cooled down to -78°C , after which the previously obtained lithium-derivative of compound 6 was added to it slowly dropwise. When the full amount was added, the cooling bath was removed and the temperature slowly rose to 20°C ,

Scheme 3. Synthesis of Monomers M1 and M2 and Their Polymerization



after which an excess of methyltrichlorosilane was distilled with toluene. The obtained solution of compound 7 in toluene was used in the following stage of synthesis without isolation or purification of the product.

A (via organolithium derivative 2): A solution of compound 2 in a THF-hexane mixture (freshly obtained from 1.78 g (7.4 mmol) of 2,5-dibromothiophene, 45 mL of THF, and 4.6 mL (7.4 mmol) of a solution of 1.6 M *n*-butyllithium in hexane) was added to a solution of freshly prepared solution of compound 7 in toluene. After standard extraction described in the procedure of the synthesis of **M1**, the reaction yield of the product was 44% (according to GPC). It was purified by column chromatography on silica gel using a mixture of hexane–toluene (v/v 5:1) as the eluent, to yield 0.59 g (15%) of the pure product as a yellowish highly viscous liquid. ^1H NMR ($\text{DMSO}-d_6/\text{CCl}_4$, δ , ppm): 0.88 (t, 6H, $\text{CH}_3\text{--CH}_2\text{--}$, $J = 6.7$ Hz), 0.89 (s, 3H, $\text{CH}_3\text{--Si}(\text{T--Br})_2$), 0.93 (s, 3H, $\text{CH}_3\text{--Si}$), 1.24–1.38 (overlapping peaks, 12H, $\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--}$ and $\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--}$), 1.63 (m, 4H, $\text{--CH}_2\text{--CH}_2\text{--T}$, $J = 7.3$ Hz), 2.76 (t, 4H, $\text{--CH}_2\text{--T}$, $J = 7.3$ Hz), 6.69 (d, 2H, $J = 3.7$ Hz), 7.04 (d, 2H, $J = 3.7$ Hz), 7.20 (d, 3H, $J = 3.7$ Hz), 7.22–7.25 (overlapping peaks, 3H), 7.27–7.31 (overlapping peaks, 2H), 7.33 (d, 2H, $J = 4.3$), 7.39 (d, 2H, $J = 3.7$ Hz). ^{13}C NMR (CDCl_3 , δ , ppm): -0.51 , -0.22 , 14.08, 22.56, 28.71, 30.15, 31.52, 31.54, 119.45, 123.99, 124.35, 124.84, 125.67, 125.80, 131.58, 132.78, 133.07, 134.26, 135.08, 137.05, 137.60, 137.83, 137.85, 138.11, 143.64, 144.50, 145.22, 145.99. ^{29}Si NMR (CDCl_3 , δ , ppm): -25.70 , -25.39 . Anal. Calcd for $\text{C}_{46}\text{H}_{48}\text{Br}_2\text{S}_8\text{Si}_2$: C, 51.47; H, 4.51; Br, 14.89; S, 23.90; Si, 5.23. Found: C, 51.22; H, 4.61; Br, 14.92; S, 24.11; Si, 5.11. MALDI MS: m/z , 1180.98 ($\text{M} + \text{Ag}$) $^+$; calculated, 1180.85.

B (via organomagnesium derivative 3). A solution of freshly prepared compound 7 in toluene was added quickly dropwise to a solution of compound 3 (freshly prepared from 1.85 g (7.6 mmol) of 2,5-dibromothiophene, 50 mL of THF, 4.7 mL (7.6 mmol) of 1.6 M *n*-butyllithium, and 10 mmol of an ether complex of magnesium bromide). After standard extraction described in the procedure of the synthesis of **M1**, the reaction yield of the product was 64% (according to GPC). It was purified by column chromatography on silica gel using a mixture of hexane–toluene (v/v 5:1) as the eluent, to yield 1.25 g (35%) of the pure product, which was fully identical to compound **M2**, obtained via organolithium derivative 2.

Poly[5'-(5'-hexyl-2,2'-bithiophen-5-yl)(methyl)silyl]-2,2'-bithiophene-5,5'-diylsilane] (P1). A solution of 0.45 g (0.7 mmol) of compound **M1** in 15 mL of THF was cooled down to -78°C , then a solution of 0.45 mL (0.7 mmol) of 1.6 M *n*-butyllithium in hexane was added dropwise to it. After that the reaction mixture was stirred for 1 h at a temperature of -78°C . Then 1.2 mmol of an ether complex of magnesium bromide was added to the reaction mixture, after which the cooling bath was removed and the temperature slowly rose to 20°C . In the next step, 3.9 mg (0.007 mmol) of [bis-(diphenylphosphino)propane]nickel(II) chloride $\text{Ni}(\text{dppp})\text{Cl}_2$ was added to the reaction mixture followed by 2 h of stirring. Then the reaction mixture was poured into 150 mL of water and 300 mL of diethyl ether. The organic layer was separated, rinsed with water to pH = 7, dried over anhydrous Na_2SO_4 and evaporated in the vacuum rotary evaporator. The reaction yield was 74% (according to GPC). It was then purified from the residual amounts of the catalyst by means of column chromatography on silica gel using toluene as the eluent. Further purification was made by fractional precipitation, utilizing toluene as the solvent and hexane as the precipitating agent. As a result, 0.20 g (60%) of the pure polymer was isolated. ^1H NMR ($\text{DMSO}-d_6/\text{CCl}_4$, δ , ppm): 0.79–0.93 (overlapping peaks, 6H, $\text{CH}_3\text{--CH}_2\text{--}$, $\text{CH}_3\text{--Si}$), 1.20–1.37 (overlapping peaks, 6H, $\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--}$ and $\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--}$), 1.52–1.67 (broad peak, 2H, $\text{--CH}_2\text{--CH}_2\text{--T}$), 2.65–2.77 (broad peak, 2H, $\text{--CH}_2\text{--T}$), 6.60 (broad peak, 1H), 6.95 (broad peak, 1H), 7.13 (broad peak, 1H), 7.19–7.34 (overlapping peaks, 5H). ^{13}C NMR (CDCl_3 , δ , ppm): -0.21 , 14.06, 22.55, 28.71, 30.14, 31.50, 31.53, 124.02, 124.37, 124.83, 125.70, 132.67, 134.26, 134.45, 137.89, 144.03, 145.25, 145.96. ^{29}Si NMR (CDCl_3 , δ , ppm): -25.29 . Anal. Calcd for $\text{C}_{23}\text{H}_{26}\text{S}_4\text{Si}$: C, 60.21; H, 5.71. Found: C, 58.69; H, 5.53.

