First Organosilicon Molecular Antennas

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Synthesis of new dendritic and "butterfly"-like oligothiophenesilanes by Suzuki coupling reactions of specially prepared branched precursors is described. Investigation of their optical properties in dilute THF solutions and in solid films revealed that both molecules show an efficient intramolecular energy transfer from the outer bithiophene to the internal terthiophenesilane units. Both experimental and theoretical estimations of the energy transfer efficiency showed the advantages of the more branched dendritic structure. The dendrimer has uniform absorption in the 280−430 nm region and almost quantitative energy transfer due to specific 3-D dendritic architecture.

Introduction

One of the most interesting features of dendrimers is the possibility of incorporation of different chromophores within one dendritic molecule that can lead to an intramolecular directional energy transfer from their peripheries to the center (a molecular antenna effect).[1] It allows tuning the emission color of the core across the entire visible spectrum, which provides an efficient tool for controlling a wavelength of light emission in organic photonic and electronic devices. During the last years, the number of light emitting luminescent dendrimers[2] has increased rapidly. Light-harvesting antennas are essential for natural photosynthetic processes[3] and currently attracting much attention. Up to now different organic dendritic structures have been reported to show the antenna effect,[4] but there are no organosilicon molecules among them, that is, containing thiophene and silicon units. There has been a considerable interest to the synthesis and investigation of silicon-containing π-conjugated materials since a discovery of strong fluorescence of the star-like molecules that have a regular arrangement of Si−Si bonds and bithienylene units.[5] Three-dimensional tetra(terthienyl)silanes were synthesized, and their hexyl end-capped derivatives were applied as donor materials for organic solar cells.[6] Recently the first dendrimers containing mono- and bithiophene units linked directly to silicon atoms have been reported.[7] These dendrimers showed high photoluminescence efficiency in the violet-blue region and allow tuning their solubility, thermal properties, and phase behavior by the choice of different end-capping groups. However, no effective energy transfer within these dendrimer molecules was observed. Here we report the synthesis of two new oligothiophenesilane compounds with different branching topology: dendrimer **1** and "butterfly"-like molecule **2**, both containing bi- and terthiophene units within the molecule (Scheme 1). Photoluminescent investigation of these compounds has shown an efficient intramolecular energy transfer between the bi- and the terthiophene units for both organosilicon molecules. For correct interpretation of the photooptical properties of these complex oligothiophenesilane compounds, two model star-shaped compounds based on bithiophenesilane **3** and terthiophenesilane **4** were prepared and investigated in detail. Each of these model molecules has one central branching silicon atom, linked to three oligothiophene units of the same conjugation length.

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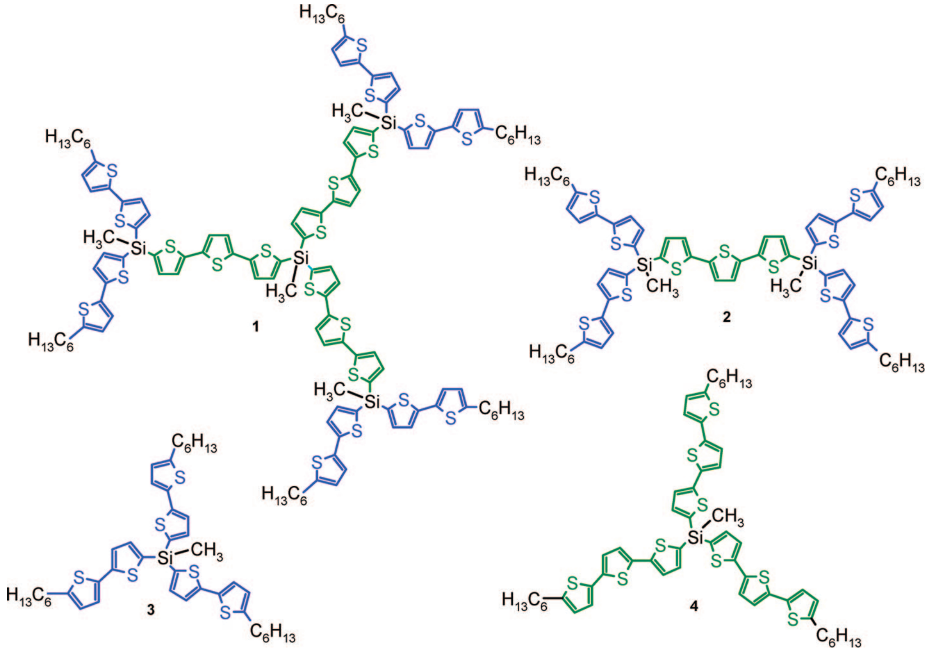
Scheme 1. Structures of Oligothiophenesilane Dendrimer (1) and "Butterfly"-like Molecule (2) as Well as Model Star-Shaped Bithiophenesilane (3) and Star-Shaped Terthiophenesilane (4)



Experimental Section

General. ^{1}H NMR spectra were recorded on a Bruker WP-250 SY spectrometer (250.13 MHz) using tetramethylsilane as the internal standard. ^{13}C NMR spectra were recorded on a Bruker DRX500 spectrometer at 125.76 MHz or on a Bruker AM300 spectrometer at 59.62 MHz, while ^{29}Si NMR spectra were recorded on a Bruker DRX500 spectrometer at 99.36 MHz or on a Bruker AM300 spectrometer at 74.48 MHz. GPC analysis was performed on a Shimadzu instrument with a RID-10A refractometer and a SPD-M10AVP diode matrix as detectors using 7.8 × 300 mm Phenomenex columns (U.S.A.) filled with the Phenogel sorbent with pore sizes of 500 Å and THF as an eluent. Steady-state luminescence and absorption spectra of solutions were performed on a multifunctional spectrometer ALS01M. All measurements were carried out at room temperature in diluted solutions ($10^{-5}-10^{-6}$ M) of UV-grade hexane or THF. Emission spectra were registered in the wavelength range of 300−700 nm for excitation wavelengths varied in the range of 250−400 nm. 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 mass spectroscope Bruker Daltonics Reflex-III in the positive ions regime using the reflect mode with the target voltage of 20 kV. 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 solution of the matrix (20 mg/mL) in chloroform in the ratio of 1:1.

