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Branched oligothiophene silanes with the efficient nonradiative energy transfer between the fragments

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The synthesis of new dendrimers and branched oligothiophene silanes containing bithiophene groups at the periphery and quaterthiophene fragments at the center of the molecule is described. Specific features of bithiophene silane bromination were shown, and the conditions for the efficient synthesis of methyltris(5-bromo-2,2´-bithiophen-5-yl)silane have been found for the first time. The optical properties of the synthesized compounds were studied. The efficiency of the electron excitation energy transfer between the fragments of branched bi- and quaterthiophene silanes was measured.

Key words: oligothiophene silane dendrimers, bromination of bithiophene silanes, molecular antennas, nonradiative energy transfer.

Reports on the synthesis and study of the properties of the luminescent polymers[1,2] and dendrimers[3,4] appear presently with increasing frequency. Among the latter, systems with the nonradiative transfer of the electron excitation energy between different fragments of the macromolecule are of great interest. Since the ordered close arrangement of fluorescent fragments with appropriate spectral properties is possible within the same dendrimer macromolecule, one can obtain systems with the efficient transfer of the energy absorbed by many peripheral fragments to the center of fluorescence emission with a certain wavelength. Such dendritic systems are often named molecular antennas.[5,6]

The dendrimers in which the monothiopene fragments are at the periphery and the bithiopene (2T) fragments directly bound to the silicon atoms are located at the center of the macromolecule have been described earlier.[7,8] The dendrimers synthesized had the fluorescence spectrum similar to that of the 2T fragments and the absorption spectrum corresponding to the sum of the absorption spectra of the mono- and bithiophene fragments. However, no efficient energy transfer between the mono- and bithiophene fragments of the macromolecule was observed. Recently we synthesized[9] the dendrimer and branched oligothiophene silane containing the 2T groups at the periphery and terthiophene (3T) fragments at the center of the molecule. In these organosilicon systems, the phenomenon of nonradiative electron excitation energy transfer from the bi- to terthiopene fragments has been observed for the first time. The efficiency of the energy transfer was 97 and 91%, for the dendrimer and branched oligothiophene silane, respectively. The study of the optical properties of the dendrimers and branched oligothiophene silanes consisting of the mono-, bi-, and terthiophene fragments showed[8,9] no π-conjugation between the chromophore fragments linked by the silicon atom. The absence of π-conjugation makes it possible to consider the oligothiophene silane dendrimers as systems of structurally organized and weakly interacting chromophore fragments. The nonradiative electron excitation energy transfer between the fragments of such a system occurs due to the inductive resonance interaction. The calculation of the electron excitation energy transfer from the bi- to terthiophene fragments by the Förster—Galanin formulas[10,11] gave good coincidence with experiment in the case of both the bi/terthiophene silane dendrimer and the corresponding branched bi/terthiophene silane. Such systems can be considered as "active light filters" shifting the spectrum of the light passing through the filters by its re-emission in a longer-wavelength range. However, difference in the spectra of bi- and terthiopene in the earlier studied compounds are not too large (50 nm between the absorption maxima and 43 nm between the fluorescence maxima). On the one hand, this provides the efficient energy transfer between the fragments considered; on the other hand, this results in a small shift between the absorbed and reemitted light. The problem of extending the spectra range of such systems is urgent for both the estimation of the transfer efficiency in macromolecules with a large spectral shift between the luminophores and their practical use.

The purpose of the present work is the synthesis and study of the regularities of the electron excitation energy transfer between the fragments of dendrimer **1** and branched oligothiophene silane **2** containing the bithiophene

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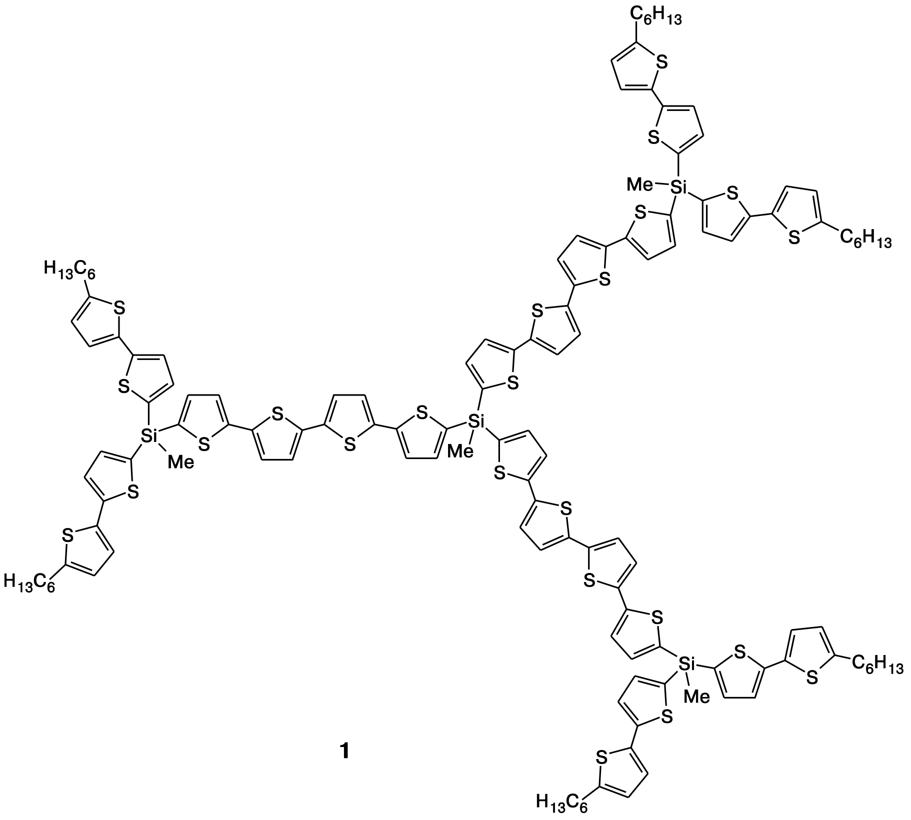
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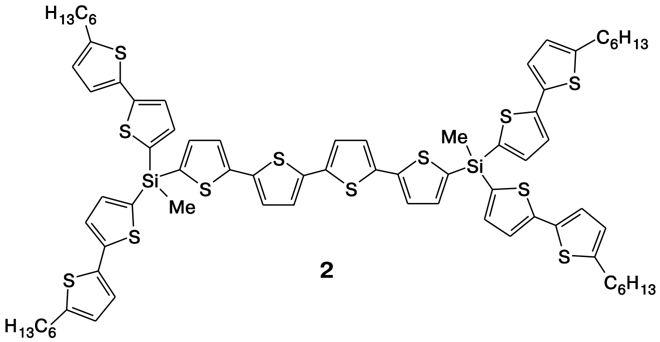
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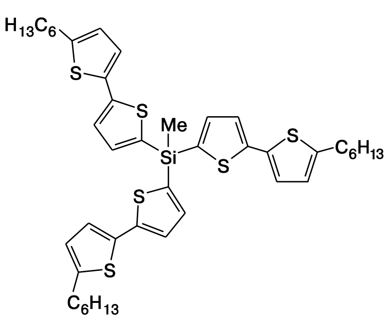
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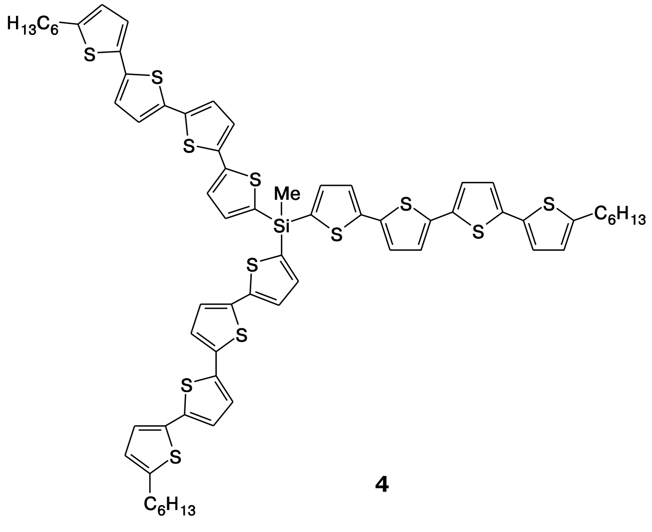
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4