Poly[5'-(5'-hexyl-2,2'-bithiophen-5-yl)(methyl)silyl]-2,2'-bithiophen-5,5'-yl(methyl)(2,2'-bithiophen-5,5'-diyl)silane] (P2). This procedure was carried out according to a technique similar to that of polymer **P1** described before from 0.51 g (0.48 mmol) of compound **M2**, 15 mL of THF, 0.3 mL (0.48 mmol) of 1.6 M *n*-butyllithium in hexane, 1.9 mmol of an ether complex of magnesium bromide, and 2.6 mg (0.005 mmol) of $\text{Ni}(\text{dppp})\text{Cl}_2$. After standard extraction, the reaction yield of the product was 69% (according to GPC). After purification similar to that used in the case of polymer **P1**, 0.19 g (44%) of pure polymer **P2** was isolated. ^1H NMR ($\text{DMSO}-d_6/\text{CCl}_4$, δ , ppm): 0.79–0.91 (overlapping peaks, 12H, $\text{CH}_3\text{--CH}_2\text{--}$, $\text{CH}_3\text{--Si}$), 1.19–1.33 (overlapping peaks, 12H, $\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--}$ and $\text{CH}_3\text{--}$

$\text{CH}_2\text{--CH}_2\text{--}$), 1.52–1.66 (broad peak, 4H, $\text{CH}_2\text{--CH}_2\text{--T}$), 2.64–2.75 (broad peak, 4H, $-\text{CH}_2\text{--T}$), 6.57 (broad peak, 2H), 6.92 (broad peak, 2H), 7.09 (broad peak, 2H), 7.16–7.31 (overlapping peaks, 10H). ^{13}C NMR (CDCl_3 , δ , ppm): –0.19, 14.07, 22.55, 28.70, 30.13, 31.49, 31.53, 123.97, 124.35, 124.82, 125.68, 125.70, 125.75, 132.86, 134.17, 134.23, 134.28, 134.73, 137.83, 137.96, 143.90, 144.05, 144.15, 145.18, 145.91. ^{29}Si NMR (CDCl_3 , δ , ppm): –25.40, –25.18. Anal. Calcd for $\text{C}_{46}\text{H}_{50}\text{S}_8\text{Si}_2$: C, 60.34; H, 5.50. Found: C, 59.79; H, 5.57.

RESULTS AND DISCUSSIONS

Among three general approaches to the synthesis of dendronized polymers (“grafting to”, grafting from” and “macromonomer strategy”)²⁶ the last one was selected for preparation of the bithiophenesilane dendronized polymers, since the creation of dendronized polymers having high molecular weights and containing no defects using the other approaches of synthesis is quite complicated. Its implementation requires, first, the preparation of precursors, which are dendritic monomers having difunctional reactive groups in the focal point, and, second, their subsequent polymerization. Among various reactions involving organometallic synthesis used in the synthesis of conjugated polymers, the Kumada reaction,³⁸ whose essence is the formation of biaryl C–C bond from arylhalogenides and their magnesium or zinc derivatives in the presence of palladium- or nickel-catalysts, is widely used. Earlier, such a reaction was applied for the synthesis of bithiophenesilane dendrimers.^{15,16} The only, but significant, disadvantage of this reaction is the formation of symmetric byproduct caused by exchange of halogen and magnesium-halogen reacting groups, which the Kumada reaction is known for. However, in the case of symmetric monomers this circumstance poses no obstacle, since the substitution of a bromine group on the thiophene ring with a magnesium bromide residue followed by the coupling reaction of the exchange products leads to the formation of the products of interest anyway. It is also known that during the synthesis of polythiophenes from their organometallic (magnesium or zinc) derivatives with the use of nickel catalysts, polymerization goes by the chain growth mechanism having “living” nature that leads to the formation of polymers with low polydispersity indices (PDIs).³⁹ That is why the reaction of the polymerization of difunctional bithiophenesilane-dendronized monomers under the Kumada conditions on the nickel catalyst was selected for the synthesis of dendronized polymers in the present work (Scheme 3).