Materials. *n*-Butyllithium (1.6 and 2.5 M solutions in hexane), thiophene, 2-bromothiophene, *N*-bromosuccinimide (Acros organics), 1,1′-bis(diphenylphosphino)ferrocene palladium(II) Pd(dppf)Cl_2 chloride and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Aldrich), and 2,4-bromthiophene (Acros organics) were used as received. Methyltrichlorosilane was distilled before use. THF and diethyl ether were dried over CaH_2 and distilled from $LiAlH_4$. 5-Bromo-2,2-bithiophene, 5-hexyl-2,2′-bithiophene, 5-hexyl-2,2′:5′,2″-terthiophene, methyltris(5′-hexyl-2,2′-bithien-5-yl)silane (**3**), methyltris(5-bromo-2-thienyl)silane (**9**), and 2-{5-[Methyl-bis(5′-hexyl-2,2′-bithienyl-5-yl)silyl]-2-thienyl}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**10**) were obtained using the procedures described elsewhere.[7−9]

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

Methyl(2,2′-bithien-5-yl)dimethoxysilane (5). A solution of 5-bromo-2,2′-bithiophene (8.28 g, 34 mmol) in 80 mL of THF was added dropwise to a suspension of magnesium (0.89 g, 37 mmol) in 10 mL of THF. The Grignard reagent was refluxed for 2 h, cooled to room temperature, and added dropwise to a solution of methyltrimethoxysilane (4.6 g, 34 mmol) in 40 mL of THF while the temperature was kept between −60 and −50 °C. The temperature was then allowed to rise to rt for 1 h, and the stirring was continued for 2 h. The reaction mixture washed with anhydrous hexane and filtered off on glass filter G4 under argon. The product was purified by distillation in vacuum (0.56 mbar, 110 °C) to give pure compound **5** (3.51 g, 40%) as a colorless liquid. MS *m/z* 270.47 (M^+, requires 270.45). ^{1}H NMR (250 MHz, $CDCl_3$, Me_4Si): δ [ppm] 0.41 (3H, s), 3.59 (6H, s), 7.01 (1H, t, $J = 7.3$ Hz), 7.22 (2H, m), 7.28 (2H, m). ^{13}C NMR (125 MHz, $CDCl_3$): δ [ppm] 4.16, 50.67, 124.17, 124.76, 124.96, 127.81, 131.79, 136.69, 136.95, 146.65. ^{29}Si NMR (100 MHz, $CDCl_3$): δ [ppm] −18.51.

5-[Bis(5′-hexyl-2,2′-bithienyl-5-yl)(methyl)silyl]2,2′-bithienyl (7). A 2.5 M solution of butyllithium in hexane (7.89 mL, 20 mmol) was added dropwise to a solution of 5-hexyl-2,2′-bithiophene (4.94 g, 20 mmol) in 90 mL of THF, while the temperature was kept between −75 and −65 °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 (0.62 g, 26 mmol) and dibromoethane (4.44 g, 24 mmol) in 5 mL of anhydrous ether) was added dropwise to the reaction mixture at −78 °C, which was stirred then for 2 h without a cooling bath. Methyl(2,2′-bithien-5-yl)dimethoxysilane (2.32 g, 9 mmol) was added to the solution of the Grignard reagent obtained. The reaction mixture was refluxed for 10 h. After

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completion of the reaction it was poured into 200 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 6.30 g of crude product, which was purified by column chromatography on silica gel (eluent toluene−hexane 1:5) to give pure compound **7** (4.00 g, 67%). MS *m/z* 707 (M^+, requires 707.22). ^{1}H NMR (250 MHz, $CDCl_3$, Me_4Si): δ [ppm] 0.88 (6H, t, $J = 6.7$ Hz), 0.92 (3H, s), 1.24−1.40 (12H, overlapped peaks,), 1.64 (4H, m, M = 5, $J = 7.3$ Hz), 2.76 (4H, t, $J = 7.3$ Hz), 6.69 (2H, d, $J = 3.05$ Hz), 7.01 (1H, d, $J = 3.05$ Hz), 7.03 (2H, d, $J = 3.7$ Hz), 7.21 (2H, d, $J = 3.7$ Hz), 7.26 (1H, d, $J = 3.7$ Hz), 7.29 (2H, d, $J = 3.7$ Hz), 7.31 (2H, d, $J = 3.7$ Hz), 7.37 (1H, d, $J = 3.7$ Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ [ppm] −0.16, 14.07, 22.56, 28.72, 30.15, 31.52, 31.55, 123.96, 124.26, 124.35, 124.79, 124.82, 125.12, 127.83, 132.96, 134.05, 134.30, 136.97, 137.78, 137.81, 144.47, 145.17, 145.94. ^{29}Si NMR (100 MHz, $CDCl_3$): δ [ppm] −25.27. Calcd (%) for $C_{37}H_{42}S_6Si$: C, 62.59; H 5.89; S 27.17; Si 3.69. Found: C, 62.84; H, 5.99; S, 27.20; Si, 3.97.

2-{5′-[Methylbis(5′-hexyl-2,2′-bithienyl-5-yl)silyl]-2,2′-bithien-5-yl}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8). A 1.6 M solution of butylllthium (1.77 mL, 2.8 mmol) in hexane was added dropwise to a solution of **7** (2.00 g, 2.8 mmol) in 75 mL of THF, while the temperature was kept between −70 and −75 °C. The reaction mixture was stirred for 60 min at −75 °C. Then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.58 mL, 2.8 mmol) was added in one portion. The reaction mixture was stirred for 1 h at −78 °C, the cooling bath was removed, and the stirring was continued for 3 h. After completion of the reaction, 300 mL of freshly distilled diethyl ether and 200 mL of degassed water containing 2.8 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 pure compound **8** (2.32 g, 99%) as blue crystals. The product was used in the subsequent synthesis without further purification. MS *m/z* 833 (M^+, requires 833.18). ^{1}H NMR (250 MHz, DMSO/CCl_4, TMS): δ [ppm] 0.87 (6H, t, $J = 6.7$ Hz), 0.93 (3H, s), 1.23−1.38 (24H, overlapped peaks), 1.62 (4H, m, M = 5, $J = 7.3$), 2.76 (4H, t, $J = 7.7$ Hz), 6.72 (2H, d, $J = 3.1$ Hz), 7.07 (2H, d, $J = 3.7$ Hz), 7.24 (2H, d, $J = 3.7$ Hz), 7.31 (2H, d, $J = 3.7$ Hz), 7.35 (2H, t, $J = 3.1$ Hz), 7.43 (2H, t, $J = 3.1$ Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ [ppm] −0.18, 14.07, 22.56, 24.76, 28.72, 30.16, 31.52, 31.55, 84.17, 123.99, 124.35, 124.82, 125.51, 125.80, 132.85, 134.29, 134.85, 137.84, 137.90, 143.61, 144.24, 145.20, 145.95. Calcd (%) for $C_{43}H_{53}BO_2S_6Si$: C, 61.99; H 6.41; S 23.09; Si 3.37. Found: C 62.00; H 6.40; S 23.04; Si 3.17.