groups at the periphery and the quaterthiophene (4T) fragments at the center of the macromolecule. Methyltris(5´-hexyl-2,2´-bithiophen-5-yl)silane (**3**) and methyltris(5´´´-hexyl-2,2´:5´,2″:5″,2´´´-quaterthiophen-5-yl)silane (**4**), being structural analogs of the fragments of the macromolecules considered, were used as objects for comparison.

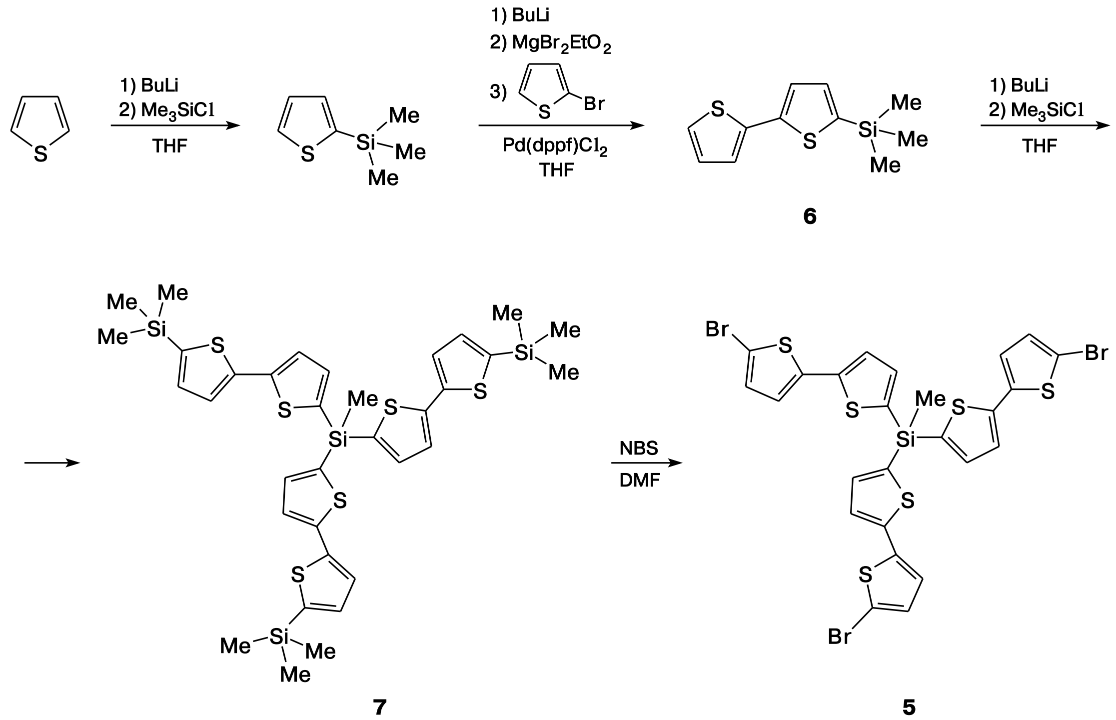
Results and Discussion

Dendrimer **1** and branched oligothiophene silane **2** were synthesized by the reactions of organoboron derivatives of thiophene silane monodendrons with bromo derivatives having the branched and linear structures following the Suzuki reaction similar to the scheme[7—9] used by us earlier for the preparation of other oligothiophene silane dendrimers.

In the case of dendrimer **1**, the branching center was methyltris(5´-bromo-2,2´-bithiophen-5-yl)silane (**5**), which was not described earlier. An attempt of the synthesis of such a compound according to the procedure used for the preparation of the trifunctional monothiophene silane branching center from 5-bromo-2-thienyllithium[7] was unsuccessful. Therefore, a basically new approach was proposed (Scheme 1). First, 2-thienyl(trimethyl)silane was synthesized in 76% yield using the described procedure.[12] Then it was lithiated with *n*-butyllithium to position 5. The lithium derivative obtained reacted with the ethereal complex of magnesium dibromide $MgBr_2 \cdot Et_2O$ to form the Grignard reagent. The interaction of the latter with 2-bromothiophene under the Kumada reaction conditions afforded 2,2´-bithiophen-5-yl(trimethyl)silane (**6**) in 89% yield. Then compound **6** was lithiated to position 5´ with *n*-butyllithium at –70 °C to form the lithium derivative, which was further reacted with methyltrichlorosilane with the formation of methyltris(5-trimethylsilyl-2,2´-bithiophen-5´-yl)silane (**7**) in 90% yield. Chromatographically pure compound **7** was isolated by column chromatography in 60% yield (Fig. 1, *a*).