The synthesis of dendronized polymers **P1** and **P2** was made in two main stages: (1) the preparation of branched monomers **M1** and **M2** and (2) their polymerization under the Kumada conditions. The synthesis of monomer **M1** and its polymerization were carried out as the model reactions in order to understand whether the progress of the reaction in the case of bithiophenesilane systems would be possible according to the chain growth mechanism at all. 5-Hexyl-2,2'-bithiophene (compound **4**) was chosen as the model compound, since it exhibits quite interesting optical characteristics¹³ and it is a structural unit of the monodendron **M2** used further. Besides, as a result of the synthesis, it forms a bithiophenesilane comb-like polymer **P1** being a structural homologue of the dendronized polymer of interest **P2**, which will provide a chance to compare the properties of these polymers both between themselves and with those of the bithiophenesilane dendrimers of different generations obtained previously.¹⁷

Synthesis of Monomers. The synthesis of bis(5-bromo-2-thienyl)(5'-hexyl-2,2'-bithiophen-5-yl)-methylsilane (monomer

M1) was carried out by reacting dichloro-(5'-hexyl-2,2'-bithiophen-5-yl)methylsilane (**5**) with a 2-fold molar excess of (5-bromo-2-thienyl)lithium (**2**) with a yield of 77%. Compound **2** was prepared *in situ* by the lithiation of 2,5-dibromothiophene (**1**) with *n*-butyllithium. The synthesis of compound **5** was performed by reacting a lithium-derivative of 5-hexyl-2,2'-bithiophene (**4**) with a 10-fold molar excess of methyltrichlorosilane for the purpose of the increasing of the yield of the target product of monosubstitution. The excess of methyltrichlorosilane was then distilled with toluene, and the solution of freshly synthesized compound **5** in toluene was used in the following reaction stage without its isolation or purification.

The synthesis of the second monomer—{5'-[bis(5-bromo-2-thienyl)(methyl)silyl]-2,2'-bithiophen-5-yl}[bis(5'-hexyl-2,2'-bithiophen-5-yl)]methyl silane (**M2**)—is similar to that previously described for **M1**. In this case the first generation of bithiophenesilane monodendron, 2,2'-bithiophen-5-yl-[bis(5'-hexyl-2,2'-bithiophen-5-yl)]methylsilane (**6**), was utilized as the initial compound, whose synthesis was performed according to the technique described earlier. However, using the modification of the focal point of {5'-[bis(5-bromo-2-thienyl)(methyl)silyl]-2,2'-bithiophen-5-yl}[bis(5'-hexyl-2,2'-bithiophen-5-yl)]methylsilane (**7**) by organolithium compound **2**, led to the reaction yield of compound **M2** of 44% only, whereas the use of organomagnesium derivative **3** allowed to increase the yield of **M2** to 64%. It may be explained by a decreased probability of the metal-bromide exchange reaction for organomagnesium derivatives as compared to their organolithium analogues that leads to formation of smaller amount of byproduct related to this process.

The purification of monomers **M1** and **M2** obtained was performed by classical column chromatography on silica gel. The purity and molecular structure of both monomers was proven by a combination of GPC analysis (Figure 1), MALDI–

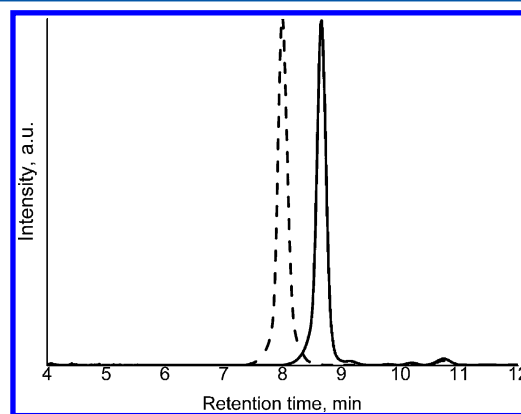


Figure 1. GPC curves for monomers **M1** (solid line) and **M2** (dashed line).

TOF MS, elemental analysis and ^1H , ^{13}C , ^{29}Si NMR spectroscopy (see Experimental Part and Figures S1–S6, S13, and S14 in the Supporting Information).

Synthesis of Polymers. Poly[(5'-hexyl-2,2'-bithiophen-5-yl)(methyl)(2,2'-bithiophen-5,5'-diyl)silane] (**P1**) was prepared by the Kumada reaction (Scheme 3) from monomer **M1**, which was first lithiated with an equimolar amount of *n*-butyllithium and then subjected to the lithium–magnesium exchange by the reaction with an ether complex of magnesium bromide. The synthesized organomagnesium derivative of monomer **M1** was

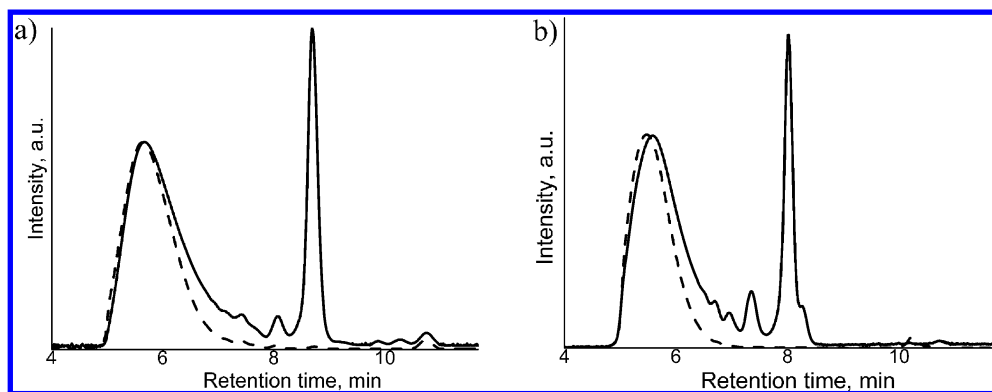


Figure 2. GPC curves of polymers **P1** (a) and **P2** (b). The solid and dashed lines correspond to the reaction mixture and the purified polymer, respectively.