Tris{5′-[methylbis(5-hexyl-2,2′-bithienyl-5-yl)silyl]-2,2′:5,2″-terthienyl-5″-yl}(methyl)silane (1). Degassed solutions of **8** (1.07 g, 1.28 mmol) and **9** (0.18 g, 0.34 mmol) in 20 mL of toluene and a 2 M solution of Na_2CO_3 (1.9 mL) were added to $Pd(PPh_3)_4$ (125 mg, 0.11 mmol), and the mixture was refluxed for 48 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 column chromatography on silica gel (eluent toluene−hexane 1:3) to give pure dendrimer **1** (0.24 g, 30%) as yellow crystals. MALDI-MS MS *m/z* 2409 (M^+, requires 2408). ^{1}H NMR (250 MHz, DMSO/CCl_4, Me_4Si): δ [ppm] 0.87 (18H, t, $J = 6.7$ Hz), 0.91 (9H, s), 0.94 (3H, s), 1.22−1.42 (36H, overlapped peaks), 1.65 (12 H, m, $J = 7.3$), 2.75 (12 H, t, $J = 7.3$ Hz), 6.67 (6H, d, $J = 3.1$ Hz), 7.01 (6H, d, $J = 3.1$ Hz), 7.18 (12H, d, $J = 3.7$ Hz), 7.28 (6H, d, $J = 3.7$ Hz), 7.31 (12H, d, $J = 4.9$ Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ [ppm] −0.27, −0.21, 14.10, 22.56, 28.72, 30.14, 31.52, 31.54, 123.97, 124.33, 124.82, 124.94, 125.03, 125.09, 132.76, 133.76, 134.24, 134.37, 136.04, 136.26, 137.84, 137.97, 143.99, 144.22, 145.17, 145.94. ^{29}Si NMR (100 MHz, $CDCl_3$): δ [ppm] −25.27, −25.13. Calcd (%) for $C_{124}H_{132}S_{21}Si_4$: C, 61.85; H, 5.53; S, 27.96; Si, 4.67%. Found: C, 61.59; H, 5.66; S, 27.60; Si, 4.45.

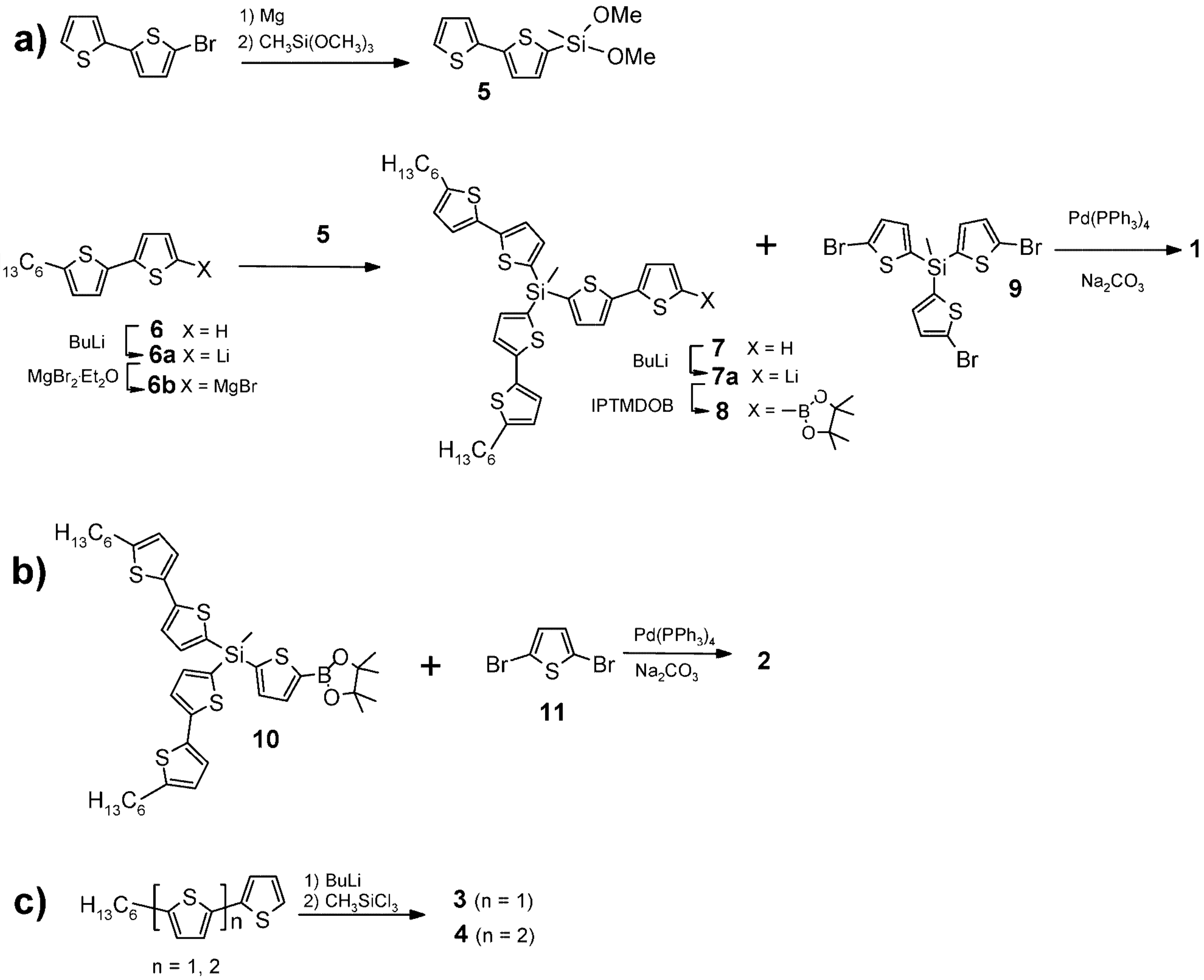
2,2′:5′,2″-Terthiene-5,5″-diylbis[bis(5′-hexyl-2,2′-bithien-5-yl)-(methyl)silane] (2). The reaction was carried out by following the procedure described above. A Suzuki coupling reaction between **10** (1.084 g, 1.44 mmol) and 2,5-dibromothiophene (0.146 g, 0.6 mmol) in the presence of $Pd(PPh_3)_4$ (83 mg, 0.07 mmol) gave 0.32 g (40%) of **2** as yellow crystals. MALDI-MS MS *m/z* 1330.09 (M^+, requires 1330.29). ^{1}H NMR (250 MHz, DMSO/CCl_4, Me_4Si): δ [ppm]: 0.88 (t, 12H, $J = 6.71$ Hz), 0.92 (s, 6H), 1.21−1.41 (overlapped peaks, 24 H), 1.63 (m, 8 H, M = 5, $J = 7.1$), 2.76 (t, 8 H, $J = 7.3$ Hz), 6.68 (d, 4H, $J = 3.1$ Hz), 7.03 (d, 4H, $J = 3.1$ Hz), 7.19−7.23 (overlapped peaks, 6H), 7.27−7.31(overlapped peaks, 4H), 7.31−7.36 (overlapped peaks, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ [ppm] −0.21, 14.10, 22.56, 28.72, 30.14, 31.52, 31.54, 123.97, 124.33, 124.82, 124.93, 125.05, 132.78, 134.24, 134.32, 136.15, 137.84, 144.03, 145.17, 145.94. ^{29}Si NMR (100 MHz, $CDCl_3$): δ [ppm] −25,27. Calcd (%) for $C_{70}H_{80}S_{11}Si_2$: C, 63.20; H, 6.06; S, 26.51; Si, 4.22. Found: C, 63.22; H, 6.14; S, 26.58; Si 4.26.