In the next reaction, NBS was used as a brominating agent, which is often applied for the selective substitution of protons of oligothiophenes in positions 2(5) for bromine atoms.[13] The replacement of the trimethylsilyl groups in oligothiophenes and their derivatives by iodine atoms using iodine chloride is also described.[14] However, to the best of our knowledge, NBS has not earlier been used for the substitution of the trimethylsilyl groups for bromine in oligothiophenes. Moreover, as can be seen from the structural formula, two silicon atoms can be distinguished in compound **7**: external silicon atoms bound to three methyl groups and one bithiophene fragment and the internal silicon atom having one methyl group and three bithiophene fragments. In our opinion, this is the difference in environment which results in selective bromination with

Scheme 1



dppf is diphenylphosphinoferrocene, NBS is *N*-bromosuccinimide the complete replacement of the external trimethylsilyl groups by bromine atom, remaining uninvolved the bonds between the central silicon atom and surrounding three bithiophene fragments.

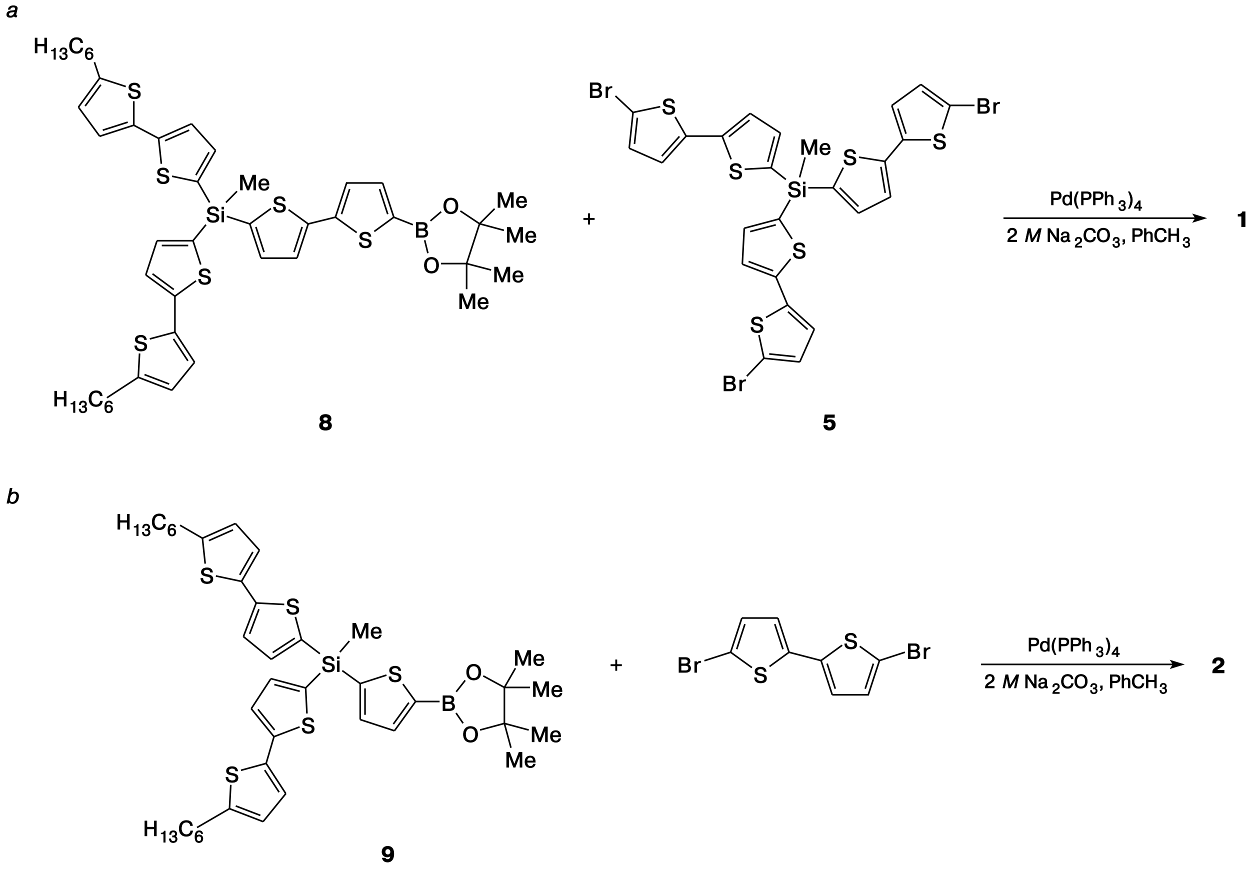
Due to rather high difference in sizes of the trimethylsilyl group and bromine atom (which results in a substantial difference in hydrodynamic radii of all intermediate and final bromination products), the reaction course was monitored by GPC. After three hours from the beginning of the synthesis, the reaction mixture contained 21% of intermediate product **I** with one bromine atom, 43% of intermediate product **II** with two bromine atoms, and 36% of trisubstituted product **III** (Fig. 1, *b*). The further occurrence of the reaction increased the content of reaction product **III** and decreased the amount of the intermediates (Fig. 1, *c*). According to the GPC data, the final reaction mixture contained 93% of the final product and 7% of the intermediate (Fig. 1, *d*). After column chromatography, pure compound **5** was isolated in 79% yield. It can be asserted on the basis of the data obtained that the bromination of compound **7** proceeds step by step with the replacement of one trimethylsilyl group, then of the second group, and finally of the third trimethylsilyl group.

The second necessary component for the synthesis of the dendrimer and branched oligothiophene silane is the organoboron derivative of thiophene silane monodendron. Compounds **8** and **9** were used as the second components for the synthesis of the dendrimer and branched oligothiophene silane, respectively. Details of the synthesis of these compounds have been described earlier.[8,9] Dendrimer **1** was synthesized by the reaction of compound **5** with 20% excess of compound **8** by the Suzuki reaction (Scheme 2, route *a*). According to the GPC data, 37% of target dendrimer **1** were formed upon refluxing for 90 h. The purification by preparative GPC allowed us to isolate dendrimer **1** in the pure form in 18% yield.

Commercially available 5,5´-dibromo-2,2´-bithiophene was used as a bromo derivative in the synthesis of branched oligothiophene silane **2** (Scheme 2, route *b*). After the completion of the Suzuki reaction, the reaction mixture contained 36% of branched oligothiophene silane **2**, according to the GPC analysis data. Purification by column chromatography gave the pure product in 21% yield.