Table 1. Molecular Characteristics of the Bithiophenesilane Dendrimers and Dendronized Polymers^a

compound	PS		LS		$M_w(\text{LS})/M_w(\text{PS})$ ratio	n	m	$[\eta]$, dL/g
	M_w	PDI	M_w	PDI				
G1(2–2)	2480	1.01	2250 ^b	1.01	0.91	4	9	0.048
G2(2–2)	4990	1.01	5150 ^b	1.01	1.03	10	21	0.055
G3(2–2)	9260	1.02	11 800 ^b	1.02	1.27	22	45	0.070
P1	16 100	1.23	20 300	1.22	1.26	37–44	74–88	0.062
P2	18 700	1.19	27 700	1.23	1.48	25–30	100–120	0.101

^aNotes: PS = molecular weight characteristics obtained using calibration according to the polystyrene standards, LS = molecular weight characteristics obtained using the dual light scattering detectors, n = average number of repeating units in the macromolecule, m = average number of bithiophene fragments in the macromolecule, and $[\eta]$ = values of intrinsic viscosity measured in THF at 25 °C. ^bData for dendrimers are taken from ref 17.

subjected to polymerization at room temperature in the presence of the nickel catalyst $\text{Ni}(\text{dppp})\text{Cl}_2$ resulting in the formation of polymer **P1**. The reaction was complete in 2 h with a reaction yield of 74% according to GPC analysis (Figure 2a).

The synthesis of poly[$\{S'-[\text{bis}(S'\text{-hexyl-2,2'-bithiophen-5-yl})(\text{methyl})\text{silyl}]-2,2'\text{-bithiophen-5,5'-yl}\}(\text{methyl})(2,2'\text{-bithiophen-5,5'-diyl})\text{silane}\}$ (**P2**) was performed according to the technique similar to that described above for **P1**, where **M2** was used as the macromonomer. As in the previous case, the polymerization reaction was complete within 2 h at room temperature (23 °C) with the reaction yield of 69% according to the GPC analysis (Figure 2b).

In both cases the purification of the polymers was made by hexane-induced fractional precipitation from their solutions in toluene. The molecular structure and purity of the polymers obtained were confirmed by GPC-analysis (Figure 2) and ^1H , ^{13}C , ^{29}Si NMR spectroscopy (see Experimental Part and Figures S7–S12 in the Supporting Information). The dendronized polymers obtained were highly soluble in low-polar organic solvents such as THF, toluene, chloroform, etc.

Molecular Characteristics. For the synthesized polymers, the values of the average molecular weights (M_w) and the polydispersity indices (PDIs) have been estimated by the following GPC-based methods: (1) using the calibration curves based on the narrow PDI polystyrene (PS) standards and (2) using a dual light scattering (LS) detector combined with a refractometer (Table 1). The data obtained indicate that despite the rigid-chain nature of the polymers under investigation, the values of their molecular weights estimated with respect to the polystyrene standards are significantly underrated in comparison to those obtained by the light

scattering method known to provide true M_w values. This experimental observation can be rationalized by a more compact conformation of the molecules of the dendronized polymers as compared to the flexible-chain molecules of PS with the same molecular weight, which is probably related to their hyperbranched structure. Moreover, the ratio of the real values of M_w to those calculated according to the PS standards when going from **P1** to **P2** increases from 1.26 to 1.48. This increase in deviation from the M_w measured by PS-based standards may be connected with an increase of the branching of the monomer repeating unit from **M1** to **M2**, resulting in a more compact conformation of the macromolecule of the dendronized polymer **P2** as compared to the PS of the same molar weight. Similar tendency of increasing the deviation between the M_w measured by GPC on the base of the PS standards and by the light scattering detector was observed in the series of dendrimers **G1–G3** as well (Table 1). It is interesting to note that the phenomenon whereas the molecular masses measured by GPC based on polystyrene standards were different from the actual molar masses has been investigated for different dendrimers and long conjugated oligomers: for the dendrimers it was found that the GPC results underestimated their molar masses,⁴⁰ while in the case of rigid conjugated oligomers an effect of overestimation of the molar masses was observed.⁴¹

The GPC measurements have shown that the polymers synthesized exhibit quite narrow polydispersity indices ($\text{PDI} = 1.22\text{--}1.23$). These data indicate that the chain growth mechanism of the Kumada polymerization³⁸ is also valid for the synthesis of the polymers from rather bulky monomer **M1** and macromonomer **M2**. Estimations based on these GPC data gives a weight-average polymerization degree $n = 44$ for **P1** and $n = 30$ for **P2**, which correspond to the number of

