Star-Shaped Oligothiophenes for Solution-Processible Organic Electronics: Flexible Aliphatic Spacers Approach

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The design, synthesis, and properties of a novel, solution-processible organic semiconductor based on star-shaped oligothiophenes linked through flexible aliphatic branches to a carbosilane core are described. This four-arm dendrimer-like molecule not only forms smooth thin films on large surfaces but also shows improved monolayer formation compared to its linear prototype, α,α'-dihexylquaterthiophene (**Hex-4T-Hex**). For the new material, three different types of structural organization (nanowires and mono- and multilayers) were found, all of which are favorable for charge transport through the material in organic field-effect transistors. These processability and structural properties, in combination with high field-effect mobility, high current modulation, and a threshold voltage of ∼0 V, suggest that star-shaped oligothiophenes with carbosilane cores are a promising new class of semiconducting materials for use in flexible organic electronics.

Introduction

There has been growing interest in π-conjugated polymers and oligomers over the last several years because of their unique semiconducting and electrooptical properties and potential applications in different electronic devices, such as organic field-effect transistors (OFETs)[1] and organic light-emitting diodes (OLEDs)[2]. Oligothiophenes are known for their stability in ambient conditions and high charge-carrier mobilities.[3] However, because of the high crystallinity and low solubility of these materials and the low viscosity of their solutions, good thin films of most commonly used oligothiophenes can be obtained only by sublimation. Sublimation, however, is not considered to be an ideal approach for deposition of materials in the production of large-area flexible electronics. Solution processing is thought to be both potentially less expensive, and hence more desirable, and more compatible with large-scale applications. One approach to the improvement of the film-forming characteristics of linear oligothiophenes is to attach them to a polymeric chain. For example, quaterthiophenes with polymerizable end groups were recently reported[4] that showed field-effect mobilities on the order of 1×10^{-3} cm^2/Vs prior to polymerization and on the order of 1×10^{-4} cm^2/Vs after polymerization. A second approach to obtaining solution-processible oligothiophenes, called the precursor route, includes incorporation of thermally removable solubilizing groups into sexithiophene, an oligomer that is otherwise nearly insoluble.[5] Field-effect mobilities up to 7×10^{-2} cm^2/Vs were achieved after thermal treatment of the precursor films at 160−250 °C. A third approach to solubilizing oligothiophenes is to attach bulky substituents such as cyclohexyl groups to the ends of the oligomer. Cyclohexyl-substituted quaterthiophene is reported to have improved solubility over the dihexyl-substituted oligomer and a mobility of 6×10^{-2} cm^2/Vs in devices obtained by solution-processing from bromobenzene solvent at 40 °C. However, observation by optical microscopy revealed that films of cyclohexyl-substituted oligothiophenes did not have continuous morphology.[6] Thus, although both the use of the precursor route and the addition of bulky side chains

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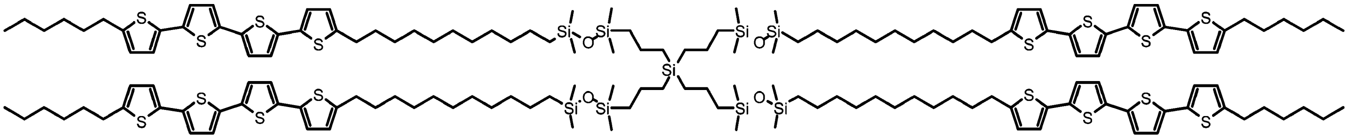
Scheme 1. Structural Formula of Carbosilane-Based Star-Shaped Oligothiophene 1



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improved the solubility of the oligomers, in neither case was the improvement sufficient for obtaining the processability required for deposition, such as by spin-coating, of continuous films of the materials onto large surfaces, especially hydrophobic ones.[7] This difficulty has been attributed to the low viscosities of the oligomer solutions. Identifying materials that combine the stability of oligomers with the processability of polymers remains a challenge.

This work presents a new approach to solving this problem: the attachment of monofunctional oligothiophene derivatives to a branched carbosilane core via flexible aliphatic spacers. First, it is found that star-shaped oligothiophenes have generally better solubility and film-forming properties than their linear counterparts, thus allowing the production of OFETs by solution processing with mobilities of about 2×10^{-4} cm^2/Vs.[8] Recently, mobilities up to 1×10^{-3} cm^2/Vs for similar star-shaped oligothiophenes have been reported,[9] and an α,α'-dihexylpentathiophene-based swivel cruciform structure with a mobility of 1.2×10^{-2} cm^2/Vs further develops the idea of utilizing branched topologies in organic semiconductors.[10] Second, our approach is on the basis of lamellar or columnar ordered structures observed for carbosilane dendrimers with terminal rodlike mesogenic groups.[11] A prerequisite for the formation of such structures is the presence of flexible aliphatic spacers between the dendritic core and the terminal mesogenic groups.[11d] The aliphatic spacers facilitate anisotropic ordering of the latter, which would otherwise not be favored by the isotropic nature of the branched dendritic structure. Thus, using this spacer concept and quaterthiophene derivatives as the mesogenic groups, we designed the carbosilane-based star-shaped oligothiophene **1** (Scheme 1). The structure includes a carbosilane branching core, flexible undecylenic spacers between the carbosilane core and the quaterthiophene (**4T**) semiconducting groups, and hexyl groups end-capping each **4T** for better solubility and reduction of trap sites.