The details of the synthesis of branched bithiophene silane **3** have been described previously.[15] The lithiation of 5-hexyl-2,2´-bithiophene with *n*-butyllithium followed by

Scheme 2



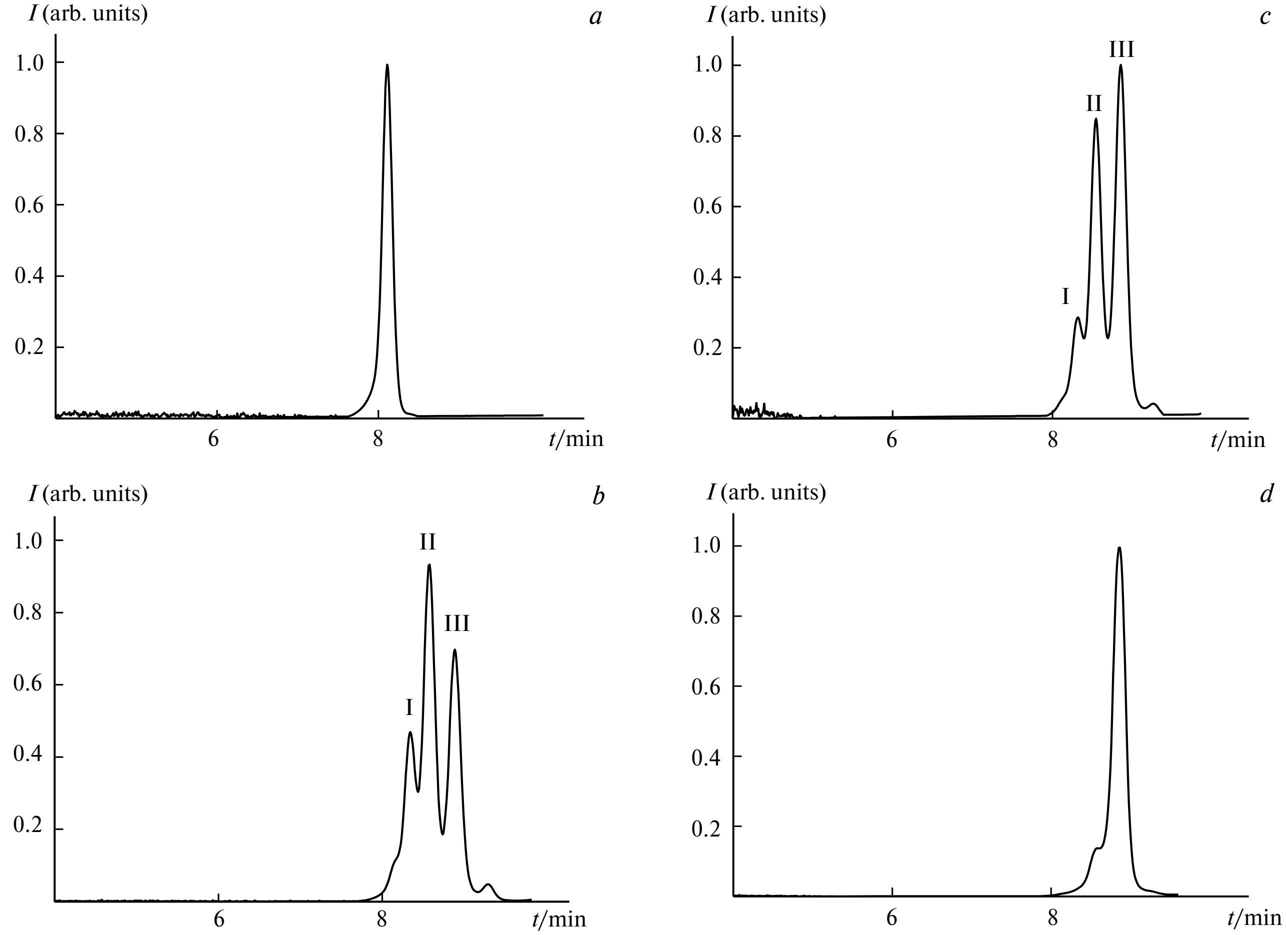


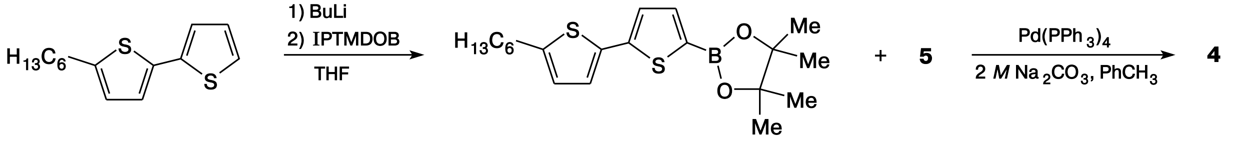
Fig. 1. GPC curves: compound **7** after purification (*a*), the reaction mixture after 3 h (*b*), 6 h (*c*), and the end of the reaction (*d*); **I**, **II**, and **III** are the mono-, bi-, and trisubstituted products, respectively; Phenogel 500 Å column, diode matrix as the detector, λ = 254 nm.

the exchange of lithium for the organoboron residue afforded[16] compound **10** in 96% yield. It was used in the Suzuki reaction with trifunctional branching center **5** to form branched quaterthiophene silane **4** (Scheme 3). After 68-h reflux, the yield was 85%. Purification was carried out by column chromatography and recrystallization. The yield of chromatographically pure compound **4** was 53%.

The structure and purity of intermediate and final compounds were confirmed by GPC analysis, ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy, and elemental analysis. The NMR spectra of all synthesized compounds contained all characteristic signals. The integral intensities of signals of protons at different structural fragments corresponded to the theoretically calculated values (see Experimental).