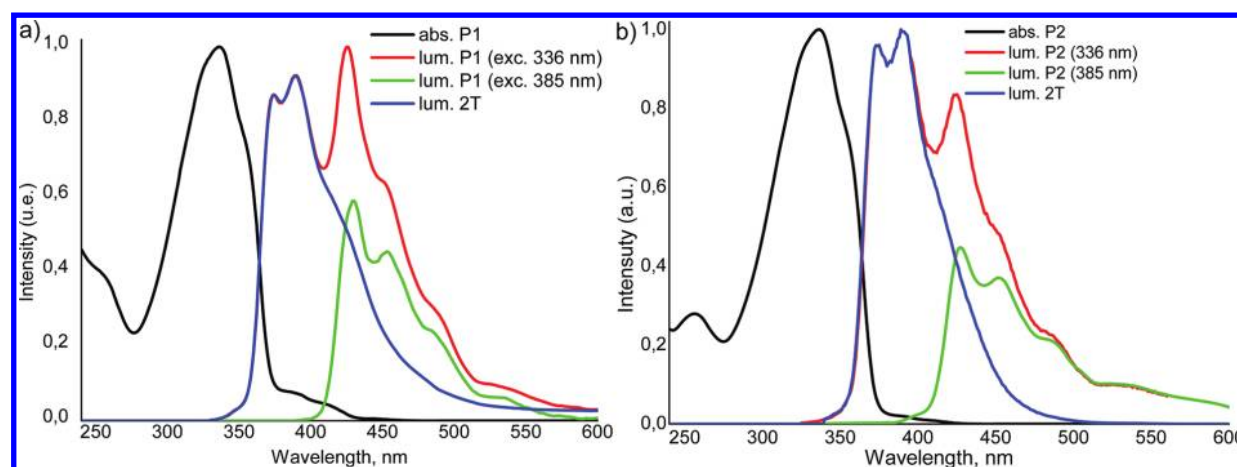


Figure 3. Absorption and luminescence spectra of dilute solutions of polymers **P1** (a) and **P2** (b) in THF. Luminescence spectra of bithiophene component (blue line) for both polymers was calculated by deduction of the luminescence of the polymer excited at 385 nm from the luminescence of the polymer excited at 336 nm.

Table 2. Optical Properties of Various Oligothiophenesilane Macromolecules and Their Low Molecular Weight Analogues^a

compound	λ_{abs} , nm	ϵ , $\text{M}^{-1}\text{cm}^{-1}$	λ_{lum} , nm	Q_F , %	Q_{ETE} , %	ref
2T	303	-	362	1 ^b	-	12
3T	354	-	407	7 ^b	-	12
Hex-2T	308	13 000	374	1.8 ^b	-	16
Hex-2T-TMS	320	19 000	380	5.8 ^b	-	16
TMS-2T-TMS	322	20 000	381	6.0 ^b	-	16
p-T ₂ SiMe ₂ ^d	326	-	371/387	24 ^c	-	12
P1	336, 385	41 000	374/389/430/453	13	50 ± 15	this work
P2	336, 385	77 000	374/389/427/452	14	70 ± 15	this work
G1(2-2)	333	174 000	374/388	30	-	17
G2(2-2)	334	420 000	375/390	31	-	17
G3(2-2)	336	870 000	376/390	30	-	17
D1(3-2)	338, 388	147 000, 114 000	427/450	10	97 ± 3	18
B1(3-2)	337, 382	84 000, 39 000	427/450	10	91 ± 3	18

^aMeasured in THF unless otherwise stated. Notes: λ_{abs} = absorption maximum, ϵ = molar extinction coefficient, λ_{lum} = luminescence maximum, Q_F = luminescence quantum yield, and Q_{ETE} = efficiency of intramolecular energy transfer. ^bIn hexane. ^cIn CH₂Cl₂. ^dLinear polymer: poly[5,5'-(dimethylsilylene)-2,2'-bithiophene].

bithiophenesilane fragments to be contained in average in one macromolecule $m = 88$ and 120 , respectively (Table 1). The corresponding number-averaged values of n and m are also shown in Table 1 as a lower limit of the respective interval. It should be noted that dendronized polymers **P1** and **P2**, both by the number of 2T fragments and by the weight-average molar weight, correspond to the fourth or even higher generation of the bithiophenesilane dendrimer, which was not possible to prepare in a regular manner.

The data obtained from the measurements of the intrinsic viscosity $[\eta]$ of the solutions of the dendronized polymers synthesized and their analogues—the bithiophenesilane dendrimers—are presented in Table 1 as well. The values of $[\eta]$ of all the macromolecules under investigation lies in a range of 0.048–0.101 dL/g, that is 2–4 times higher than the $[\eta]$ of more flexible polyallylcarbosilane dendrimers of various generations.⁴² Besides, $[\eta]$ slightly increases with the increase of the molecular weight of the dendronized polymer, which is also observed in the studied family of bithiophenesilane dendrimers. At the same time, the dependency of the reduced viscosity on the concentration of the solution is more pronounced for the dendronized polymers than for the dendrimers, for which the reduced viscosity is practically

independent of the dilution of their solutions (see Figure S15 in the Supporting Information). All in all, there are similarities in the hydrodynamic behavior of the bithiophenesilane dendrimers and dendronized polymers investigated, which confirm the conclusion about the compact conformation of the dendronized polymers.

Optical Properties. The absorption and luminescence spectra of the dilute solutions of dendronized polymers **P1** and **P2** in THF are presented in Figure 3. The absorption spectrum of polymer **P1** is almost identical to that of the star-like bithiophenesilane molecules.¹³ The value of the molar extinction coefficient ϵ , being 41 000 $\text{L mol}^{-1}\text{cm}^{-1}$ at a wavelength of 336 nm, calculated for one monomer unit, corresponds to the sum of ϵ for two bithiophenesilane fragments (Table 2). Thus, the formation of the absorption spectrum of the dendronized polymer occurs in the same way as in the case of the bithiophenesilane dendrimer.¹⁹ At the same time, a weak long-wave band in the 370–400 nm range, which is impossible to explain by the absorption of the bithiophenesilane fragments, was observed in the absorption and excitation spectra of polymer **P1**. The luminescence spectrum of polymer **P1** excited at 336 nm lies in the range from 360 to 540 nm and has a complex structure and differs from the luminescence of

this polymer excited at 385 nm (Figure 3a). The letter spectra coincides with luminescence of dendrimer **D1(3–2)**, which shows luminescence from its 3T fragments.¹⁸ The mathematical deconvolution of the luminescence spectral contour of polymer **P1** excited at 336 nm led the fact that it consists of the luminescence spectra of two components—bithiophenesilane (2T) with the main maxima at 374 and 389 nm and terthiophenesilane (3T) with the main maxima at 430 and 453 nm. It means that beside the 2T repeating units, polymer **P1** contains a certain amount of 3T fragments. Calculations carried out on the basis of the measured absorption spectra of polymer **P1** revealed that the molar ratio of 2T to 3T fragments in this polymer is close to 25: 1. Therefore, upon the average, one macromolecule of **P1** contains 3–4 terthiophene units, two of which located, most probably, at the ends of the polymer main chain, as shown in Scheme 2.

