Rational Design of Dendritic Organic Electronic Semiconductors – Comparative Analysis of the Structure and Phase Behavior of Carbosilane Dendrimers Based on α-α'-Dilakylquatrothiophene

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Methods of synthesis

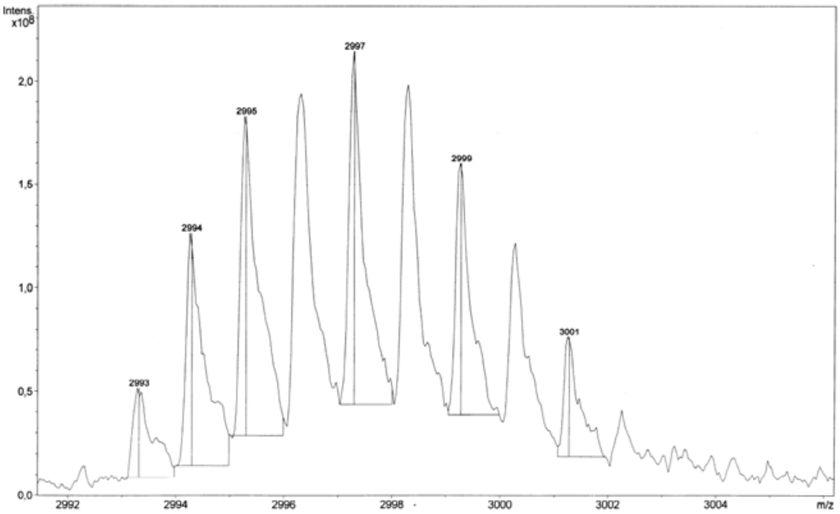

Figure 1. The MALDI-MS spectrum of a quaterthiophene-containing carbosilane dendrimer **1.**

Tetraallylsilane and polyallylcarbosilane dendritic matrices were prepared as described in ISPM RAS procedure [Ponomarenko S.A., Rebrov E.A., Boyko N.I., Muzafarov A.M., Shibaev V.P. Synthesis of liquid-crystal carbosilane dendrimers of the first to fifth generations containing terminal cyanobiphenyl groups // Vysokomolek. soed. 1998. T.40. P.1253-1265].

THF and diethyl ether were dried over CaH_2 and absolutized over $LiAlH_4$. Hexane was also dried over CaH_2. DMFA was dried over BaO. Toluene was dried over sodium.

Unless otherwise indicated, all reactions were carried out in inert atmosphere using anhydrous solvents. Before carrying out the reactions, the glassware was kept in an oven at 150°C for 2 hours, then it was collected hot and cooled in a stream of argon.

3,3',3",3'''-[Silantetrayltetrakis(propane-3,1-diyl)]tetrakis{1-[11-(5'''-hexyl-2,2':5',2":5",2'''-quaterthiophen-5-yl)undecyl]-1,1,3,3-tetramethyldisiloxane} (1).

Method A:

In a 100 ml three-necked flask equipped with a magnetic stirrer, a cooler and a septum filled with argon, 380 mg of compound **10** (0.16 mmol), 83 mg of $Pd(PPh_3)_4$ (0.07 mmol) and degassed solutions of 270 mg of compound **7** (0.72 mmol) were placed in 20 ml of toluene and 2 ml (4 mmol) of a 2M aqueous solution of Na_2CO_3. The reaction mixture was stirred at boiling for 30 h. The reaction was monitored for completeness by GPC analysis. After completion of the reaction, the contents were poured into a mixture of 100 ml of water, 6 ml of 1M hydrochloric acid solution and 200 ml of toluene. The organic layer was separated, washed with water and dried over anhydrous sodium sulfate. After removal of the solvent and drying in vacuum (1 mbar), 690 mg of a dark green solid were obtained. The crude product was purified by column chromatography on silica gel (eluent: toluene), followed by recrystallization from a mixture of hexane and toluene. According to GPC, the final product contained 98% of compound **1**. Yield: 250 mg (51%). MALDI MS (α-cyano-4-hydroxycinnamic acid, $[M+H]^+$): 2997. Calculated (%) for $C_{160}H_{244}O_4S_{16}Si_9$: 2997.52, C 64.11, H 8.20, Si 8.43, S 17.11. Found (%): C 64.11, H 8.40, Si 8.37, S 17.04. ^1H-NMR (250 MHz, $CDCl_3$, δ, ppm, *J*/Hz): 0.02 (48H, s), 0.40-0.65 (24H, overlapping peaks), 0.89 (12H, t, *J* = 6.9), 1.16-1.45 (96H, overlapping peaks with a maximum at 1.27 ppm), 1.66 (16H, m, *J* = 7.5), 2.77 (16H, t, *J* = 7.5), 6.67 (8H, d, *J* = 3.7), 6.93 -6.98 (16H, overlapping peaks), 7.00 (8H, d, *J* = 3.7).