To study the optical properties of compounds **1** and **2**, the absorption and fluorescence spectra of their dilute solutions were measured. The fluorescence quantum yield was determined by comparison with the known quantum yields of the standards using the method of measuring fluorescence of dilute solutions.[17] Solutions of the fol-

Scheme 3



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IPTMDOB is 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane lowing compounds were used as standards: *p*-terphenyl ($\Phi_F = 0.90$), 2,5-diphenyloxazole (PPO, $\Phi_F = 0.91$), anthracene ($\Phi_F = 0.27$), 1,4-di(5-phenyloxazol-2-yl)benzene (POPOP, $\Phi_F = 0.98$), and rhodamine 6G ($\Phi_F = 0.94$). The quantum yield values of compounds **1** and **2** given in the present work are average, calculated with allowance for measurements relatively to each of five standards. In order to calculate the efficiency of the electron excitation energy transfer ($Q_{\text{ETE}}{}^{2\text{T}\to4\text{T}}$), we used the measured absorption and fluorescence spectra obtained upon the excitation with the light with the wavelength $\lambda^{2\text{T};4\text{T}}$, at which both the 2T and 4T fragments absorb the light, and with the light with the wavelength $\lambda^{4\text{T}}$, at which only the 4T fragments absorb. The fraction of the light absorbed by the 2T and 4T fragments in the region of overlap of their absorption spectra was determined by the decomposition of the total absorption spectrum to the components taking into account the spectral shape of the absorption bands of compounds **3** and **4**. The procedure of calculation of the efficiency of the electron excitation energy transfer between the fragments of the dendrite macromolecule and approaches of using absorption spectra of the model compounds have been described earlier.[9]

The absorption and fluorescence spectra of dilute solutions of compounds **1** and **2** in THF, as well as the fluorescence spectra of bi- and quaterthiophene silanes **3** and **4**, respectively, in the absence of electron excitation energy transfer are shown in Figs 2 and 3. It is well seen that the fluorescence spectra of compounds **1** and **2** coincide with the fluorescence spectrum of quaterthiophene silane **4** upon excitation at the absorption band maxima of both quaterthiophene (416 and 410 nm) and bithiophene (333 nm) fragments.

Thus, the character of fluorescence of the synthesized compounds indicates the efficient transfer of the energy absorbed by the bithiophene fragments to the quaterthiophene fragments. The integral fluorescence intensity divided into the absorption coefficient of the exciting radiation is somewhat lower upon excitation to the absorption region of the bithiophene fragments than upon the excitation of only the quaterthiophene fragments. Therefore, the energy transfer efficiency is lower than 100%. The calculations taking into account the fraction of radiation absorbed by the bi- and quaterthiophene fragments give the efficiency of the transfer equal to 94 and 85% for compounds **1** and **2**, respectively.

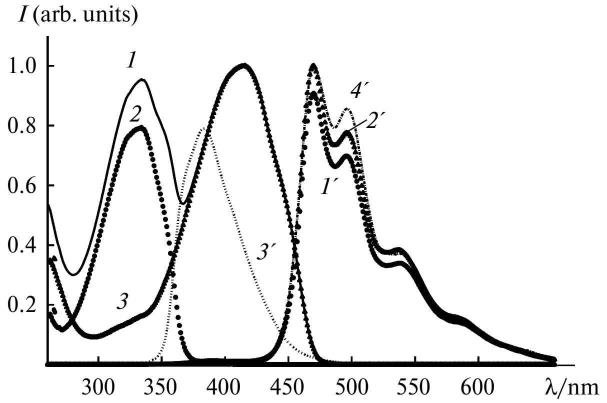

Fig. 2. Absorption (*1—3*) and fluorescence (*1´—4´*) spectra of compounds **1**, **3**, and **4** in THF: the absorption of compound **1** (*1*) and bithiophene (*2*) and quaterthiophene fragments (*3*); the fluorescence of compound **1** at $\lambda_{\text{exc}} = 333$ (*1´*) and 416 nm (*2´*) and of compounds **3** (*3´*) and **4** (*4´*).

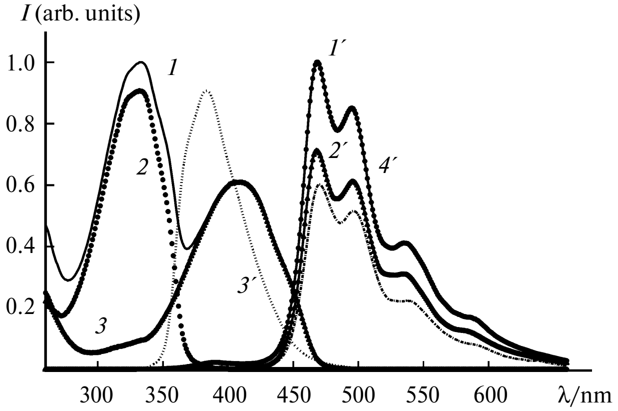

Fig. 3. Absorption (*1—3*) and fluorescence (*1´—4´*) spectra of compounds **2**, **3**, and **4** in THF: the absorption of compound **2** (*1*) and bithiophene (*2*) and quaterthiophene fragments (*3*); the fluorescence of compound **2** at $\lambda_{\text{exc}} = 333$ (*1´*) and 410 nm (*2´*) and of compounds **3** (*3´*) and **4** (*4´*).

The results obtained by the study of the optical properties of dilute molecular solutions of compounds **1—4** in THF are listed in Table 1.

It seems interesting to compare the obtained data with the results of studying the optical properties of the dendrimer and branched oligothiophene silane containing the bithiophene fragments at the periphery and the terthiophene fragments at the center of the macromolecule.[9] As in the macromolecules with the bi- and terthiophene fragments and in the compounds with the bi- and quaterthiophene, the molar absorption coefficients of the corresponding bands are equal to the sum of the absorption coefficients of the fragments. In the both cases, the fluorescence quantum yield of the fragments, which are energy acceptors, corresponds to that of the respective to model compound. The spectral distribution of fluorescence photons upon the excitation of both the donating fragments and the fragments acting as energy acceptors corresponds to the fluorescence spectrum of the corresponding energy acceptor. The efficiency of the energy transfer in the systems with the quaterthiophene fragments as an energy acceptor is by 3—4% lower than that in the systems with the terthiophene fragments. Probably, this is due to the larger length of the quaterthiophene fragments, because the efficiency of the transfer following the dipole-dipole

Table 1. Results of studying the optical properties* of the synthesized compounds

Compound	$\lambda^{abs}{}_{max}$/nm	$\varepsilon \cdot 10^{-3}$ /L mol^{-1} cm^{-1}	Q_F (%)	$\lambda^{fl}{}_{max}$/nm	Q_{ETE} (%)
1	334±1	126±9	12±2	470±1.5	94±3
	416±1	138±10	13±2	496±1.5	—
				537±1.5	—
2	333±1	80±7	11±2	468±1.5	87±3
	408±1	48±4	13±2	496±1.5	—
				534±1.5	—
3	332±1	61±6	19±3	384±1.5	—
4	412±1	138.3±10	13±2	469±1.5	—

* $\lambda^{abs}{}_{max}$ and $\lambda^{fl}{}_{max}$ are the wavelengths of the absorption and fluorescence maxima.

mechanism depends substantially on the distance between the energy donor and acceptor.