Methyltris(5″-hexyl-2,2′:5′,2″-terthien-5-yl)silane (4). A 2.5 M solution of butyllithium in hexane (0.51 mL, 1.27 mmol) was added dropwise to a solution of 5-hexyl-2,2′:5′,2″-terthiophene (0.42 g, 1.27 mmol) in 30 mL of dry THF, keeping the temperature in the interval between −65 °C and −50 °C. Then the cooling bath was removed and the temperature was allowed to rise to 0 °C. After cooling the reaction mixture again to −78 °C methyltrichlorosilane (0.045 mL, 0.39 mmol) was added. Then cooling bath was removed, and the temperature was allowed to rise to room temperature. After completion of the reaction it was poured into 200 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, and the solvent was evaporated. Purification by column chromatography on silica gel (eluent hexane−toluene mixture, 5:1) gave pure product (0.3 g, 74%). MALDI-MS *m/z* 1037.73 (M^+, requires 1037.75). ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ [ppm] 0.89 (9H, t, $J = 6.7$ Hz), 0.95 (3H, s), 1.28−1.42 (18H, overlapped peaks,), 1.67 (6H, m, M = 5, $J = 7.3$ Hz), 2.78 (6H, t, $J = 7.3$ Hz), 6.66 (3H, d, $J = 3.7$ Hz), 6.96 (6H, t, $J = 3.05$ Hz), 7.08 (3H, d, $J = 3.7$ Hz), 7.24 (3H, d, $J = 3.7$ Hz), 7.31 (3H, d, $J = 3.7$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] −0.14, 14.15, 22.64, 28.81, 29.77, 30.26, 31.62, 123.53, 123.64, 124,91, 124.93, 124.98, 133.67, 134.46, 135.02, 137.47, 138.01, 144.55, 145.81. ^{29}Si NMR (60 MHz, $CDCl_3$): δ [ppm] −25.35. Calcd (%) for $C_{37}H_{42}S_6Si$: C, 63.66; H, 5.83; S, 27.81; Si, 2.71. Found: C, 63.75; H, 5.95; S, 27.32; Si, 2.76.

Results and Discussion

Synthesis. Compounds **1** and **2** were synthesized by a convergent approach as shown in Scheme 2a,b. The synthetic strategy, which was developed previously for bithiophenesilane dendrimers,[7a,b] was extended here successfully for larger oligothiophenesilanes. It includes the synthesis of monodendrons by a reaction between the corresponding thienylmethoxysilane and 5′-hexyl-2,2′-bithien-5-yl magnesium bromide, followed by a preparation of their pinacolineboronic derivatives (**8**, **10**) and, finally, linking them to corresponding branching cores having functional 2-bromothienyl groups (**9**, **11**) via Suzuki reactions.

Scheme 2. Synthesis of New Organosilicon Compounds



Dendrimer **1** was prepared according to this procedure in several steps (Scheme 2a). First, methyl(2,2′-bithien-5-yl)dimethoxysilane (**5**) was synthesized by the reaction between 2,2′-bithien-5-yl magnesium bromide, prepared in situ from 5-bromo-2,2′-bithiophene, magnesium, and methyltrimethoxysilane. To improve the yield of the monosubstituted silane, the latter was used in a twofold excess. Second, bithiophenesilane monodendron **7** was obtained by the reaction between compound **5** and 5′-hexyl-2,2′-bithien-5-ylmagnesium bromide (**6b**). The latter was prepared in situ from 5-hexyl-2,2′-bithiophene by its lithiation with *n*-butyllithium in THF followed by the lithium–magnesium exchange using magnesium(II) bromide ethyl etherate complex. The overall reaction yield of monodendron **7** was very high (94% according to GPC analysis). Subsequent lithiation of compound **7** followed by the treatment with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (IPTMDOB) gave rise to pinacolatoborolane-functionalized monodendron **8** in 99% isolated yield. Finally, compound **8** was reacted with methyltris(5-bromo-2-thienyl)silane (**9**)[7a] under Suzuki conditions to yield dendrimer **1**, having three internal terthienyl and six external bithienyl units with hexyl end groups. The reaction yield was 55% (as determined by GPC analysis of the reaction mixture) and the isolated yield was 30% (after purification by classical column chromatography).

“Butterfly”-like oligothiophenesilane **2** was prepared by a similar technique (Scheme 2b). Preparation of borylated monodendron **10** was described in detail before.[7b] A Suzuki coupling reaction between **10** and 2,5-dibromothiophene (**11**) gave the desired compound **2** with 62% reaction and 41% isolated yield.

Star-shaped oligothiophenesilanes **3** and **4** were obtained by lithiation of 5-hexyl-2,2′-bithiophene or 5-hexyl-2,2′:5′,2″-terthiophene, respectively, followed by the reaction with methyltrichlorosilane (Scheme 2c).

Purification of the target compounds was made by a classical column chromatography on silica gel, leading to chromatographically pure substances as was checked by TLC. GPC analysis has also shown that all of them are monodisperse individual compounds (Figure 1). Both branched oligothiophenesilane compounds **1** and **2**, as well as model star-shaped compounds **3** and **4**, are highly soluble in common organic solvents such as toluene, THF, chloroform, and so forth. Their purity and molecular structures were confirmed by GPC, ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy, elemental analysis, and MALDI-TOF measurements (see Experimental Section and Supporting Information).