Method B:

In a 100 ml three-neck flask, equipped with a refrigerator, a valve for argon in/out from the refrigerator, a stopper and a magnetic stirrer, 700 mg (1.0 mmol) of compound **13** were added and filled with argon. Then, in a stream of argon, a solution of 38.5 mg ($2.0\cdot10^4$ mol) of tetraallylsilane in 20 ml of absolute toluene was added. The reaction mixture was heated until complete dissolution of the reagents (40°C) and was degassed by careful vacuuming to boiling of toluene with the refrigerator switched on, followed by filling the reaction flask with argon. Then 10 µl of Karsted catalyst ($1.0\cdot10^{-6}$ mol Pt) was added. The reaction mixture was stirred in argon at 50°C for 16 hours. To isolate the product, the reaction mixture was poured onto a column of silica gel (75 ml) in hot toluene (60°C). A brown precipitate fell out of the first fraction (100 ml) while cooling, which was filtered and dried, yielding 318 mg (63% of theory) of a product containing 28.73% of a fully substituted dendrimer, 19.45% of a dendrimer with the replacement of three of the four groups, 15.61% of dimer, 2.13% of silane, 14.18% of monomer and 19.90% of high molecular weight products (didendrimer and more). Pure dendrimer **1** was isolated by preparative GPC (column 10^4 Å, eluent: THF, 40°C). Yield: 63 mg (11% of theory). ^{1}H-NMR ($CDCl_3$, TMS, ppm, *J*/Hz): 0.02 (48H, s), 0.40-0.65 (24H, overlapping peaks), 0.89 (12H, t, *J* = 6.9), 1.16-1.45 (96H, overlapping peaks with a maximum at 1.27 ppm), 1.66 (16H, m, *J* = 7.5), 2.77 (16H, t, *J* = 7.5), 6.67 (8H, d, *J* = 3.7), 6.93-6.98 (16H, overlapping peaks), 7.00 (8H, d, *J* = 3.7).

G1(Und-4T-Hex) - compound 2 was obtained according to the procedure described above for compound **1** (**Method B**) from 1.33 g (1.9 mmol) of compound **13**, 120 mg ($1.7 \cdot 10^{-4}$ mol) of the G1(Allyl)$_8$ polyallylcarbosilane dendrimer and 25 µl of Karsted catalyst ($3.5 \cdot 10^6$ mol Pt) in 40 ml of absolute toluene. The reaction mixture was stirred in argon at 70°C for 30 h. According to GPC, the reaction yield was 63% (taking into account the use of a 40% excess of silane **13**). To isolate the product, the reaction mixture, which is a frozen gel at room temperature, was heated to 80°C to completely dissolve and form a clear, light yellow solution and passed through a column of silica gel (50 ml) in toluene at 55°C. The first 150 ml were evaporated and dried in a vacuum oven at 50°C. 1.43 g of light yellow crystals were obtained, containing 44% of dendrimer, 7% of didendrimer, 20% of dimer, 23% of monomer and 6% of impurity, according to GPC. Pure dendrimer **2** was isolated by preparative GPC (column 104 Å, eluent: THF, 40°C). Yield: 560 mg (39% of theory). According to the results of ^{1}H-NMR analysis, the product contains ~15% of the double bond, i.e. seven groups of eight were replaced on average. Elemental analysis: calculated for $C_{336}H_{528}O_8S_{32}Si_{21}$ (%): C, 63.91; H, 8.48; S, 16.25; Si, 9.34. Found: C, 62.98; H, 8.76; S, 14.66; Si, 10.94. Deviations from the calculated values by 1.5–2% also indicate incomplete substitution in the reaction product. MALDI MS: 6301 (M^+), 5601 (M^+ - 700), 5901 (M^+ - 1400), 4201 (M^+ - 2100).

G3(Und-4T-Hex) - compound 3 was obtained according to the procedure described above for compound **1** (**Method B**) from 1.26 g (1.8 mmol) of compound **13**, 144 mg ($4.0 \cdot 10^{-5}$ mol) of the G3(allyl)32 polyallylcarbosilane dendrimer and 25 µl of Karsted catalyst ($3.5 \cdot 10^{-6}$ mol Pt) in 40 ml of absolute toluene. The reaction mixture was stirred in argon at 70°C for 10 h. According to GPC, the reaction yield was 35% (taking into account the use of a 40% excess of silane **13**). To isolate the product, the reaction mixture, being a frozen gel at room temperature, was heated to 80°C to completely dissolve and form a clear, light yellow solution, then it was passed through a column of silica gel (50 ml) in toluene at 55°C. The first 150 ml were evaporated and dried in a vacuum oven at 50°C. 1.23 g of light yellow crystals were obtained, containing 25% of dendrimer, 7% of didendrimer, 38% of dimer, 14% of monomer and 6% of impurity in it, according to GPC. Pure dendrimer **3** isolated by preparative GPC (column 104 Å, eluent: THF, 40ºC). Yield: 321 mg (31% of theory). According to the results of ^{1}H-NMR analysis, the product contains ~ 40% of double bond, i.e. 19 groups out of 32 were replaced on average. Elemental analysis. Calculated for $C_{1392}H_{2218}O_{32}S_{128}Si_{93}$ (%): C, 63.86; H 8.54; S, 15.67; Si, 9.98. Found: C 59.93; H 8.52; S, 12.18; Si, 13.01. Deviations from the calculated values by 3-4% also indicate incomplete substitution in the reaction product. MALDI MS: 16279 (M^+ - 14×700), which corresponds to the product with the substitution of 18 groups of 32 (the calculated value for the product of full substitution M^+ = 26028).