So, its can be assumed that the synthesized compounds and those studied earlier[9] are molecular dendritic antennas with the efficient electron excitation energy transfer following the Förster—Galanin mechanism. Therefore, in the synthesis of the oligothiophene silanes, one can beforehand estimate the efficiency of the energy transfer between the fragments using for this purpose the Förster—Galanin expression and the spectral data for the compounds modeling the corresponding energy donors and acceptors of the fragments of the system.

Thus, in the present work we synthesized for the first time dendrimer **1** and branched oligothiophene silane **2** containing the bithiophene fragments at the periphery and the quaterthiophene fragments at the center of the macromolecule, as well as star-like quaterthiophene silane **4**. The new scheme for the synthesis of the bromo derivatives of bithiophene silanes by the replacement of the trimethylsilyl groups by *N*-bromosuccinimide was developed. The efficient energy transfer from the peripheral group of the dendritic molecules to the internal groups was demonstrated.

Experimental

Solutions of butyllithium in hexane (1.6 and 2.5 mol L^{-1}), thiophene, 2-bromothiophene, *N*-bromosuccinimide, and 5,5´-dibromo-2,2´-bithiophene (Acros), as well as 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (IPTMDOB) and tetrakis(triphenylphosphine)palladium(0) Pd(PPh$_3$)$_4$ (Aldrich), were used as received. Methyltrichlorosilane and trimethylchlorosilane were distilled prior to use; THF and diethyl ether were pre-dried over calcium hydride and dehydrated by distillation over lithium aluminum hydride.

^{1}H NMR spectra were recorded on a Bruker WP-250 SY spectrometer (250.13 MHz) using Me$_4$Si as the internal standard. ^{13}C and ^{29}Si NMR spectra were obtained on a Bruker DRX500 spectrometer. GPC analysis was carried out on a Shimadzu instrument (Japan), a RID-10A refractometer and an SPD-M10AVP diode matrix served as detectors (Phenomenex column (USA) 7.8×300 mm in size packed with the Phenogel sorbent with the pore size 500 Å, THF as the eluent).

Absorption and luminescence spectra were measured in a range of 200—600 nm in dilute THF solutions with the concentration 10^{-5}—10^{-6} mol L^{-1} to avoid self-absorption. Absorption spectra were recorded on a Shimadzu UV-2501PC spectrophotometer (Japan). An ALS01M multifunctional adsorption luminescence spectrometer was used for the measurement of luminescence. The three-channel optical system was used in the spectrometer for the synchronous measurement of electronic absorption, excitation and luminescence (fluorescence or phosphorescence) spectra of the samples. The high sensitivity to low concentrations of luminescent substances was achieved by the use of the method of single photon counting in successive time intervals with an automated control of the measured radiation intensity.

All reactions, if not otherwise stated, were carried out under an inert atmosphere and in anhydrous solvents. The solvent was removed by evacuation (down to 1 Torr) on heating to 40 °C.

2-Thienyl(trimethyl)silane was synthesized from thiophene (38.11 g, 0.453 mol), a 2.5 *M* solution of BuLi in hexane (151 mL, 0.377 mol), and trimethylchlorosilane (41.08 g, 0.377 mol) according to an earlier described procedure.[12] According to the GPC analysis, after the end of the reaction the mixture contained 82% of the product. Pure 2-thienyl(trimethyl)silane (45 g, 76%) was isolated after distillation, b.p. 165—168 °C (748 Torr). ^{1}H NMR (CDCl$_3$), δ: 0.32 (s, 9 H, Me$_3$Si); 7.19 (dd, 1 H, H(4), J_1 = 3.1 Hz, J_2 = 4.3 Hz); 7.27 (dd, 1 H, H(5), J_1 = 1.2 Hz, J_2 = 3.1 Hz); 7.60 (dd, 1 H, H(3), J_1 = 4.3 Hz, J_2 = 1.2 Hz).

2,2´-Bithiophen-5-yl(trimethyl)silane (6). Tetrahydrofuran (70 mL) was added dropwise to a 2.5 *M* solution (30.71 mL) of BuLi in hexane (75.8 mmol), maintaining the temperature below –10 °C. Then a solution of 2-thienyl(trimethyl)silane (12 g, 75.8 mmol) in THF (90 mL) was added slowly, maintaining the temperature in the interval from –10 to 0 °C. An ethereal solution of the complex of magnesium bromide with ether (freshly prepared from magnesium (2.32 g, 97 mmol) and dibromoethane (8 mL, 92 mmol) in 40 mL of anhydrous ether) was poured to the obtained lithium derivative. The resultant Grignard reagent was added dropwise to a solution of the Pd(dppf)Cl$_2$ catalyst (0.17 g, 0.23 mmol) and 2-bromothiophene (12.51 g, 77 mmol) in THF (150 mL) at 0—10 °C. After heating to ~20 °C, the reaction mixture was stirred for 2 h. According to the GPC analysis, after the standard isolation the reaction mixture contained 89% of the product. The purification was carried out by column chromatography with silica gel (hexane as the eluent) followed by distillation *in vacuo*. Pure compound **6** was obtained in a yield of 12.03 g (67%). ^{1}H NMR (DMSO—CCl$_4$), δ: 0.31 (s, 9 H, Me$_3$Si); 7.02 (dd, 1 H, H(4′), J_1 = 3.7 Hz, J_2 = 5.5 Hz); 7.13 (d, 1 H, H(4), J = 3.7 Hz); 7.20 (dd, 1 H, H(3′), J_1 = 1.2 Hz, J_2 = 3.7 Hz); 7.23 (d, 1 H, H(3), J = 3.7 Hz); 7.34 (dd, 1 H, H(5′), J_1 = 1.2 Hz, J_2 = 5.5 Hz). ^{13}C NMR (CDCl$_3$), δ: 0.36; 124.25; 124.83; 125.49; 128.24; 135.16; 137.89; 140.23; 142.88. ^{29}Si NMR (CDCl$_3$), δ: –6.37. Found (%): C, 55.38; H, 6.01; S, 26.98; Si, 11.58. $C_{11}H_{14}S_2Si$. Calculated (%): C, 55.41; H, 5.92; S, 26.89; Si, 11.78.