Experimental Section

General. ^{1}H NMR spectra were recorded using a Bruker WP-250 SY spectrometer (250.13 MHz) in CDCl$_3$ solutions. The phase transitions were studied by differential scanning calorimetry (DSC) using a Mettler TA-4000 thermosystem at scanning rates of 10 and 1 K/min. Sample weights were typically chosen to be between 5 and 10 mg. MALDI-TOF analysis was performed on a Bruker Daltonics system with an impulse N$_2$-laser at 337 nm and α-cyano-4-hydroxycinnamic acid as a matrix material.

GPC analysis was performed on a Shimadzu instrument (Japan) with an RID-10A refractometer and an SPD-M10AVP diode matrix as detector, using 7.8×300 mm Phenomenex columns (United States) filled with Phenogel sorbent with pore sizes of 500 and 1×10^3 Å and tetrahydrofuran (THF) as eluent. Use of the SPD-M10AVP diode matrix detector made it possible to obtain 3D GPC chromatograms with UV−vis absorbency spectra versus elution time, 2D chromatograms with absorbency at fixed wavelength (i.e., 400 nm) versus elution time, or plots of UV−vis absorbency spectra at fixed elution times.

Atomic force microscopy (AFM) was performed using a Digital Instruments Multimode equipped with a Nanoscope IIIa controller (Veeco Instruments, Santa Barbara, CA). Imaging was done in the tapping mode using standard silicon cantilevers: Nanoworld Pointprobe NCH ($k \approx 42$ N/m, $f_0 \approx 330$ kHz). Height and phase images were recorded simultaneously. For more correct measurements of surface steps (or layer thickness), the set-point amplitude, A_{sp}, was chosen to be close to A_0 to further reduce the tip-to-surface interaction.

Optical microscopy observations were performed with an optical reflection microscope (Zeiss axioplan) equipped with a differential interference contrast (DIC) module. The micrograph was acquired with an Axio Cam digital camera.

OFETs were made by drop casting or spin-coating of compound **1** from hot toluene, xylene, or mesitylene solutions (0.5−2 mg/mL, 80 °C) onto a hot substrate (70 °C). In these experiments, we used heavily doped n++-Si wafers as the gate electrode, with a 200 nm thick layer of thermally grown SiO$_2$ as the gate-insulating layer. Using conventional lithography, we defined gold source and drain contacts. Ring transistors with a channel length of 40 μm and channel width of 1000 μm were used. Hexamethyldisilazane (HMDS) or octyldimethylchlorosilane (ODMCS) was applied as a primer on top of the SiO$_2$.

Materials. *n*-Butyllithium in hexane (1.6 and 2.5 M) and *N*-bromosuccinimide obtained from Acros Organics were used without further purification. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (IPTDOB), tetrakis(triphenylphosphine) palladium(0) (Pd(PPh$_3$)$_4$), and platinum(0) 1,3-divynyl-1,1,3,3-tetramethyldisiloxane complex in xylene (Karstedt's catalyst) were obtained from Sigma-Aldrich Co. and used without further purification. THF and diethyl ether were dried over CaH$_2$ and distilled from LiAlH$_4$. 5-Hexyl-2,2′-bithiophene and 5-(10-undecenyl-1)-2,2′-bithiophene were obtained from H. C. Starck GmbH and used without further purification. The synthesis of tetraallylsilane is described elsewhere.[12a] Glassware was dried in a drybox at 150 °C for 2 h, assembled while hot, and cooled in a stream of nitrogen.

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(7) By a "continuous film," we mean "uninterrupted, unbroken" film, which is not necessarily perfect or complete but has a direct connection between all its different parts through the same material.