G5(Und-4T-Hex) - compound 4. A solution of 702 mg (1.0 mmol) of compound **13** and 82 mg ($5.0 \cdot 10^{-6}$ mol) of G5(Allyl)128 polyallylcarbosilane dendrimer was placed in a 100 ml three-neck flask with a magnetic stirrer, a refrigerator and a thermometer, filled with nitrogen and added 17 ml of anhydrous toluene. The solution was saturated with nitrogen, heated to 60°C (until compound **13** was completely dissolved) and 10 µl of Karsted catalyst ($1.0 \cdot 10^{-6}$ mol Pt) was added. The reaction mixture was stirred while heating to 80°C for 20 hours. After the reaction was completed, 70 ml of ethanol was added to the reaction mixture, heated to boiling and boiled for 4 hours. The resulting suspension was filtered on a hot filtration funnel. After drying the precipitate in vacuum, 625 mg of crude product was obtained as a yellow powder. Purification was performed by precipitating from a hot toluene solution (15 ml, 80°C) with ethanol (70 ml). The procedure was repeated twice. As a result, 486 mg (92% of theory) of the product was obtained in the form of a yellow powder, which is a mixture of dendrimer **3** and dimer **14**. Pure dendrimer **4** was isolated by preparative GPC (column 104 Å, eluent: THF, 40ºC). Yield: 108 mg (20% of theory). According to the results of ^{1}H-NMR analysis, the resulting product contained 55-60 terminal quaterthiophene fragments of the possible 128, and the remaining 68-73 terminal fragments were unreacted allyl groups.

5-Hexyl-2,2'-bitiophene (6a). To a mixture of 2.47 g (0.102 mol) of magnesium and 20 ml of absolute ether, a solution of 15.24 g (93.4 mmol) of 2-bromothiophene in 100 ml of absolute ether was added dropwise, after which the reaction mixture was boiled for 5.5 hours. The resulting solution of 2-thienyl magnesium bromide was dropped to the mixtures of 21 g (85 mmol) of 2-hexyl-5-bromothiophene and 0.19 g (0.3 mmol) of $Pd(dppf)Cl_2$ in 100 ml of absolute ether, maintaining the temperature in the range from 0°C to 10°C. After warming to room temperature, the reaction mixture was stirred for 2 hours. After completion of the reaction, 200 ml of ice-cold water was added to the reaction mixture, and it was extracted twice with freshly distilled diethyl ether (200 ml). The organic phase was separated, washed until neutral, dried over Na_2SO_4, and the solvent was evaporated. 21.91 g of crude product was obtained. After purification by distillation in vacuum (0.22 mbar), 16.65 g (78.26%) of compound **6a** was obtained. T_B = 120 ... 122°C/0.22 mbar. ^{1}H-NMR (250 MHz, $CDCl_3$, δ, ppm, *J*/Hz): 0.91 (t, 3H, *J* = 6.7); 1.25-1.46 (overlapping peaks, 6H); 1.69 (m, 2H, *J* = 7.3); 2.80 (t, 2H, *J* = 7.3); 6.69 (dd, 1H, J_1 = 1.2, J_2 = 3.1); 6.99 (m, 2H); 7.11 (dd, 1H, J_1 = 1.2, J_2 = 3.7); 7.16 (dd, 1H, J_1 = 1.2, J_2 = 3.7).

2-(10-Undecene-1-yl)-thiophene (6b). From 86 ml (0.21 mmol) of 2.5 M solution of *n*-butyl lithium in hexane, 21.65 g (0.26 mol) of thiophene and 50.0 g (0.21 mol) of 11-bromundecane-1 in 120 ml of absolute THF. The reaction mixture was stirred for 1 hour at 50°C. After a standard reaction isolation, 49.74 g of crude product was obtained, which was purified by distillation in vacuum. 35.84 g (71% of theory) of compound **6b** was obtained. T_B = 119 ... 121°C /1 mbar. ^{1}H-NMR (250 MHz, δ in $CDCl_3$, TMS, ppm, *J* / Hz): 1.22-1.45 (overlapping peaks with a maximum at 1.29, 12H, –CH_2–CH_2–CH_2–), 1.68 (m, 2H , *J* = 7.3, –T–CH_2–CH_2–), 2.05 (m, 2H, *J* = 7.3, CH_2=CH–CH_2–), 2.83 (t, 2H, *J* = 7.3, –T–CH_2–CH_2–) , 4.97 (m, 2H, CH_2=CH–CH_2–), 5.81 (m, 1H, CH_2=CH–CH_2–), 6.79 (dd, 1H, *J*1 = 1.2, *J*2 = 3.7, thiophene-H), 6.92 (dd, 1H, *J*1 = 3.7, *J*2 = 4.9, thiophene-H), 7.12 (dd, 1H, *J*1 = 1.2, *J*2 = 4.9, thiophene-H). ^{13}C-NMR (δ in $CDCl_3$): 28.99, 29.16, 29.40, 29.51, 29.54, 29.96, 31.85, 33.86, 114.14, 122.67, 123.85, 126.58, 139.14, 145.77.