Optical properties of compounds **1**–**4** were investigated in their dilute solutions in THF as well as in thin films by UV–vis absorption and fluorescence emission spectroscopy.

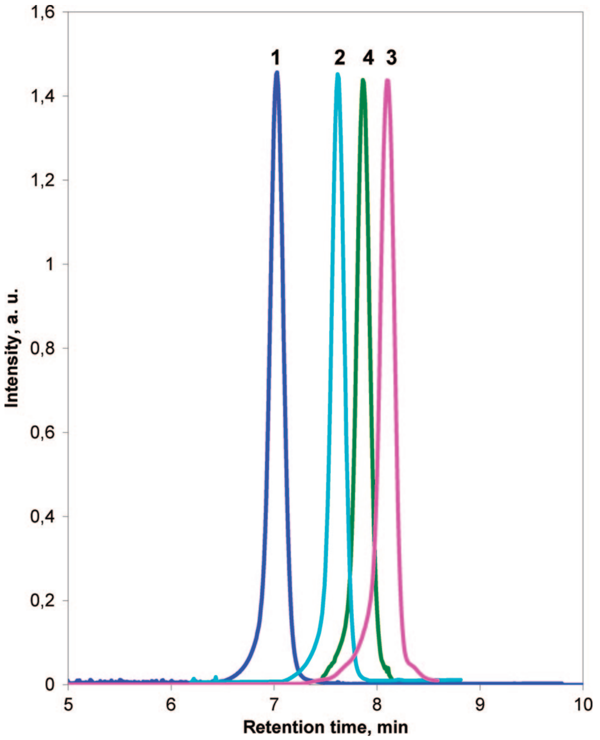


Figure 1. GPC curves of oligothiophenesilane dendrimer (**1**), "butterfly"-like oligothiophenesilane (**2**), star-shaped bithiophenesilane (**3**), and star-shaped terthiophenesilane (**4**).

Optical Properties in Dilute Solutions. Earlier investigation of the optical properties of a number of bithiophenesilane dendrimers and model compounds (5-hexyl-2,2′-bithienylsilane and 5,5′-bis(trimethylsilyl)-2,2′-bithiophene), corresponding to repeating fragments of the dendrimer molecules linked through silicon atoms, have shown that photons are absorbed by these fragments independently of each other and there is no π-conjugation between the chromophores in the dendrimers.[7] Namely, it was shown that α-substitution of 5-hexyl-2,2′-bithiophene with trimethylsilyl group leads to increase of the molar extinction coefficient ε (from 12 000 $M^{-1}\cdot cm^{-1}$ to 20 000 $M^{-1}\cdot cm^{-1}$) and to slight red shift of the absorption and luminescence spectra (on 8−10 nm) due to an inductive effect of the trimethylsilyl substituent. Absorption spectra of the bithiophenesilane dendrimers coincide with those of the model bithiophenesilane compounds, but they are red-shifted on 14−16 nm. The value of molar extinction coefficient ε of the bithiophenesilane dendrimer corresponds to ε of the model bithiophenesilane compound multiplied by the number of bithiophenesilyl units in the dendritic molecule. All these data allow considering the oligothiophenesilane dendrimers as a system of chromophoric units, which are structurally organized in the space and weakly interact between each other. In this case the absorption spectrum of the dendrimer will correspond to a sum of the absorption spectra of its fragments. Position and intensity of the absorption spectra of each chromophoric fragment in such a system is determined by the influence of the local field of surrounding fragments and the solvent molecules. Electronic excitation energy transfer between the fragments will take place because of inductive−resonance interactions, and it should be nicely described by the Förster formula.[10] These conceptions were taken as a basis for consideration of the electronic excitation energy transfer processes in compounds **1** and **2**. Bithiophene units are the energy donors in these compounds and terthiophene units the acceptors. For modeling the absorption and the luminescence spectra of the donor and the acceptor fragments we have used the spectra of compounds **3** and **4**. According to the data obtained previously their optical properties should best of all correspond to those of compounds **1** and **2**.[7,9]

Features of the absorption and luminescence spectra of dilute molecular solutions of compounds **1**−**4** in THF indicates the effective electronic excitation energy transfer from bi- to terthiophene units. In fact, both under excitation in the region of mostly donor absorbance (328 nm) and in the region of acceptor absorbance (388 or 382 nm for compounds **1** or **2**, respectively) only the luminescence, corresponding to the emission of compound **4**, is observed (Figures 2 and 3). The luminescence intensity under excitation at 328 nm and 388/382 nm is proportional to absorbance of the solutions for the corresponding wavelengths (Figures 2 and 3).

Estimation of the energy transfer efficiency on the base of the luminescence quantum yield values measured under the excitation at 328 nm and 388/382 nm gives 100% for compound **1** and 90% for compound **2**. However, such estimation could not be considered as ultimate, since on the wavelength of 328 nm the light is absorbed by both donor (2T fragment) and acceptor (3T fragment). More precise values of the energy transfer efficiency were obtained by taking into account an impact of the acceptor absorbance. For this purpose the absorbance spectra of compounds **1** and **2** were deconvoluted into the components corresponding to the absorbance spectra of their constituent fragments. Reliability of the deconvolution was confirmed by a good agreement of the calculated spectra for components 2T and 3T with the experimental spectra of model compounds **3** and **4** (Figures 2 and 3). The spectra of 2T- and 3T-components of compound **1** in Figure 2 are red-shifted on 2 and 3 nm, respectively, as compared to the spectra of model compounds **3** and **4**. Such a shift to longer wavelengths corresponds to the shift observed in the spectra of the first generation bithiophenesilane dendrimer as compared to the spectra of model star-shaped compound **3** (compounds **1** and **5** in ref 7b). A ratio of the absorption spectra amplitudes of 2T- and 3T-components coincides with the ratio of the molar extinction coefficients multiplied by the number of bi- or terthiophenesilane fragments in compounds **1** and **2**. Namely, for compound **1** we have the ratio: $20\,000 \times 6/38\,000 \times 3 = 2/1.9$; for compound **2** we have $20\,000 \times 4/38\,000 \times 1 = 4/1.9$. The spectra of 2T- and 3T-components obtained allow estimation of an impact of bi- and terthiophenesilane fragments in the total absorption of compounds **1** and **2**.