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

2-(5′-Hexyl-2,2′-bithien-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolan (2). *n*-Butyllithium (2.5 M in hexane, 8.0 mL, 20 mmol) was added to anhydrous THF (50 mL) at −78 °C under nitrogen. A solution of 5-hexyl-2,2′-bithiophene (5.0 g, 20 mmol) in dry THF (50 mL) was then added dropwise. The reaction mixture was stirred for 1 h at −78 °C; the bath was removed, and the temperature was allowed to rise to 0 °C. After that, the reaction mixture was cooled again to −78 °C, and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.9 g, 4.3 mL, 20 mmol) was added in one portion via syringe. The mixture was stirred for 30 min at −78 °C and the bath was then removed; the solution was stirred for an additional 3 h while the temperature was increased slowly to 22 °C. The reaction mixture was next poured into 300 mL of ether and 100 mL of ice−water mixed with 21 mL of 1 M HCl. The organic phase was separated, washed with water, dried over sodium sulfate, and evaporated to yield the product as a blue solid. The product was used without further purification. Yield: 7.21 g (96%). GC-MS, 97%. MS *m*/*z* 376 ($M^{\cdot+}$). ^{1}H NMR ($CDCl_3$, TMS, ppm): 0.88 (3H, t, J = 6.9 Hz), 1.20−1.45 (18 H, overlapping peaks with maximum at 1.34 ppm), 1.67 (2H, m, J = 7.5 Hz), 2.77 (2H, t, J = 7.5 Hz), 6.67 (1H, d, J = 3.7 Hz), 7.03 (1H, d, J = 3.7 Hz), 7.14 (1H, d, J = 3.7 Hz), 7.49 (1H, d, J = 3.7 Hz).

1-[11-(2,2′-Bithien-5-yl)undecyl]-1,1,3,3-tetramethyldisiloxane (3). 5-Undec-10-en-1-yl-2,2′-bithiophene (4.10 g, 13 mmol) was dissolved in 85 mL of 1,1,3,3-tetramethyldisiloxane under argon, after which 25 μL of Karstedt's catalyst was added. The reaction was complete after 3 h of stirring at 17−27 °C. The crude product was purified by column chromatography on silica gel (eluent hexane) and dried under a vacuum (1 mbar). Yield: 4.0 g (69%). MALDI-TOF (α-cyano-4-hydroxycinnamic acid, $[M+H]^+$): 449, calcd 452.87. Calcd for $C_{23}H_{40}O_1S_2Si_2$: 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, ppm): 0.05 (6H, s), 0.15 (6H, d, J = 2.9 Hz), 0.52 (2H, t, J = 7.5 Hz), 1.19−1.45 (16 H, overlapping peaks with maximum at 1.27 ppm), 1.67 (2H, m, M=5, J = 7.5 Hz), 2.78 (2H, t, J = 7.5 Hz), 4.67 (1H, m, M=7, J = 2.8 Hz), 6.66 (1H, d, J = 3.9 Hz), 6.97 (1H, d, J = 3.9 Hz), 6.98 (1H, d, J = 3.9 Hz), 7.08 (1H, dd, J_1 = 3.9 Hz, J_2 = 1.5 Hz), 7.15 (1H, dd, J_1 = 5.1 Hz, J_2 = 1.5 Hz).

3,3′,3′′,3′′′-[Silanetetrayltetrakis(propane-3,1-diyl)]tetrakis{1-[11-(2,2′-bithien-5-yl)undecyl]-1,1,3,3-tetramethyldisiloxane} (4). Tetraallylsilane (100 mg, 0.52 mmol) and **3** (1.08 g, 2.39 mmol) were dissolved in 12 mL of anhydrous hexane under argon, and 10 μL of Karstedt's catalyst was then added. The reaction was complete after the solution was stirred at 23−26 °C for 4 h. The crude product was purified by gradient column chromatography on silica gel (eluents: hexane, toluene) and lyophilized to give 98% pure compound. Yield: 960 mg (92%). MALDI-TOF (α-cyano-4-hydroxycinnamic acid, $[M+H]^+$): 2001, calcd 2000. Calcd. for $C_{104}H_{180}O_4S_8Si_9$: Si, 12.61; S, 12.80. Found: Si, 12.25; S, 12.92. ^{1}H NMR ($CDCl_3$, TMS, ppm): 0.02 (48H, s), 0.40−0.65 (24H, overlapping peaks), 1.18−1.44 (72 H, overlapping peaks with maximum at 1.26 ppm), 1.67 (8H, m, J = 7.5 Hz), 2.77 (8H, t, J = 7.5 Hz), 6.65 (4H, d, J = 3.4 Hz), 6.96 (4H, d, J = 3.9 Hz), 6.98 (4H, d, J = 3.9 Hz), 7.07 (4H, dd, J_1 = 3.7 Hz, J_2 = 1.5 Hz), 7.14 (4H, dd, J_1 = 5.1 Hz, J_2 = 1.5 Hz).