5-(10-Undecene-1-yl)-thiophene-2-yl-magnesium-bromide (6c). A solution of 5.23 g of compound **6b** (22 mmol) in 25 ml of anhydrous THF was added dropwise to a solution of 22 mmol of *n*-butyl lithium in 25 ml of a mixture of THF-hexane at –10ºC.

Then, the cooling bath was removed, the temperature was allowed to rise to 20°C and the reaction mixture was cooled again to –17°C. Then, freshly prepared magnesium bromide ether complex obtained from 1.00 g (42 mmol) of magnesium and 2.4 ml (28 mmol) of dibromoethane in 20 ml of anhydrous ether was added dropwise to the reaction mixture. The reaction mixture was stirred for 1 h without cooling to ensure the completion of the exchange reaction of lithium to magnesium. The resulting Grignard reagent was not isolated, but immediately used in subsequent reactions.

5-(10-Undecene-1-yl)-2,2-bithiophene (6d). A freshly prepared solution of 75.8 mmol of compound **6c** was added dropwise to a mixture of 12.36 g of 2-bromothiophene (75.8 mmol), 278 mg of Pd(dppf)Cl_2 (0.4 mmol) and 150 ml of anhydrous THF, while maintaining the temperature from 0 to 10ºC. The cooling bath was removed, while stirring at room temperature was continued for 2 hours. Then the reaction mixture was cooled and poured into 300 ml of ice water, followed twice by extraction with toluene. The organic phase was separated, washed with water and dried over anhydrous sodium sulfate. After evaporation of the solvent on a rotary evaporator, 24.00 g of crude product was obtained. Further purification of the product was carried out by the method of column chromatography (eluent: hexane), as a result, 21.61 g of pure compound **6d** was obtained (89% of theory). T_m = 26ºC. ^{1}H-NMR (250 MHz, $CDCl_3$, δ, ppm, *J*/Hz): 1.22-1.45 (overlapping peaks with a maximum at 1.28, 12H, $–CH_2–CH_2–CH_2–$), 1.67 (m, 2H, *J* = 7.3), 2.03 (m, 2H, *J* = 7.3), 2.77 (t, 2H, *J* = 7.3), 4.95 (m, 2H), 5.80 (m, 1H), 6.67 (d, 1H, *J* = 3.7), 6.98 (dd, 2H, J_1 = 3.7, J_2 = 4.9), 7.08 (dd, 1H, J_1 = 3.7, J_2 = 1.2), 7.15 (dd, 1H, J_1 = 4.9, J_2 = 1.2). ^{13}C-NMR (δ in $CDCl_3$): 28.94, 29.07, 29.13, 29.35, 29.47, 29.49, 30.15, 31.61, 33.83, 114.12, 122.95, 123.35, 123.68, 124.68, 127.65, 134.73, 137.95, 139.23, 145.34.

5-Bromo-5'-hexyl-2,2'-bithiophene (6e). From 9.77 g (39.0 mmol) of 5-hexyl-2,2’-bithiophene (**6a**) and 7.00 g (39.4 mmol) of NBS in 60 ml of dry DMFA. Purification of the product was performed by recrystallization from methanol (200 ml), followed by silica gel column chromatography (eluent: hexane). 9.54 g (74%) of pure compound **6e** was obtained. ^{1}H- NMR (250 MHz, $CDCl_3$, δ, ppm, *J*/Hz): 0.90 (t, 3H, *J* = 6.7), 1.23-1.45 (overlapping peaks, 6H), 1.67 (m, 2H, *J* = 7.3), 2.78 (t, 2H, *J* = 7.3), 6.68 (dd, 1H, J_1 = 3.7, J_2 = 1.2), 6.83 (d, 1H, *J* = 3.7), 6.92 (d, 1H, *J* = 3.7), 6.95 (d, 1H, *J* = 3.7).