For determination of the energy transfer efficiency Q_{ETE} on the base of absorption and luminescence spectra obtained under excitation by light with the wavelength $\lambda_{\mathrm{ext}}^{(\mathrm{DA})}$, on which both the donor and the acceptor absorb the light, and by light with the wavelength $\lambda_{\mathrm{ext}}^{(\mathrm{A})}$, on which only the acceptor absorbs the light, the following equation can be easily obtained:

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(10) Förster, T. *Discuss. Faraday Soc.* **1959**, *27*, 7.

$$Q_{\mathrm{ETE}} = \frac{F_{\mathrm{A}}(\lambda_{\mathrm{lum}}, \lambda_{\mathrm{ext}}^{(\mathrm{DA})}) \times \mathrm{A}_{\mathrm{A}}(\lambda_{\mathrm{ext}}^{(\mathrm{A})})}{F_{\mathrm{A}}(\lambda_{\mathrm{lum}}, \lambda_{\mathrm{ext}}^{(\mathrm{A})}) \times \mathrm{A}_{\mathrm{D}}(\lambda_{\mathrm{ext}}^{(\mathrm{DA})})} - 1 \qquad (1)$$

where $\mathrm{A}_{\mathrm{D}}(\lambda_{\mathrm{ext}}^{(\mathrm{DA})})$ is absorbability of the energy donor on the excitation wavelength $\lambda_{\mathrm{ext}}^{(\mathrm{DA})}$; $\mathrm{A}_{\mathrm{A}}(\lambda_{\mathrm{ext}}^{(\mathrm{A})})$ is absorbability of the energy acceptor on the excitation wavelength $\lambda_{\mathrm{ext}}^{(\mathrm{A})}$; $F_{\mathrm{A}}(\lambda_{\mathrm{lum}}, \lambda_{\mathrm{ext}}^{(\mathrm{DA})})$ is intensity in the luminescence spectra of the energy acceptor under excitation at $\lambda_{\mathrm{ext}}^{(\mathrm{DA})}$; and $F_{\mathrm{A}}(\lambda_{\mathrm{lum}}, \lambda_{\mathrm{ext}}^{(\mathrm{A})})$ is intensity in the luminescence spectra of the energy acceptor under excitation at $\lambda_{\mathrm{ext}}^{(\mathrm{A})}$.

Apparently for the energy transfer efficiency calculation one should use such a spectral region of the acceptor luminescence, on which the donor and the acceptor luminescence spectra do not overlap. As follows from Figures 2 and 3, for determination of Q_{ETE} in compounds **1** and **2** the suitable interval is situated between 475 and 525 nm. The energy transfer efficiency determined by this method was found to be equal to 97±3% for compound **1** and 91±3% for compound **2**.

Since the presence of the inductance−resonance interactions between bi- and terthiophenesilane fragments in compounds **1** and **2** raises no doubts, it is worth estimating the electronic excitation energy transfer efficiency by Förster equation for the case of dipole−dipole interactions. Calculations of a critical energy transfer distance by this equation require knowledge of decay time or luminescence quantum yield of the donor under absence of the acceptor and an overlap integral of the donor luminescence spectra and the

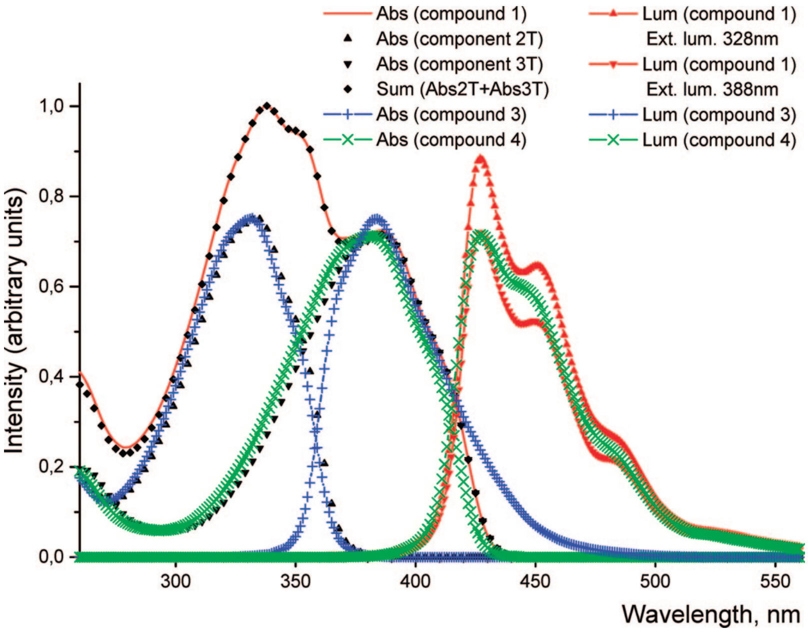

Figure 2. Absorption and luminescence spectra of dilute solutions of compounds **1**, **3**, and **4** in THF. Model absorption spectra of 2T and 3T components of compound **1** are also shown.

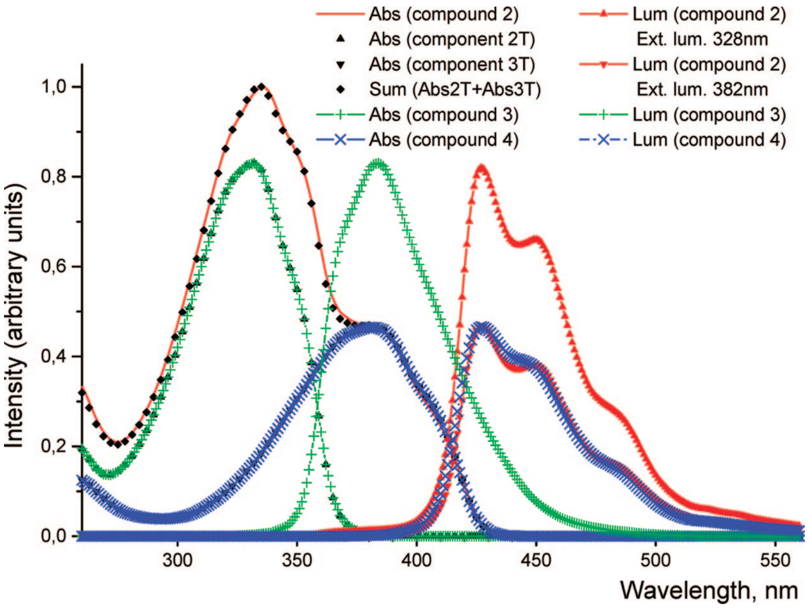

Figure 3. Absorption and luminescence spectra of dilute solutions of compounds **2**, **3**, and **4** in THF. Model absorption spectra of 2T and 3T components of compound **2** are also shown.