3,3′,3′′,3′′′-[Silanetetrayltetrakis(propane-3,1-diyl)]tetrakis{1-[11-(5′-bromo-2,2′-bithien-5-yl)undecyl]-1,1,3,3-tetramethyldisiloxane} (5). A solution of **4** (900 mg, 0.45 mmol) in a mixture of 6 mL of anhydrous dimethylformamide and 6 mL of anhydrous toluene was cooled to −10 °C. In the dark, a solution of *N*-bromosuccinimide (380 mg, 2.1 mmol) in 6 mL of anhydrous DMF was added dropwise. After 30 min of the mixture being stirred, the cooling bath was removed and the reaction mixture was stirred at 22 °C for 4 h. The mixture was then poured into 100 mL of water and 200 mL of dichloromethane. The organic layer was isolated, washed with water, and dried over sodium sulfate. After the solvent was removed and the mixture dried under vacuum (1 mbar), 1.20 g of yellowish oil was obtained. The crude product was purified by column chromatography on silica gel (eluent: toluene) and dried under vacuum (1 mbar) to give 99.8% pure compound. Yield: 923 mg (89%). Calcd. for $C_{23}H_{40}O_1S_2Si_2$: 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, ppm): 0.02 (48H, s), 0.40−0.65 (24H, overlapping peaks), 1.17−1.45 (72 H, overlapping peaks with maximum at 1.26 ppm), 1.66 (8H, m, J = 7.5 Hz), 2.77 (8H, t, J = 7.5 Hz), 6.64 (4H, d, J = 3.7 Hz), 6.80 (4H, d, J = 3.7 Hz), 6.89 (4H, d, J = 3.7 Hz), 6.92 (4H, d, J = 3.7 Hz).

3,3′,3′′,3′′′-[Silanetetrayltetrakis(propane-3,1-diyl)]tetrakis{1-[11-(5′′′-hexyl-2,2′:5′,2′′:5′′,2′′′-quaterthien-5-yl)undecyl]-1,1,3,3-tetramethyldisiloxane} (1). Compound **5** (380 mg, 0.16 mmol) was placed into a three-neck 100 mL flask equipped with a magnetic stirrer, cooler, and argon inlet. The flask was filled with $Pd(PPh_3)_4$ (83 mg, 0.07 mmol) and kept under argon. Degassed solutions of **2** (270 mg, 0.72 mmol) in 20 mL of toluene and 2 M aq Na_2CO_3 (4 mmol) were then added. The mixture was heated at reflux temperature for 30 h. The progress of the reaction was monitored by 3D GPC analysis (see the Supporting Information). After completion, the mixture was poured into a mixture of 100 mL of water, 6 mL of 1 M HCl, and 200 mL of toluene. The organic layer was isolated, washed with water, and dried over sodium sulfate. After the solvent was removed and the mixture dried under vacuum (1 mbar), 690 mg of a dark green solid was obtained. The crude product was purified by column chromatography on silica gel (eluent: toluene) followed by recrystallization from a hexane−toluene mixture. The final compound obtained was 98% pure according to 3D GPC. Yield: 250 mg (51%). MALDI-TOF (α-cyano-4-hydroxycinnamic acid, $[M+H]^+$): 2997, calcd 2997.52. Calcd. for $C_{160}H_{244}O_4S_{16}Si_9$: 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. ^{1}H NMR ($CDCl_3$, TMS, ppm): 0.02 (48H, s), 0.40−0.65 (24H, overlapping peaks), 0.89 (12H. t, J = 6.9 Hz), 1.16−1.45 (96 H, overlapping peaks with maximum at 1.27 ppm), 1.66 (16H, m, J = 7.5 Hz), 2.77 (16H, t, J = 7.5 Hz), 6.67 (8H, d, J = 3.7 Hz), 6.93−6.98 (16H, overlapping peaks), 7.00 (8H, d, J = 3.7 Hz).

Results and Discussion

Synthesis of compound **1** successfully combined two general approaches: (1) a Grignard coupling reaction followed by hydrosilylation, as is commonly used in the synthesis of carbosilane dendrimers,[12] and (2) bromination followed by organometallic thiophene−thiophene bond formation via Suzuki coupling, as is extensively utilized in the synthesis of pure oligothiophenes and their derivatives.[13,14] The synthesis used in this work consists of three steps (Scheme 2). In the first step, 2-(5′-hexyl-2,2′-bithien-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolan (**2**) with one