2-(5'-Hexyl-2,2'-bithiophene-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7). A 2.5M solution of *n*-butyl lithium in hexane (8.0 ml, 20 mmol) was added to 50 ml of anhydrous THF at –78 ° C in a nitrogen atmosphere. A solution of 5.0 g of compound **6a** (20 mmol) in 50 ml of dry THF was then added dropwise. The reaction mixture was stirred for 1 h at –78 ° C, after which the cooling bath was removed, and the temperature spontaneously rose to 0°C. Then the mixture was cooled again to –78°C, after which 3.9 g of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.3 ml, 20 mmol) was added in one portion. The mixture was stirred for 30 minutes at –78 ° C, after which the cooling bath was removed again, and while the temperature slowly rose to 22 ° C, stirring was continued for another 3 hours. After that, the reaction mixture was poured into 300 ml of ether and 100 ml of ice water mixed with 21 ml of 1M hydrochloric acid solution. The organic phase was separated, washed with water, dried over anhydrous sodium sulphate and evaporated to isolate the product as a blue solid. The use of the product in further reactions was carried out without further purification. Yield: 7.21 g (96% of theory). GLC-MS, 97%. MS *m/z* 376 (M^+). ^{1}H-NMR ($CDCl_3$, TMS, ppm, *J*/Hz): 0.88 (3H, t, *J* = 6.9), 1.20-1.45 (18H, overlapping peaks with a maximum at 1.34 ppm), 1.67 (2H , m, *J* = 7.5), 2.77 (2H, t, *J* = 7.5), 6.67 (1H, d, *J* = 3.7), 7.03 (1H, d, *J* = 3.7), 7.14 (1H, d, *J* = 3.7), 7.49 (1H, d, *J* = 3.7).

1-[11-(2,2'-Bitiophene-5-yl)-undecyl]-1,1,3,3-tetramethyldisiloxane (8). 4.10 g of compound **6d** (13 mmol) was dissolved in 85 ml of 1,1,3,3-tetramethyldisiloxane in an argon atmosphere, after which 25 µl of Karsted catalyst was added. The reaction was complete after 3 hours of stirring at 17-27ºC. The crude product was purified by silica gel column chromatography (eluent: hexane), followed by drying in vacuum (1 mbar). Yield: 4.0 g (69% of theory). MALDI MS (α-cyano-4-hydroxycinnamic acid, $[M+H]^+$): 449. Calculated (%) for $C_{23}H_{40}OS_2Si_2$: 452.87, C 61.00, H 8.90, Si 12.40, S 14.16. Found (%): C 61.14, H 9.01, Si 12.67, S 14.10. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm, *J*/Hz): 0.05 (6H, s), 0.15 (6H, d, *J* = 2.9), 0.52 (2H, t, *J* = 7.5), 1.19 -1.45 (16H, overlapping peaks with a maximum at 1.27 ppm), 1.67 (2H, m, M = 5, *J* = 7.5), 2.78 (2H, t, *J* = 7.5), 4.67 (1H, m, M = 7, *J* = 2.8), 6.66 (1H, d, *J* = 3.9), 6.97 (1H, d, *J* = 3.9), 6.98 (1H, d, *J* = 3.9), 7.08 (1H, dd, J_1 = 3.9 , J_2 = 1.5), 7.15 (1H, dd, J_1 = 5.1, J_2 = 1.5).

3,3',3'',3'''-[Silantetrayltetrakis(propane-3,1-diyl)]tetrakis{1-[11-(2,2'-bithiophene-5-yl)-undecyl]-1,1,3,3-tetramethyldisiloxane} (9). 100 mg of tetraallyl silane (0.52 mmol) and 1.08 g of compound **8** (2.39 mmol) were dissolved in 12 ml of anhydrous hexane in argon atmosphere, after which 10 µl of Karsted catalyst was added. The reaction was complete after stirring for 4 hours at 23-26ºC. The crude product was purified by column chromatography (gradient elution) on silica gel using hexane and toluene as eluents, followed by lyophilization, resulting in a target product of 98% purity (GPC). Yield: 960 mg (92% of theory). MALDI MS (α-cyano-4-hydroxycinnamic acid, $[M+H]^+$): 2001. Calculated (%) for $C_{104}H_{180}O_4S_8Si_9$: 2000, Si 12.61, S 12.80. Found (%): Si 12.25, S 12.92. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm, *J*/Hz): 0.02 (48H, s), 0.40-0.65 (24H, overlapping peaks), 1.18-1.44 (72H, overlapping peaks with a maximum with 1.26 ppm), 1.67 (8H, m, *J* = 7.5), 2.77 (8H, t, *J* = 7.5), 6.65 (4H, d, *J* = 3.4), 6.96 (4H, d, *J* = 3.9), 6.98 (4H, d, *J* = 3.9), 7.07 (4H, dd, J_1 = 3.7, J_2 = 1.5), 7.14 (4H, dd, J_1 = 5.1, J_2 = 1.5).