It should be noted that the presence of the 3T units in **P1** was detected by spectral-luminescence methods only because of their very low content (3–4%) and similarity of their chemical composition to 2T units. Therefore, they can be considered as defects of the polymer chain, formation of which can be related to a small (1–2%) decomposition of the monomer **M1** during its lithiation with *n*-butyllithium (see Scheme S1 in the Supporting Information). The lithium derivatives of the mono- and bithiophene fragments thus formed undergo the lithium–magnesium exchange reaction and participate in the following polymerization under the Kumada conditions. In the polymerization reaction they can serve either as monofunctional blocking agents, which form 2T or 3T end groups, thus limiting the macromolecule length, or as bifunctional comonomer units (presumably, magnesium derivatives of 2,5-disubstituted thiophene), forming a few (1–2 per one macromolecule) defects of 3T units in the main chain of polymer **P1**.

In spite of a small amount of 3T units in **P1**, they significantly change its luminescence spectra as compared to those of the bithiophenesilane dendrimers **Gn(2–2)** (Scheme 1).¹⁷ It was found that under the excitation of **P1** into the spectral range of the maximal absorption of bithiophenesilane and weak absorption of terthiophenesilane (336 nm), the integral intensity of the fluorescence of bithiophenesilane and terthiophenesilane amounts to 69% and 31% respectively, which points out to the phenomenon of the nonradiative energy transfer of the electronic excitation from bi- to terthiophenesilane fragments. In the case of excitation at 336 nm (2T), the fluorescence quantum yield Q_F amounts to 13%, whereas under excitation at 385 nm (3T) its value drops to 8%. Thus, the Q_F of 2T fragments in polymer **P1** is significantly lower than that in the bithiophenesilane dendrimers (20–30%), but not approaching zero as it takes place in the case of efficient (90–97%) intramolecular energy transfer in the “dendritic molecular antenna” from bi- and terthiophene fragments of **B1(3–2)** and **D1(3–2)** (Scheme 1).¹⁸ Therefore, the efficiency of nonradiative energy transfer in polymer **P1** is lower than that in the dendritic “molecular antenna” consisting of bi- and terthiophene fragments. The calculations of the energy transfer efficiency Q_{ETE} from 2T to 3T fragments carried out on the basis of the measured absorption and luminescence spectra of polymer **P1** by the method described before¹⁸ yielded a value of Q_{ETE} close to 50%. The critical distance of energy transfer by inductive resonance mechanism for the system bithiophene–silicon–terthiophene amounts to 20–25 Å meaning that the average distance between a terthiophene

fragment (acceptor) and a group of bithiophene fragments (donors) must not exceed 25 Å. In the case of the linearly arranged main chain of polymer **P1**, it amounts to approximately 100–110 Å (see Figure S16a in the Supporting Information), which should correspond to the efficiency of energy transfer of lower than 4%. Hence it is possible to conclude that a macromolecule of the polymer forms a coil with quite dense packing, in the case of which a bigger number of bithiophene fragments is located closer than 20–25 Å apart from the terthiophene fragment. It is in good agreement with the data obtained by the GPC and viscometry methods, also pointing out to the compact conformation of such macromolecules (see Figure S16c in the Supporting Information).

The formation of the absorption spectrum of dendronized polymer **P2** (Figure 3b) is similar to that of polymer **P1**. The value of the molar extinction coefficient ϵ , being 77000 L mol^{−1} cm^{−1} at a wavelength of 336 nm, calculated for one monomer unit, corresponds to the sum of ϵ for four bithiophenesilane fragments. During excitation spectra measurements performed at 490 nm (in the luminescence range of 3T), a long wavelength band corresponding to the excitation spectrum of 3T was present in the excitation spectrum. Thus, the macromolecule of polymer **P2** also contains terthiophenesilane fragments. Calculations carried out on the basis of the measured absorption spectra of polymer **P2** revealed that the molar ratio of 2T to 3T fragments in this polymer is close to 68: 1. Therefore, one macromolecule of polymer **P2** contains approximately 2 terthiophene repeating units in average, which, most probably, located at the ends of the polymer chains as shown in Scheme 2. During excitation into the spectral range of the maximal absorption of 2T and weak absorption of 3T (336 nm), the integral intensity of the luminescence of 2T and 3T amounts to 69% and 31% respectively. At the same time, excitation at 336 nm (2T) and 385 nm (3T) results in Q_F of 14% and 8%, respectively. The calculations of the energy transfer efficiency from 2T to 3T fragments carried out on the basis of the measured absorption and luminescence spectra of polymer **P2** yielded a value of Q_{ETE} close to 70%. In the case of the most elongated configuration of the macromolecule of polymer **P2**, its 17 repeating units (68 bithiophene fragments falling on one terthiophene fragment) have a length of approximately 150–160 Å (see Figure S16d in the Supporting Information). In this case, the average distance of 2T structural units from 3T structural units amounts to 80–85 Å, which results in an efficiency of energy transfer of below 1%. In order to the energy transfer efficiency will be equal to 70%, as it was observed, the distance between the most part of the 2T fragments and the 3T fragment must not exceed a value of 18–22 Å that is possible in compact conformations of the macromolecules only (see Figure S16f in the Supporting Information).