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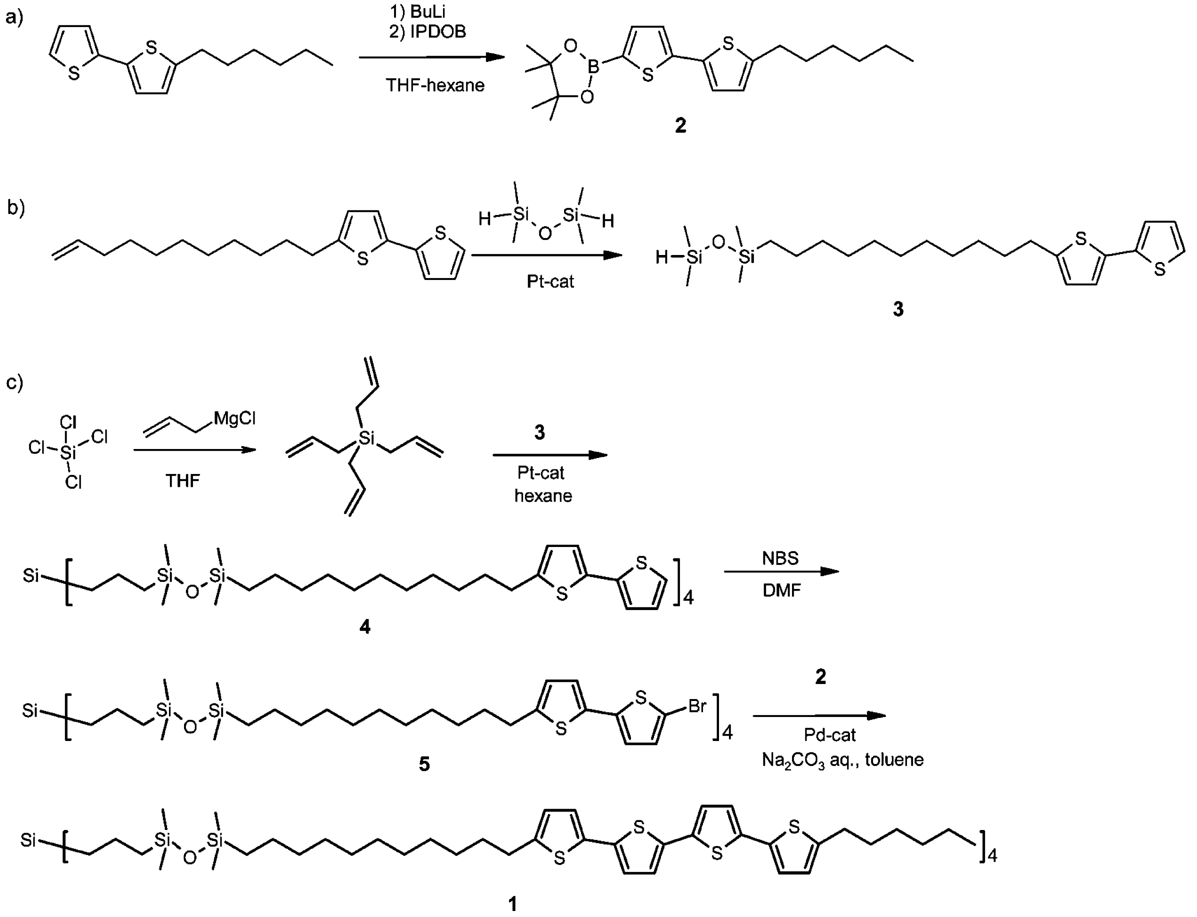
Scheme 2. Synthesis of Carbosilane Star-Shaped Compound 1



functional group (pinacolatoborolane) is obtained (Scheme 2a). In the second step, 1-[11-(2,2′-bithien-5-yl)undecenyl]-1,1,3,3-tetramethyldisiloxane (**3**) with two functional groups, Si−H and an active proton at the 5′-position of 2,2′-bithiophene, is made (Scheme 2b). The third step (Scheme 2c) includes synthesis of tetraallylsilane from tetrachlorosilane by Grignard coupling with allylmagnesium chloride followed by hydrosilylation with compound **3**. The result is branched carbosilane **4** with four bithiophene arms. These bithiophene groups are then quantitatively brominated with NBS and coupled via Suzuki coupling with **2** to make the desired compound **1**. The progress of the last step is monitored by 3D GPC analysis with in-line UV−vis absorbance measurements by a diode array detector. The structure and purity of the intermediate and final compounds were evaluated by ^{1}H NMR, GPC, MALDI-TOF, and elemental analysis (see Experimental Section and the Supporting Information).