3,3',3'',3'''-[Silantetrayltetrakis(propane-3,1-diyl)]tetrakis{1-[11-(5'-bromo-2,2'-bitiophene-5-yl)-undecyl]-1,1,3,3-tetramethyldisiloxane} (10). A solution of 900 mg of compound **9** (0.45 mmol) in a mixture of 6 ml of anhydrous DMFA and 6 ml of anhydrous toluene was cooled to –10ºC. In the dark, a solution of 380 mg of NBS(2.1 mmol) in 6 ml of anhydrous DMFA was added dropwise. After 30 minutes of stirring, the cooling bath was removed, after which the reaction mixture was stirred at 22 ºC for 4 hours. The contents were then poured into 100 ml of water and 200 ml of dichloromethane. The organic layer was separated, washed with water and dried over anhydrous sodium sulfate. After removal of the solvent and drying in vacuum (1 mbar), 1.20 g of product was obtained as a yellowish oil. The crude product was purified by silica gel column chromatography (eluent: toluene) and dried under vacuum (1 mbar). As a result, the target compound was obtained with 99.8% purity. Yield: 923 mg (89% of theory). Calculated (%) for $C_{23}H_{40}OS_2Si_2$: C 53.86, H 7.65, Br 13.78, S 11.06, Si 10.90. Found (%): C 53.91, H 7.79, Br 13.84, S 11.16, Si 10.77. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm, *J*/Hz): 0.02 (48H, s), 0.40-0.65 (24H, overlapping peaks), 1.17-1.45 (72H, overlapping peaks with a maximum at 1.26 ppm), 1.66 (8H, m, *J* = 7.5), 2.77 (8H, t, *J* = 7.5), 6.64 (4H, d, *J* = 3.7), 6.80 (4H, d, *J* = 3.7) , 6.89 (4H, d, *J* = 3.7), 6.92 (4H, d, *J* = 3.7).

4,4,5,5-Tetramethyl-2-[5'-(10-undecyl)-2,2'-bithiophene-5-yl]-1,3,2-dioxaborolane (11). To 70 ml of anhydrous THF, cooled to –74ºC, 5.6 ml of a 2.5M solution of *n*-butyl lithium in hexane was added dropwise. A solution of 4.46 g of compound **6d** (14 mmol) in 120 ml of anhydrous THF was then added dropwise, followed by stirring for 30 minutes at –70ºC. After that, the cooling bath was removed, allowing the temperature to rise. When the mixture warmed to 0ºC, the reaction mixture was cooled again to –

74ºC and 3.3 ml of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (16 mmol) was added to it in one portion. After stirring for 30 hours at –74ºC, the cooling was removed, the temperature raised to 20ºC and stirring was continued for 3 hours. After this, the reaction mixture was poured into 200 ml of ice water mixed with 15 ml of 1M hydrochloric acid solution and extracted with 500 ml of diethyl ether. The organic phase was separated, washed with water, dried over anhydrous sodium sulfate and filtered, and the solvent was removed completely by evaporation in a rotary evaporator, resulting in 6.03 g (97% of theory) of a dark blue crystalline product. The product of synthesis was used in subsequent reactions without further purification. T$_m$ = 52ºC. GLC-MS analysis: M$^+$ 99%, *m/e* = 444. ^{1}H-NMR (250 MHz, δ in CDCl$_3$, TMS, ppm, *J*/Hz): 1.22-1.45 (overlapping peaks with a maximum at 1.28, 12H, –CH$_2$–CH$_2$–CH$_2$–), 1.34 (s, 12H, –CH$_3$), 1.67 (m, 2H, *J* = 7.3, –T–CH$_2$–CH$_2$–), 2.04 (m, 2H, *J* = 7.2, CH$_2$=CH–CH$_2$–), 2.79 (t, 2H, *J* = 7.3, –T–CH$_2$–CH$_2$–), 4.97 (m, 2H, CH$_2$=CH–CH$_2$–), 5.81 (m, 1H, CH$_2$=CH–CH$_2$–), 6.68 (d, 1H, *J* = 3.7, thiophene-H), 7.06 (d, 1H, *J* = 3.7, thiophene-H), 7.16 (d, 1H, *J* = 3.7, thiophene-H), 7.50 (d, 1H, *J* = 3.7, thiophene-H). ^{13}C-NMR (δ in CDCl$_3$): 24.77, 28.95, 29.08, 29.14, 29.34, 29.47, 29.49, 30.19, 31.59, 33.82, 84.10, 114.12, 124.08, 124.19, 124.88, 134.69, 137.91, 139.22, 144.79, 146.10.

5-Hexyl-5'''-(10-undecene-1-yl)-2,2':5',2'':5'',2'''-quaterthiophene (12). In inert atmosphere, a solution of 7.35 g of compound **11** in 120 ml of toluene and 21 ml of a 2M aqueous solution of sodium carbonate was added to 4.61 g of compound (**6e**) and 0.090 g of Pd(PPh$_3$)$_4$. The reaction mixture was boiled for 18 hours. After cooling, the reaction mixture was poured into 200 ml of ice-cold water, 45 ml of 1N solution of hydrochloric acid and 300 ml of toluene. The organic phase was separated and washed twice with 200 ml of water. The yellow precipitate was filtered and dissolved in 350 ml of toluene, the solution was dried over anhydrous magnesium sulfate, filtered and the solvent was evaporated. The result was 1.28 g of the crude product as a yellow solid. The filtrate was dried over anhydrous magnesium sulfate, filtered and the solvent was distilled off, and the residue was recrystallized from 900 ml of *n*-hexane. As a result, 5.8 g of the crude product as a brownish yellow solid was obtained. After recrystallization from toluene, 4.81 g of pure **12** was obtained as a yellow powder. Yield: 1.28 + 4.81 = 6.09 g (77% of theory). MS: *m/z* = 566 (M$^+$). ^{1}H-NMR (250 MHz, CDCl$_3$, TMS, ppm, *J* / Hz): 0.90 (t, 3H, *J* = 6.9), 1.23-1.44 (overlapping peaks with a maximum value of 1 , 29 ppm, 18H), 1.68 (m, 4H, 2.4 (t, 2H, *J* = 7.2) 5.81 (m, 1H), 6.68 (d, 2H, *J* = 3.7), 6.98 (d, 2H, *J* = 3.7), 6.99 (d, 2H, *J* = 3.7), 7.03 (d, 2H, *J* = 3.7).