Comparison of the optical characteristics (molar extinction coefficients, energy transfer efficiency, luminescence quantum yield) of the synthesized bithiophenesilane-containing dendronized polymers, dendrimers, and low molecular weight analogues of their structural fragments may be found in Table 2. The data presented there suggest that the basic optical properties exhibited by the obtained dendronized polymers are better than those of their low-molecular analogues (i.e., their molar extinction coefficients and luminescence quantum yield are higher) and somewhat poorer than those of the dendrimers with similar compositions (i.e., the energy transfer efficiency is lower as compared to dendrimer **D1(3–2)**).

Thermal Properties. The phase behavior and thermal stability of the dendronized polymers obtained were studied by means of the DSC and TGA methods (Table 3). The data recorded are shown in Figure 4. According to the results of DSC analysis (Figure 4a), both polymers turn out to be

Table 3. Thermal Properties of the Bithiophenesilane-Containing Dendrimers and Dendronized Polymers^a

compound	T_g , °C	T_m , °C	ΔH_m , J/g	$T_{dec}(A)$, °C	$T_{dec}(B)$, °C
G1(2–2)	–14	–	–	405	305
G2(2–2)	–2	–	–	430	310
G3(2–2)	–1	–	–	430	400
P1	19	–	–	415	340
P2	17	–	–	400	300
D1(3–2)	–2	–	–	405	290
B1(3–2)	–25	72	33.14	400	290

^aNotes: T_g = glass transition temperature, T_m = melting temperature, ΔH_m = melting enthalpy, $T_{dec}(A)$ = temperature at 1% weight loss measured by TGA in argon, and $T_{dec}(B)$ = temperature at 1% weight loss measured by TGA in air.

amorphous, whereas their glass transition temperatures T_g are practically the same being 19 and 17 °C for P1 and P2 respectively. This is significantly higher than T_g of the corresponding bithiophenesilane dendrimers of different generations G1(2–2), G2(2–2), and G3(2–2), and even T_g of those containing terthiophene units D1(3–2) and B1(3–2) – all these dendrimers has T_g in the range from –25 to –1 °C. No crystallization of polymers P1 and P2 was observed as opposite to dendrimer B1(3–2). These results might be explained by higher M_w of the dendronized polymers as compared to the molar weight of the dendrimers (see Table 1) and low content of the terthiophenesilane units in these polymers.

TGA analysis (Figure 4b) demonstrated the stability of the dendronized polymers P1 and P2 to thermal-oxidative destruction up to 340 and 300 °C (1 wt % weight loss), and up to 415 and 400 °C (1 wt % weight loss) in the case of thermal decomposition. These results are comparable with those obtained for bithiophenesilane-containing dendrimers (Table 3).

Cyclic Voltammetry. Electrochemical properties of polymers P1 and P2 and dendrimers G1(2–2), G2(2–2), and D1(3–2) were studied by cyclic voltammetry (CVA). The measurements were carried out in the 1,2-dichlorobenzene:

acetonitrile (4: 1) mixture of solvents using 0.1 M Bu₄NPF₆ as supporting electrolyte. The results are summarized in Table 4. All compounds showed an irreversible oxidation with two waves for P1, P2 (Figure 5), G1(2–2), and D1(2–3) and with

Table 4. Electrochemical Properties of the Bithiophenesilane-Containing Dendrimers and Dendronized Polymers^a

compound	E_{ox} , V	$E^{1/2}_{ox}$, V	$E_{cl}(HOMO)$, eV
G1(2–2)	1.29, 1.50	1.23, 1.44	–5.63
G2(2–2)	1.29, 1.48, 1.64	1.23, 1.42, 1.58	–5.63
P1	1.36, 1.60	1.30, 1.54	–5.70
P2	1.30, 1.58	1.24, 1.52	–5.64
D1(3–2)	1.34, 1.55	1.28, 1.49	–5.68

^aNotes: E_{ox} = oxidation potential vs SCE; $E^{1/2}_{ox}$ = standard oxidation potential calculated as $E^{1/2}_{ox} = E_{ox} - 0.06$ V; $E(HOMO)$ calculated as $E(HOMO) = -E^{1/2}_{ox} - 4.40$ eV (see ref 43 for detail).

three waves for G2(2–2) (see Figure S17B in the Supporting Information). The fact of irreversible oxidation can be

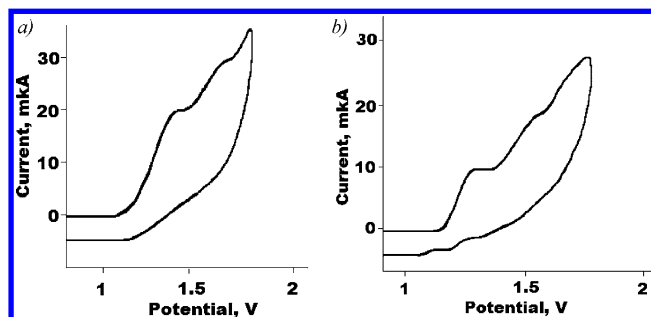


Figure 5. Electrochemical oxidation curves of P1 (a) and P2 (b).