Table 1. Optical Properties of Dilute Solutions of Compounds 1−4 in THF

	absorption				luminescence	Q_{ETE} (%)	
compound	$\lambda_{\max}$ (nm)	ε ($\mathrm{M^{-1}\ cm^{-1}}$)	ε/n ($\mathrm{M^{-1}cm^{-1}}$)	Q_F (%)	$\lambda_{\max}$ (nm)	experimental	calculation
1	338	147000	24500	10 ± 2	427	97 ± 3	98
	388	114000	38000	10 ± 2	450		
2	337	84000	21000	9 ± 2	427	91 ± 3	94
	382	39000	39000	10 ± 2	450		
3	332	61000	20333	19 ± 3	384		
4	381	93000	31000	9+ /- 2	427		

Footnotes: ε - molar extinction coefficient, n - number of chromophors, ETE - energy transfer efficiency of the electronic excitation, Q_F - luminescence quantum yield.

acceptor absorption spectra, as well as the orientation factor. The donor luminescence quantum yield was taken equal to the quantum yield of compound **3**. Calculation of the overlap integral, when both the luminescence spectra of the donor and that of the molar extinction coefficient of the acceptor (Figures 2 and 3) are known, is not a matter of concern. The orientation factor was calculated based on the conceptions for the compounds structure and, hence, the accuracy of its calculation is limited to these assumptions. For different reciprocal orientations between bi- and terthiophene fragments within compounds **1** and **2** the calculated value of the energy transfer critical distance lays between 17 Å and 24 Å. The distance between a donor and the closest to it acceptor is equal to 8.5 Å. The energy transfer critical distance for such pairs is calculated to be 17 Å for both compounds **1** and **2**. In this case the calculated energy transfer efficiency would be equal to 99.8% for both compounds, which contradicts the experimental data. The reason for such discrepancy lays in the fact that in compounds **1** and **2** there are from five (in compound **2**) to nine (in compound **1**) interacting fragments for a sphere with a diameter of 16−30 Å. Under such dense packing probability, the energy transfer between any two fragments will be determined by all the surrounding fragments. Hence, the energy transfer efficiency from the bithiophene excited donor D_1 to the terthiophene acceptor A for compound **2** should be calculated in accordance with the eq 2

$$Q_{\mathrm{ETE}} = \frac{\kappa_{\mathrm{D_1A}}}{\kappa_{\mathrm{D_1A}} + \sum_{j=2}^{4} \kappa_{\mathrm{D_1D}_j} + \frac{1}{\tau_{\mathrm{D}}^{0}}} \qquad (2)$$

and for compound **1** as a probability of the energy transfer from the excited bithiophene donor $\mathrm{D_1}$ to any of three terthiophene acceptors $\mathrm{A}_{j=1,2,3}$

$$Q_{\mathrm{ETE}} = \frac{\sum_{j=1}^{3} \kappa_{\mathrm{D_1A}_j}}{\sum_{j=1}^{3} \kappa_{\mathrm{D_1A}_j} + \sum_{j=2}^{6} \kappa_{\mathrm{D_1D}_j} + \frac{1}{\tau_{\mathrm{D}}^{0}}} \qquad (3)$$

where $\kappa_{\mathrm{D_1A}_j}$ is the energy transfer rate constant from donor $\mathrm{D_1}$ to acceptor A_j; $\kappa_{\mathrm{D_1D}_j}$ is the energy transfer rate constant from donor $\mathrm{D_1}$ to donor D_j; and τ_{D}^{0} is the luminescence decay time of donor $\mathrm{D_1}$ in absence of the surroundings.

The calculations taking into account interactions of all the fragments gives the energy transfer efficiency values of 98% and 94% for compounds **1** and **2**, respectively. These are in good agreement with the experimentally found values of 97 ± 3% for compound **1** and 91 ± 3% for compound **2**. Therefore, the energy transfer efficiency in different branched oligothiophenesilane systems depends not only on the reciprocal orientation and the distance between the fragments being the donor and the acceptor of energy but also on the number of the energy acceptor fragments lying on the distance that is less than the critical energy transfer distance from the donor. In accordance to the Förster formula for the case of dipole−dipole coupling the larger is the luminescence quantum yield of the donor and the higher is the critical energy transfer distance. The consequence of this is that the resulting Q_{ETE} of a system consisting from a large number of donor and acceptor fragments will be the higher; the larger is Q_{F} of the donor.

The results obtained under investigation of the optical properties of dilute molecular solutions of compounds **1−4** in THF are summarized in Table 1.

Comparing the optical properties of dendrimer **1** and "butterfly"-like compound **2**, one can see that the main difference is the intensity of the absorption in the terthiophene region that is about twice higher for the dendrimer. It can be explained by an increase of 3T/2T ratio in the dendrimer molecule. Thus, the dendrimer has more uniform absorption in the 280−430 nm region that could be an advantage for possible applications of such materials: in photonics for optical spectra conversion or in organic solar cells. High molar extinction coefficients ε of both compounds are also favorable for such kind of applications.

Optical Properties in Thin Films. Optical properties of compound **1** were further investigated in the solid state both in PMMA thin film and in the bulk. The results of the optical property investigation of a solid solution of compound **1** in PMMA thin film (thickness $d = 7\ \mu$m; concentration $C = 10^{-3}$ M) are presented in Figure 4. As can be seen the absorption and luminescence spectra of compound **1** both in THF and in PMMA coincides. In both cases the efficient electronic excitation energy transfer process from bi- to terthiophenesilane fragments is observed. Taking into account the contribution of the acceptor partial absorption on the wavelength of primary absorption of the donor (335 nm) the energy transfer efficiency is equal to 96 ± 4%. Therefore, for the solid solution of compound **1** in PMMA the same peculiarities of the energy transfer between the fragments of the oligothiophenesilane dendrimer can be observed as they were found in THF solutions.