1-[11-(5'''-Hexyl-2,2':5',2'':5'',2'''-quaterthiophene-5-yl)undecyl]-1,1,3,3-tetramethyl-disiloxane (13). 1.25 g of compound **12** and 40 ml of anhydrous toluene, placed in a 250 ml three-necked flask, dry and filled with nitrogen, equipped with a magnetic stirrer, a reflux condenser and a thermometer, were purged with nitrogen and heated to 70ºC. To the resulting clear solution 16 ml of tetramethyldisiloxane (12.0 g) and 10 µl of Karsted catalyst were added, after which the reaction mixture was stirred for 21 hours. After removing the solvent on a rotary evaporator, 2.59 g of a yellow solid was obtained, which was heated to 50 ºC, and purified by chromatography on silica gel (eluent: toluene). 1.365 g (87% of theory) of pure compound **13** was obtained as a solid yellow substance. FD MS: *m/z* = 700 (M$^+$). ^{1}H-NMR (250 MHz, CDCl$_3$, TMS, ppm, *J*/Hz): 0.06 (s, 6H), 0.16 (d, 6H, *J* = 2.5), 0.53 (t, 2H, *J* = 7.6), 0.90 (t, 3H, *J* = 6.85), 1.21-1.44 (overlapping peaks with a maximum at 1.27 ppm, 22H), 1.68 (m, 4H, M = 5, *J* = 7.5), 2.79 (t, 4H, *J* = 7.6 Hz), 4.7 (m, 1H, M = 7, *J* = 2.8), 6.68 (d, 2H, *J* = 3.7), 6.97 (d, 2H, *J* = 3.7), 6.99 (d, 2H, *J* = 3.7), 7.03 (d, 2H, *J* = 3.7).

X-Ray Scattering

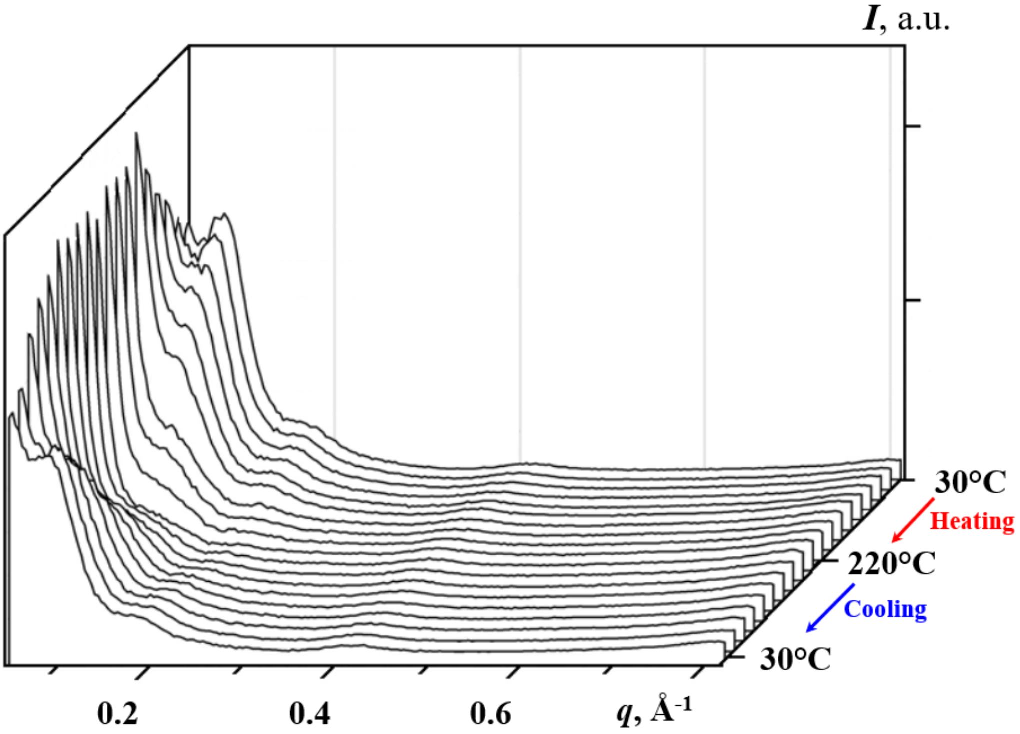

Figure 2. Small-angle X-Ray spectra of compound **4** in the heating to a melting temperature – cooling cycle.