Thermal Properties. DSC measurements of compound **1** elucidate its crystalline behavior. The compound melts at 189 °C, with a transition enthalpy of 42.5 J/g. This corresponds to 127.4 kJ/mol or, bearing in mind that the molecule has four quaterthiophene (**4T**) groups, to 31.85 kJ/(mole of **4T** groups). Interestingly, melting starts at ca. 150 °C with some slow, low-energy processes, and then intensifies at 185 °C and finishes at 190 °C. Careful investigation at slow scanning rates (1 °C/min, see the Supporting Information) allowed for resolution of the melting process into two peaks: one at 160 °C with an enthalpy of 4.3 J/g and another at 188 °C with an enthalpy of 34.6 J/g. These two processes are fully reversible and could be attributed to crystal$_1$−crystal$_2$ and crystal$_2$−isotropic melt phase transitions, respectively. It could not be excluded that crystal$_2$ is actually a highly ordered smectic phase like those found in other dialkyl-substituted oligothiophenes.[14a,15] Detailed X-ray investigation of the structure of different phases formed by compound **1** is under way. TGA analysis showed that compound **1** is a thermostable material, even in the presence of oxygen. There is no evidence of decomposition up to 275 °C in air and up to 375 °C under a nitrogen atmosphere.

Solution-Processing and Film-Forming Properties. Despite its high crystallinity, compound **1** is soluble in different organic solvents, e.g., toluene, THF, chloroform, etc., under slight heating (40−60 °C), with maximum attainable concentrations of 10−20 mg/mL. These values are comparable to the solubility of its monomer analogue, α,α′-dihexylquaterthiophene, also known as **Hex-4T-Hex**.[15] However, in contrast to **Hex-4T-Hex**, compound **1** forms a gel at room temperature (20 °C). More importantly, the new material has better film-forming properties; homogeneous substrate coverage is achieved by the spin-coating of **1**, whereas **Hex-4T-Hex** forms discontinuous layers as proven by optical microscopy and AFM investigations.

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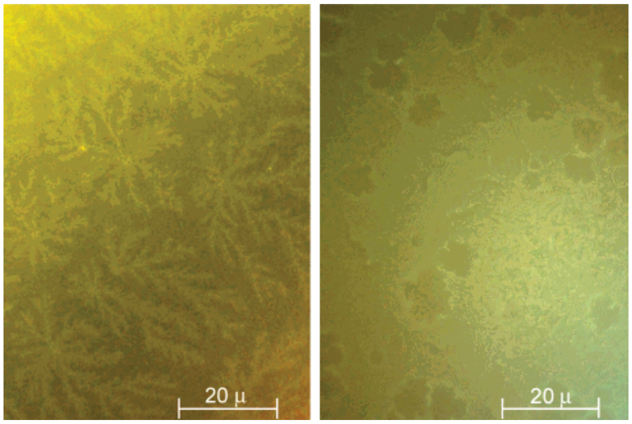

Figure 1. Optical micrographs of thin films of (a) **Hex-4T-Hex** and (b) compound **1**, obtained by dip-coating from a 1 mg/mL toluene solution onto Si wafers.

For comparison purposes, 1 mg/mL toluene solutions of both substances were dip-coated onto either Si wafer or mica under the same conditions. On Si wafer, **Hex-4T-Hex** has a strong tendency to crystallize into dendrite-like structures, leaving most of the substrate uncovered (Figure 1a). Compound **1**, however, covers most of the substrate surface with a uniform layer, although a small number of holes due to dewetting (Figure 1b) are seen. Dewetting is a general problem in solution processing[16] and deserves further investigation. In the case of low-molecular-weight crystallizable compounds (i.e., **Hex-4T-Hex**), dewetting usually leads to the formation of large crystals that are separated from each other rather than to a homogeneous film. Compound **1**, however, with a molar weight around 3000, is an example of a material that combines high crystallinity with good film-forming properties.

Further evidence of continuous film morphology was obtained by AFM (Figure 2). The AFM images of thin films of **1** show platelike domains, which consist of multilayers with an average thickness of 5.3−5.4 nm. These domains are interconnected with each other, leaving just a small part of the substrate (ca. 15%) uncovered from dewetting processes. It is worth noting that a very similar film morphology was obtained for **Hex-4T-Hex** that was deposited by a vacuum evaporation technique.[17] This comparison leads to the conclusion that wet-processing of compound **1** gives thin films of comparable coverage to those obtained from sublimated **Hex-4T-Hex**. Thus, attaching quaterthiophene residues to a carbosilane branching core via flexible spacers does indeed improve the film-forming ability of quaterthiophenes.