Absorption and luminescence spectra of a thin (3−5 nm) film of compound **1** are shown in Figure 5. As can be seen, these spectra are different from the absorption and luminescence

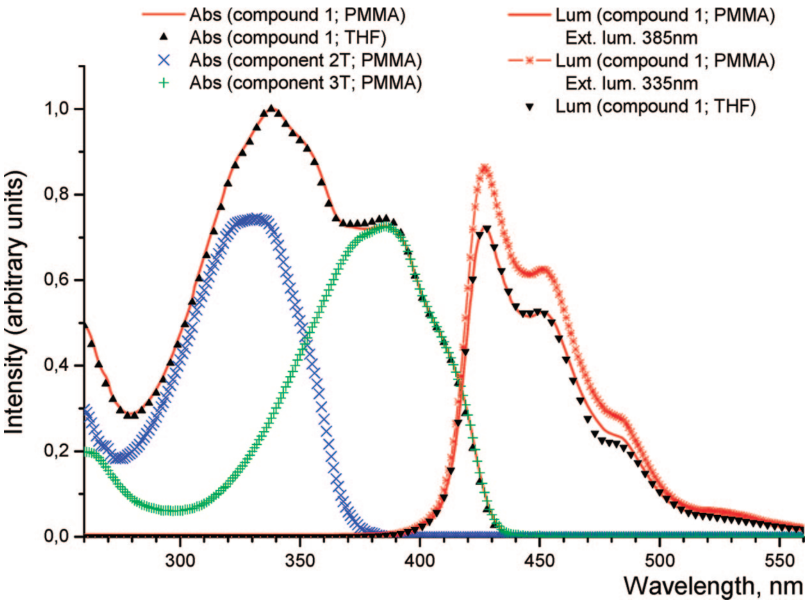

Figure 4. Absorption and luminescence spectra of compound **1** in PMMA thin film and THF solution. Model absorption spectra of 2T and 3T components of compound **1** are also shown.

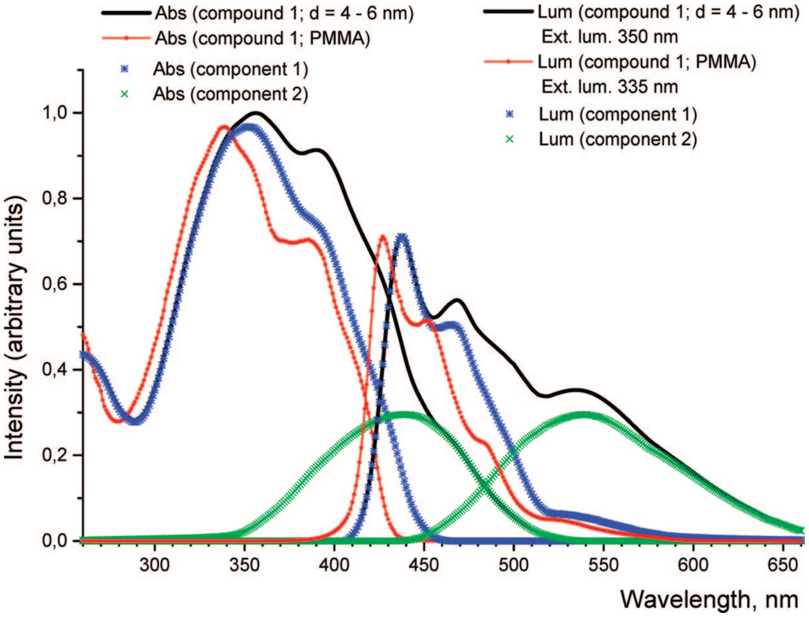

Figure 5. Absorption and luminescence spectra of thin film of compound **1** (*d* = 3−5 HM). Model absorption and luminescence spectra (components **1** and **2**).

spectra of compound **1** in THF or PMMA. The absorption spectra of the thin film of compound **1** can be presented as a sum of two absorption bands: a band close by the shape to the absorption band of compound **1** in PMMA (component **1** in Figure 5) and a weak unstructured band with the maxima at 440 nm (component **2** in Figure 5). The luminescence spectra of compound **1** can also be presented as a superposition of two bands: a band corresponding to the luminescence spectra of compound **1** in PMMA and a band with the intensity maxima at 550 nm, being a mirror symmetrical to the absorption spectra of component **2**. To estimate the energy efficiency transfer from bithiophenesilane fragments, which do not participate in the intermolecular complex formation, to terthiophenesilane fragments in the film being only 3−5 nm thick is not possible because of very weak (D = 0.04−0.06) absorption of the sample.

The peculiarities observed in the absorption and luminescence spectra of the thin film of compound **1** could be explained by interactions between the fragments of closely located dendritic molecules. Probably, fragments of the internal dendrimer sphere (terthiophenes), belonging to different molecules, interact only weakly. At the same time, the peripheral fragments (bithiophene), belonging to different dendritic molecules, could form intermolecular complexes (dimers). We suggest that the absorption and luminescent spectra of the first component in Figure 5 comes from terthiophenesilane fragments of compound **1**, which are isolated by the bithiophenesilane fragments of adjacent dendritic molecules. Obviously, the spectra of such fragments would be similar to the spectra of compound **1** in liquid or solid solution. Spectra of the second component could belong to complexes formed by bithiophenesilane fragments, which would not participate in the energy transfer of the electronic excitation. Most probably, the presence of such complexes will lead to quenching of the acceptor luminescence that follows from the mutual position of the absorption spectra of component **2** and luminescence spectra of component **1** in Figure 5.

Dendritic molecules are located sufficiently far from each other even at high concentrations in the "solid solution" of compound **1** in PMMA and therefore they do not interact. As a result the energy transfer efficiency from bi- to terthiophene fragments remains high and favors availability of branched oligothiophenesilane systems like compound **1** for solar light spectra conversion applications as solid solutions in transparent polymeric matrixes like it were discribed recently for other materials.[11] The advantage of our systems is high molar extinction coefficient in the region of 250−420 nm that permits their usage as thin film coatings to harvest this highly energetic part of solar spectra.

To sum up, we have successfully synthesized the first oligothiophenesilane dendrimer **1** and "butterfly"-like oligothiophenesilane **2**, both of which showed very effective energy transfer from the outer bithiophene to the internal terthiophenesilane units. The dendrimer has some advantages such as more uniform absorption in the 280−430 nm region and almost quantitative energy transfer efficiency due to specific structural organization of bi- and terthiophenesilane units in the 3-D dendritic architecture. Albeit an intramolecular energy transfer is known for different organic dendrimers and called as the "molecular antenna effect",[1,4] this work describes the first organosilicon molecular antennae. From the point of view of searching for an organic silicon[12] we believe that a combination of π-conjugated oligomers with the silicon units, for instance, in the oligothiophenesilane dendrimers, could be the right direction, and the results reported here are one of the first important contributions to it. The estimation of the materials properties of the oligothiophenesilane dendrimers in real devices of organic electronics and photonics is in progress now and will be in focus of our further publications.

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Supporting Information Available: ^{13}C- and ^{29}Si-NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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