Methyltris(5-trimethylsilyl-2,2′-bithiophen-5′-yl)silane (7). A 2.5 *M* solution (5 mL) of butyllithium in hexane was added dropwise to a solution of compound **6** (3.12 g, 0.013 mol) in THF (50 mL), maintaining the temperature below –55 °C. Then the temperature was increased to 0 °C, the mixture was cooled to –75 °C, after which methyltrichlorosilane (0.47 mL, 0.004 mol) was poured, and the mixture was stirred for 30 min at –73 °C. According to the GPC analysis, the reaction mixture contained 90% of silane **7**. To isolate this compound, the mixture was poured to 200 mL of ice-cold water and 300 mL of freshly distilled diethyl ether. The organic layer was washed with distilled water (3×100 mL), dried over sodium sulfate, and concentrated on a rotary evaporator. The purification was carried out by column chromatography with silica gel (toluene—hexane (1 : 10) mixture as the eluent). Pure compound **7** was obtained in a yield of 1.74 g (58%). ^{1}H NMR (DMSO—CCl$_4$), δ: 0.30 (s, 27 H); 0.95 (s, 3 H); 7.15 (d, 3 H, H(3), J = 3.7 Hz); 7.30 (d, 3 H, H(4), J = 3.7 Hz); 7.32 (d, 3 H, H(4′), J = 3.7 Hz); 7.34 (d, 3 H, H(3′), J = 3.7 Hz). ^{13}C NMR (CDCl$_3$), δ: 0.32; 0.36; 125.64; 126.01; 134.31; 135.21; 138.34; 140.87; 142.38; 145.04. ^{29}Si NMR (CDCl$_3$), δ: –25.18, –6.29. Found (%): C, 54.09; H, 5.68; S, 25.64; Si, 14.78. $C_{34}H_{42}S_6Si_4$. Calculated (%): C, 54.06; H, 5.60; S, 25.47; Si, 14.87.

Methyltris(5′-bromo-2,2′-bithiophen-5-yl)silane (5). To a solution of compound **7** (1.00 g, 1.32 mmol) in DMF NBS (1.06 g, 5.9 mmol) was added in the dark at 0—10 °C. After the end of the reaction, the reaction mixture was poured to a mixture of ice-cold water (100 mL) and freshly distilled diethyl ether (100 mL). The organic layer was washed with distilled water (3×100 mL), dried over sodium sulfate, concentrated on a rotary evaporator, and purified by column chromatography (toluene—hexane (1 : 5) mixture as the eluent). After purification the product was isolated in a yield of 0.810 g (79%). ^{1}H NMR (CDCl$_3$), δ: 0.96 (s, 3 H); 6.96 (d, 3 H, H(3), J = 3.7 Hz); 6.98 (d, 3 H, H(4), J = 3.7 Hz); 7.16 (d, 3 H, H(4′), J = 3.7 Hz); 7.31 (d, 3 H, H(3′), J = 3.7 Hz). ^{13}C NMR (CDCl$_3$), δ: 0.12; 112.12; 124.90; 125.85; 131.17; 134.45; 138.38; 138.77; 144.07. ^{29}Si NMR (CDCl$_3$), δ: –25.01. Found (%): C, 38.77; H, 1.92; Br, 30.77; S, 24.73; Si, 3.64. $C_{25}H_{15}Br_3S_6Si$. Calculated (%): C, 38.72; H, 1.95; Br, 30.91; S, 24.81; Si, 3.62.

Methyltris{5′-[methylbis(5′-hexyl-2,2′-bithiophen-5-yl)silyl]-2,2′:5′,2″:5″,2‴-quaterthiophen-5‴-yl}silane (1). Solutions of compound **8** (1.04 g, 1.25 mmol) and compound **5** (0.269 g, 0.35 mmol) in toluene (30 mL) and a 2 *M* solution of Na$_2$CO$_3$ (1.9 mL) were poured into a flask containing Pd(PPh$_3$) (72 mg, 0.06 mmol), and the mixture was heated to boiling. The reaction mixture was refluxed for 90 h, anhydrous toluene (30 mL) was added, and a toluene—water azeotropic mixture was distilled off. The product was purified by column chromatography (toluene as the eluent) followed by recrystallization from a toluene—hexane (1 : 2) mixture. Pure dendrimer **1** was isolated in a yield of 0.186 g (18%). ^{1}H NMR (DMSO—CCl$_4$), δ: 0.87 (t, 18 H, J = 6.7 Hz); 0.92 (s, 9 H); 0.94 (s, 3 H); 1.22—1.42 (m, 36 H); 1.62 (m, 12 H, J = 7.3 Hz); 2.73 (t, 12 H, J = 7.3 Hz); 6.69 (d, 6 H, J = 3.7 Hz); 7.04 (d, 6 H, J = 3.7 Hz); 7.16—7.27 (m, 18 H); 7.28—7.43 (m, 18 H). ^{13}C NMR (CDCl$_3$), δ: –0.27; –0.20; 14.10; 22.56; 28.72; 30.14; 31.52; 31.54; 123.97; 124.34; 124.37; 124.40; 124.83; 124.93; 125.05; 125.08; 125.12; 132.77; 133.78; 134.24; 134.39; 135.74; 135.92; 136.18; 136.34; 137.85; 137.99; 143.96; 144.19; 145.18; 145.95. ^{29}Si NMR (CDCl$_3$), δ: –25.28, –25.13. Found (%): C, 61.79; H, 5.29; S, 28.83; Si, 4.23. $C_{136}H_{138}S_{24}Si_4$. Calculated (%): C, 61.54; H, 5.24; S, 28.99; Si, 4.23.