explained by electrochemical instability trithienylsubstituted silanes. It is known from the literature that mono- and disubstituted thienylsilanes are electrochemically unstable,⁴³ whereas tetrasubstituted thienylsilanes can be oxidized reversibly.¹⁰ The onsets of the first oxidation peaks for P1, P2, G1(2–2), G2(2–2), and D1(3–2) have the values of $E^{1/2}$ equal to 1.30, 1.24, 1.23, 1.23, and 1.38 V vs a saturated calomel electrode (SCE), respectively. The HOMO level was calculated using these data as described before.⁴⁴ Peaks of the reduction process were not observed for all the polymers and dendrimers under investigation up to a value of –2.2 V for the discharge

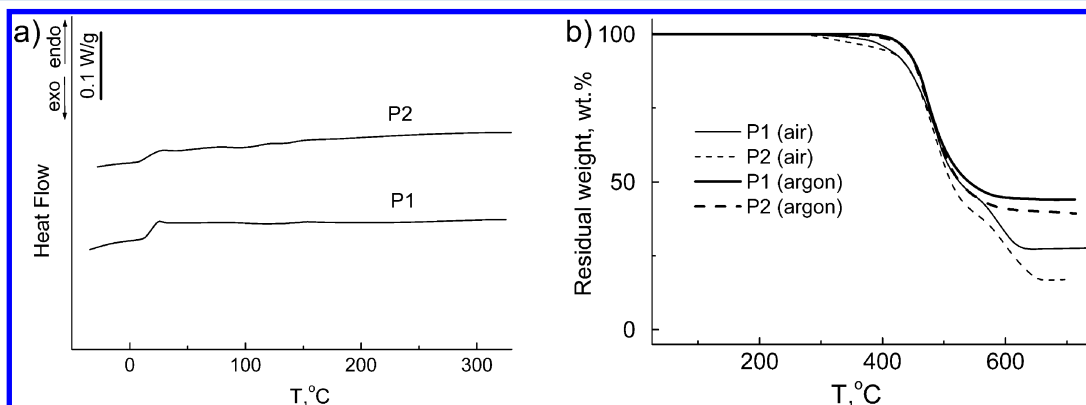


Figure 4. DSC (a) and TGA (b) curves of dendronized polymers P1 and P2.

background. As can be seen from the results obtained, the HOMO energy levels of bithiophenesilane dendrimers **G1(2–2)** and **G2(2–2)** (–5.63 eV) almost coincide with the HOMO energy level of polymer **P2** (–5.64 eV), while the HOMO energy level of polymer **P1** is much closer to the HOMO energy level of dendrimer **D1(3–2)**, containing both 2T and 3T fragments. Bearing in mind that the oxidation processes in such systems are governed by the most conjugated oligothiophene fragments, these results can be explained by the fact that concentration of 3T fragments in polymer **P2** is too small to be detected by CVA method and only 2T fragments are responsible for its oxidation. In contrast, the oxidation behavior of polymer **P1** is governed namely by 3T fragments. These results are in good agreement with optical measurements, which have shown that the ratio of 2T to 3T fragments in polymers **P1** and **P2** are 25: 1 and 68: 1, respectively.

CONCLUSIONS AND OUTLOOK

Thus, as a result of the present work, for the first time an efficient approach to the synthesis of bithiophenesilane dendronized polymers was developed and polymers **P1** and **P2** have been obtained. Both of them have low DPI (1.22–1.23), indicating that the polymerization under Kumada conditions used for their synthesis has a chain growth mechanism, like it was found before for much smaller monomer units of 3-hexylthiophene.³⁸ The polymers synthesized exhibited good solubility in a broad range of organic solvents, high thermal and thermal-oxidative stability up to 320 and 415 °C respectively, and interesting molecular and photo-optical properties. The measurements of the viscosity of the dilute solutions of the synthesized dendronized polymers and their analogues – the bithiophenesilane dendrimers – have shown that all of them have rather low values of the intrinsic viscosity [η] (0.048–0.101 dL/g) that slightly increases with increasing the molar weight of the macromolecule. Similarities found in the hydrodynamic behavior of the bithiophenesilane dendrimers and dendronized polymers investigated, indicate that the dendronized polymers synthesized adopt the compact conformation in solutions.

Studies of the spectral-luminescent characteristics of the dilute solutions of dendronized polymers **P1** and **P2** pointed out to the presence of both bi- and terthiophene structural units in the polymers, whereas the ratio of the number of bithiophenesilane fragments to that of terthiophenesilane fragments is 25:1 in the case of polymer **P1** and 68:1 in the case of polymer **P2**. As a result, the nonradiative transfer of the electronic excitation energy from bi- to terthiophene fragment by the inductive resonance mechanism takes place for both polymers with an efficiency of 50 and 70% respectively. The obtained information affords ground to state that the configuration of the molecules of dendronized bithiophenesilane polymers possesses a shape of a coil with compact packing. Further works on bithiophenesilane-containing dendronized polymers with improved luminescence efficiency and their application in organic optoelectronics devices is in progress.

ASSOCIATED CONTENT

Supporting Information

NMR ¹H, ¹³C, and ²⁹Si spectra, MALDI–TOF MS spectra, data of viscosity measurements, molecular models of **P1**, **P2**, cyclic voltammetry oxidation curves for **G1(2–2)**, **G2(2–2)**, and **D1(3–2)**, and schematic demonstration of formation of

terthiophene units in polymer chains of **P1**. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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Notes

The authors declare no competing financial interest.

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