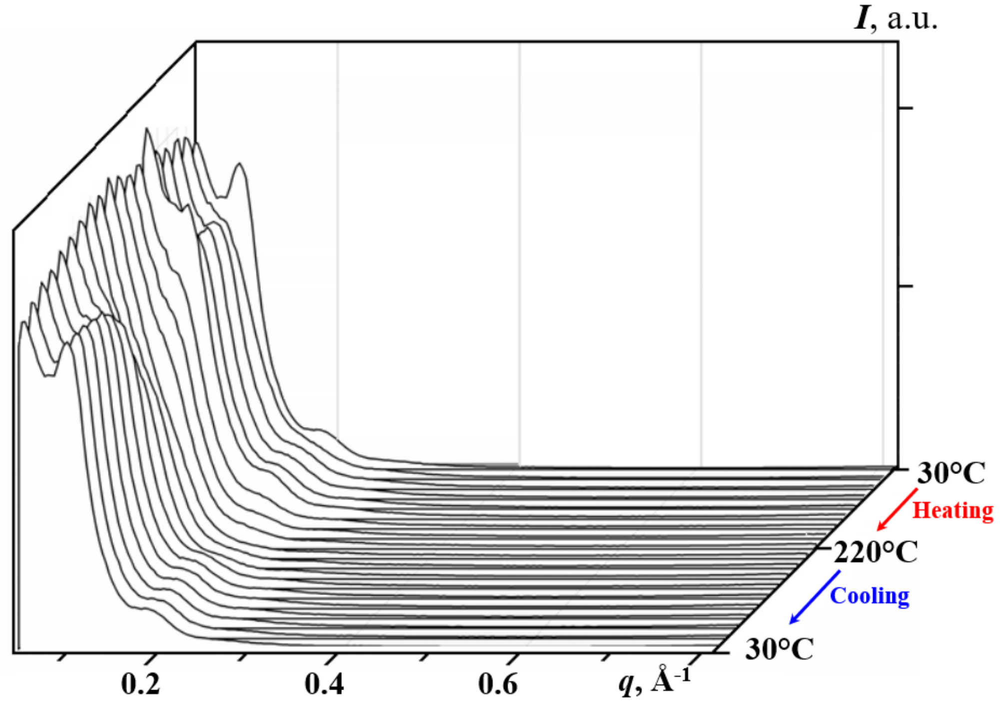

Figure 3. Small-angle X-Ray spectra of compound **5** in the heating to a melting temperature – cooling cycle.

Differential scanning calorimetry

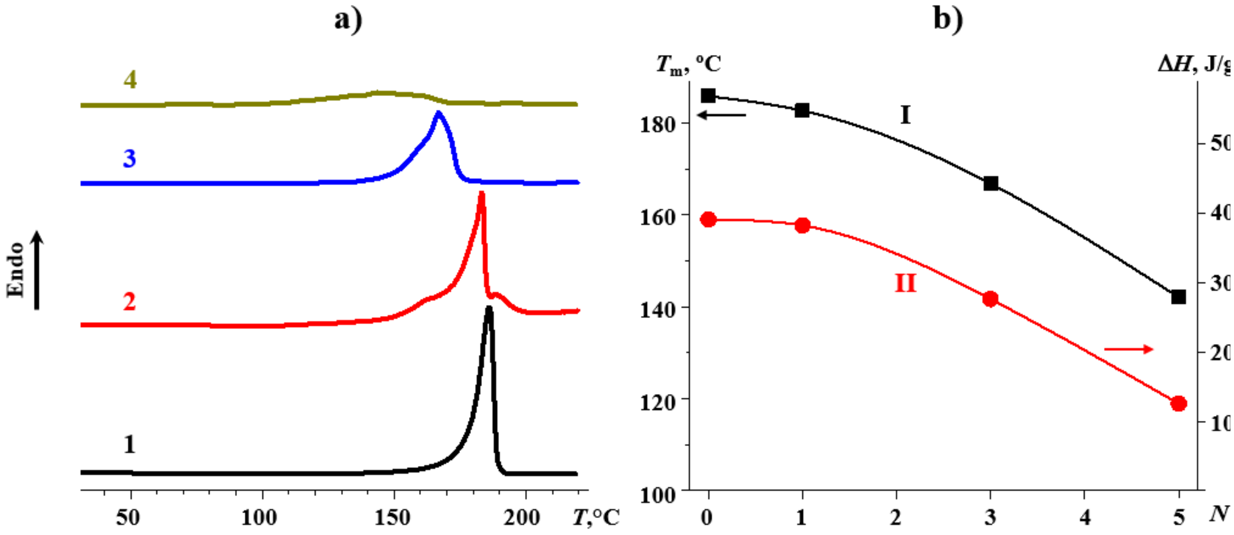

Figure 4. DSC traces of the first transition of compounds **1**-**4** (a) and dependencies of the transition temperature (I) and its heat (II) vs. dendrimer number (b).