5,5‴-Bis[bis(5′-hexyl-2,2′-bithiophenyl-5-yl)(methyl)silyl]-2,2′:5′,2″:5″,2‴-quaterthiophene (2). The synthesis was carried out similarly to the previous procedure from compound **9** (0.45 g, 0.6 mmol), 5,5′-dibromo-2,2′-bithiophene (0.085 g, 0.26 mmol), and Pd(PPh$_3$)$_4$ (35 mg, 0.03 mmol). The reaction mixture was refluxed for 86 h and poured into a separatory funnel containing toluene (50 mL) and water (100 mL). The organic layer was washed to the neutral pH of the medium and dried over Na$_2$SO$_4$, and the solvent was evaporated. The product was purified by column chromatography (toluene—hexane (1 : 5) mixture as the eluent). Pure compound **2** was isolated in a yield of 0.078 g (21%). ^{1}H NMR (CDCl$_3$), δ: 0.88 (t, 12 H, J = 6.7 Hz); 0.93 (s, 6 H); 1.21—1.41 (m, 24 H); 1.66 (m, 8 H, J = 7.3 Hz); 2.77 (t, 8 H, J = 7.3 Hz); 6.66 (d, 4 H, J = 3.7 Hz); 7.01 (d, 4 H, J = 3.7 Hz); 7.05 (d, 2 H, J = 3.7 Hz); 7.10 (d, 2 H, J = 3.7 Hz); 7.18 (d, 4 H, J = 3.7 Hz); 7.24—7.33 (m, 8 H). ^{13}C NMR (CDCl$_3$), δ: –0.20; 14.09; 22.56; 28.72; 30.14; 31.52; 31.54; 123.97; 124.34; 124.82; 124.95; 125.07; 132.78; 134.24; 134.38; 135.88; 136.23; 137.84; 143.98; 145.18; 145.95. ^{29}Si NMR (CDCl$_3$), δ: –25.27. Found (%): C, 62.98; H, 5.85; S, 27.04; Si, 4.00. $C_{74}H_{82}S_{12}Si_2$. Calculated (%): C, 62.93; H, 5.85; S, 27.24; Si, 3.98.

Methyltris(5′-hexyl-2,2′:5′,2″:5″,2‴-quaterthien-5-yl)silane (4). The synthesis was carried out similarly to the procedure of synthesis of compound **1** from compound **10** (0.80 g, 2.12 mmol), compound **5** (0.42 g, 0.55 mmol), and Pd(PPh$_3$)$_4$ (125 mg, 0.11 mmol). The reaction mixture was refluxed for 68 h, after which anhydrous toluene was added and a toluene—water azeotropic mixture was distilled off. The product was purified by column chromatography (toluene as the eluent) and recrystallization. Pure compound **4** was isolated in a yield of 0.37 g (53%). ^{1}H NMR (CDCl$_3$), δ: 0.88 (t, 9 H, J = 6.7 Hz); 0.96 (s, 3 H); 1.23—1.43 (m, 18 H); 1.67 (m, 6 H, J = 7.3 Hz); 2.79 (t, 6 H, J = 7.3 Hz); 6.67 (d, 3 H, J = 3.7 Hz); 6.96 (d, 3 H, J = 3.7 Hz); 6.98 (d, 3 H, J = 3.7 Hz); 7.04 (d, 6 H, J = 3.7 Hz); 7.11 (d, 3 H, J = 3.7 Hz); 7.26 (d, 3 H, J = 3.7 Hz); 7.33 (d, 3 H, J = 3.7 Hz). Found (%): C, 61.64; H, 5.18; S, 30.03. $C_{67}H_{66}S_{12}Si$. Calculated (%): C, 62.67; H, 5.18; S, 29.96.

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References

1. J. M. Lupton, in *Organic Light Emitting Devices. Synthesis, Properties and Applications*, Eds K. Müllen, U. Scherf, Wiley-VCH Verlag GmbH & Co. KgaA, Weinheim, 2006, Ch. 8, p. 215.
2. Y. Shirota, *J. Matter. Chem.*, 2000, **10**, 1.
3. A. Adronov, J. M. J. Fréchet, *Chem. Commun.*, 2000, **18**, 1701.
4. S. A. Ponomarenko, O. V. Borshchev, Yu. N. Luponosov, A. M. Muzafarov, *Vse materialy. Entsiklopedicheskii spravochnik* [*All Materials. Encyclopaedic Handbook*], 2008, **2**, 13 (in Russian).
5. C. Devadoss, P. Bharathi, J. S. Moore, *J. Am. Chem. Soc.*, 1996, **118**, 9635.
6. M. R. Shortreed, S. F. Swallen, Z.-Y. Shi, W. Tan, Z. Xu, C. Devadoss, J. S. Moore, R. Kopelman, *J. Phys. Chem. B*, 1997, **101**, 6318.
7. S. A. Ponomarenko, A. M. Muzafarov, O. V. Borshchev, E. A. Vodop´yanov, N. V. Demchenko, V. D. Myakushev, *Izv. Akad. Nauk*, *Ser. Khim.*, 2005, 673 [*Russ. Chem. Bull., Int. Ed.*, 2005, **54**, 684].
8. O. V. Borshchev, S. A. Ponomarenko, N. M. Surin, M. M. Kaptyug, M. I. Buzin, A. P. Pleshkova, N. V. Demchenko, V. D. Myakushev, A. M. Muzafarov, *Organometallics*, 2007, **26**, 5165.
9. Y. N. Luponosov, S. A. Ponomarenko, N. M. Surin, O. V. Borshchev, E. A. Shumilkina, A. M. Muzafarov, *Chem. Mater.*, 2009, **21**, 447.
10. T. Förster, *Discuss. Faraday Soc.*, 1959, **27**, 7.
11. M. D. Galanin, I. M. Frank, *Zh. Eksp. Teor. Fiz.*, 1951, **21**, 114 [*J. Exp. Theor. Phys.* (*Engl. Transl.*), 1951, **21**].
12. R. A. Benkeser, R. B. Currie, *J. Am. Chem. Soc.*, 1948, **70**, 1780.
13. P. Baeuerle, F. Wuerthner, G. Goetz, F. Effenberger, *Synthesis*, 1993, 1099.
14. C.-Q. Ma, E. Mena-Osteritz, T. Debaerdemaeker, M. M. Wienk, R. A. J. Janssen, P. Bauerle, *Angew. Chem., Int. Ed.*, 2007, **46**, 1679.
15. E. A. Shumilkina, O. V. Borshchev, S. A. Ponomarenko, N. M. Surin, A. P. Pleshkova, A. M. Muzafarov, *Mendeleev Commun.*, 2007, **17**, 34.
16. S. A. Ponomarenko, E. A. Tatarinova, A. M. Muzafarov, S. Kirchmeyer, L. Brassat, A. Mourran, M. Moeller, S. Setayesh, D. de Leeuw, *Chem. Mater.*, 2006, **18**, 4101.
17. G. A. Crosby, J. N. Demas, *J. Phys. Chem.*, 1971, **75**, 991.

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