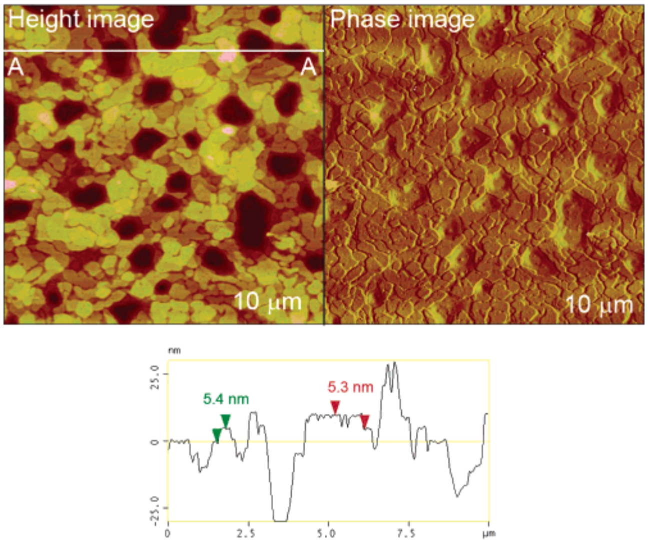

Figure 2. AFM height and phase images (10 μm × 10 μm each) and cross-section through the A−A line of a thin layer of compound **1**, obtained by dip-coating from a 1 mg/mL toluene solution onto a Si wafer.

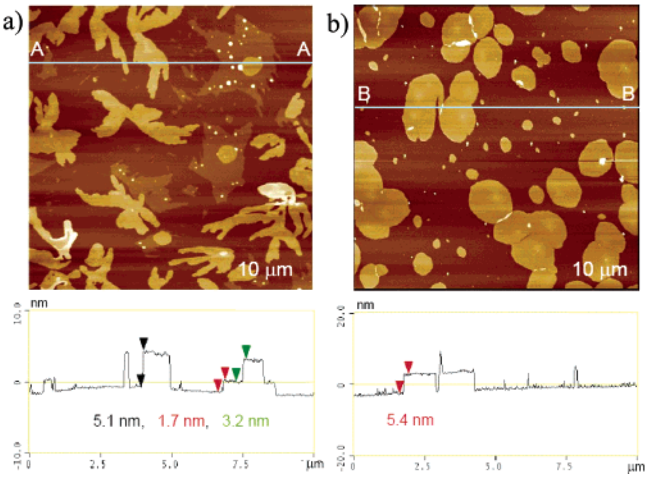

Figure 3. AFM height images (10 μm × 10 μm each) and cross-sections through A−A and B−B lines, respectively, of the monolayer islands of (a) **Hex-4T-Hex** and (b) compound **1**, obtained by dip-coating from a 1 mg/mL toluene solution onto mica.

Investigation of Monolayer Formation. AFM measurements of samples dip-coated on mica allowed us to look closer into the process of monolayer formation. **Hex-4T-Hex** simultaneously forms islands of mono- and bilayers (Figure 3a), with the first layer having a significantly smaller thickness (1.7 ± 0.3 nm) than the second (3.2 ± 0.3 nm), and a bilayer 5.1 ± 0.3 nm thick.

Bearing in mind that **Hex-4T-Hex** in bulk has a layer periodicity of 2.85 nm,[15] it can be concluded that the molecules in the second layer stand almost perpendicular to the surface, as is postulated for its sexithiophene homologue **Hex-6T-Hex**,[18] and that the molecules in the first layer have a different orientation or are less-ordered, probably because of disordered or tilted alkyl tails. In contrast, compound **1** has a strong tendency to form only a monolayer with a thickness of ca. 5.4 ± 0.3 nm (Figure 3b), which is somewhat less than expected for a fully extended conformation of this “4-mer” molecule (8.6 nm, Figure 4a). This suggests that the flexible carbosilane−siloxane core and at least part of the aliphatic spacers are in a compact conformation, leading to an overall diminished size of the molecule. Taking into account the strong tendency of quaterthiophene groups to

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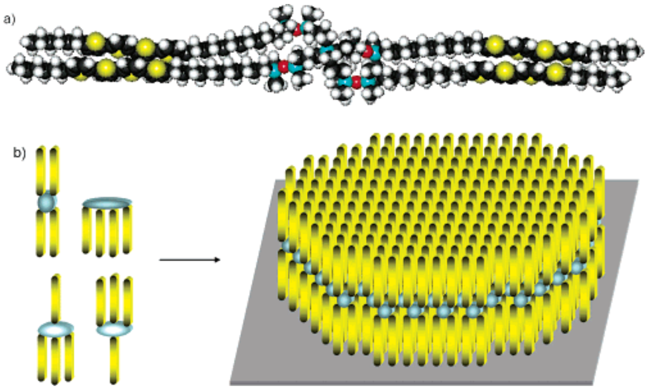

Figure 4. (a) Molecular model of compound **1** in its extended conformation. (b) Schematic representation of different conformations of compound **1** as a core with four arms, and its self-organization into a monolayer.

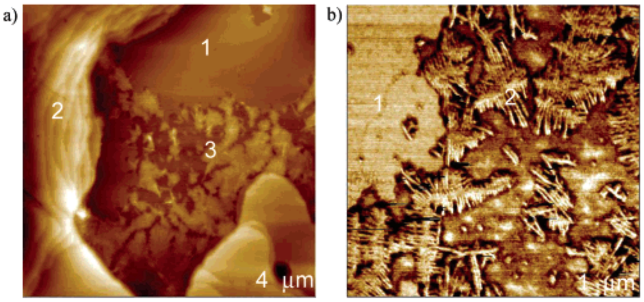

Figure 5. (a) AFM height image (4 μm × 4 μm) of the sample of compound **1** showing different levels of structural organization: (1) a monolayer, (2) multilayers, and (3) nanowires. (b) AFM phase image (1 μm × 1 μm) of the same sample at the edge between the monolayer (1) and nanowires (2).

aggregate because of $\pi-\pi$ interactions, it is reasonable to model compound **1** as a core with four rigid rods interacting in pairs (Figure 4b). Such ordering seems to be a general phenomenon for different four-arm molecules[19] (see Discussion in the Supporting Information).

Different Levels of Structural Organization. Further investigation into the structural organization of star-shaped compound **1** was made by AFM of the samples annealed near the melting temperature. It was found that annealing leads to dewetting of the film and the formation of droplets. These droplets, however, have lamellar ordering and are interconnected by at least a monolayer of the material (Figure 5a). In an AFM image of the edge of a droplet, one can observe three different levels of structural organization in the material: (1) a monolayer, (2) multilayers and (3) nanowires. In high resolution AFM images (Figure 5b), one can clearly see nanowires that are connecting different parts of the monolayer. The nanowires are located parallel to the surface, have a very similar width of around 10 nm, and have the same height as a monolayer (ca. 5.2 nm). Moreover, most of the nanowires are parallel to each other and are organized into sheaves, with some of the nanowires crossing these sheaves perpendicularly. One can suppose that these nanowires represent an initial step of monolayer formation during crystallization of the material from the isotropic phase.

Further ordering of the layers gives a multilayer structure. The origin of the nanowire coexisting with the layered structure is not clear yet, but it may be correlated to the structural transition observed in the thermal analysis. Further investigation is needed to clarify this issue.

It should be noted that the formation of different nanostructures by oligothiophenes is known in the literature. For instance, it has been shown that oligoethylenoxy-endcapped sexithiophenes form one-dimensional nanowires in the form of long ribbonlike aggregates or helical nanoribbons.[16b,20] Thiophene dendrimers have also been shown to aggregate into nanowires on graphite surfaces.[21] However, none of the nanostructures described were reported to be as organized as those presented here. This finding opens up new possibilities for the control of semiconducting nanowire formation and ordering.

OTFT Measurements. Semiconducting properties of compound **1** were evaluated in organic field-effect transistors. Transistors made by drop-casting from toluene solution showed typical mobilities of $1-2 \times 10^{-3}$ cm^2/Vs (at source-drain voltage $V_{sd} = -2$ V) with on/off ratios reaching 1×10^4 at $V_{sd} = -2$ V and 1×10^5 at $V_{sd} = -20$ V. Transistors made by spin-coating from toluene solution showed typical mobilities of $2-5 \times 10^{-3}$ cm^2/Vs with on/off ratios of 1×10^4 to 1×10^5. Annealing under a vacuum at 70 °C did not influence the mobility or on/off ratio of the devices studied here, although the threshold voltages decreased from −3 to −1 V upon annealing. The highest-performance spin-coated sample after annealing under vacuum at 70 °C had a mobility of 1×10^{-2} cm^2/Vs with an on/off ratio of 1×10^6 and a threshold voltage close to 0 V (Figure 6a). This sample also exhibited the expected transfer characteristics (Figure 6b). It is worth noting that all transistors were prepared and characterized in air, indicating compound **1**'s high stability against oxidative doping.

For further optimization of the transistor behavior, we evaluated different solvents and primers Often, OFETs show better transistor characteristics when high boiling point solvents are employed for deposition of the semiconductor.[5a,16a,22] Therefore, in addition to toluene, we chose to evaluate deposition from xylenes and mesitylene. The concentrations used were in the range of 0.5 to 2 mg/mL (Table 1). As a primer, in addition to our standard HDMS, we have also evaluated the use of octyldimethylchlorosilane (ODMCS). The latter is known to form a self-assembled monolayer of *n*-octylsilane on the SiO_2 surface.[23] Summarizing the results obtained, we conclude that there is a clear optimum in the concentration for spin-coating of compound **1** that is close to 1 mg/mL. Mesitylene solutions work well

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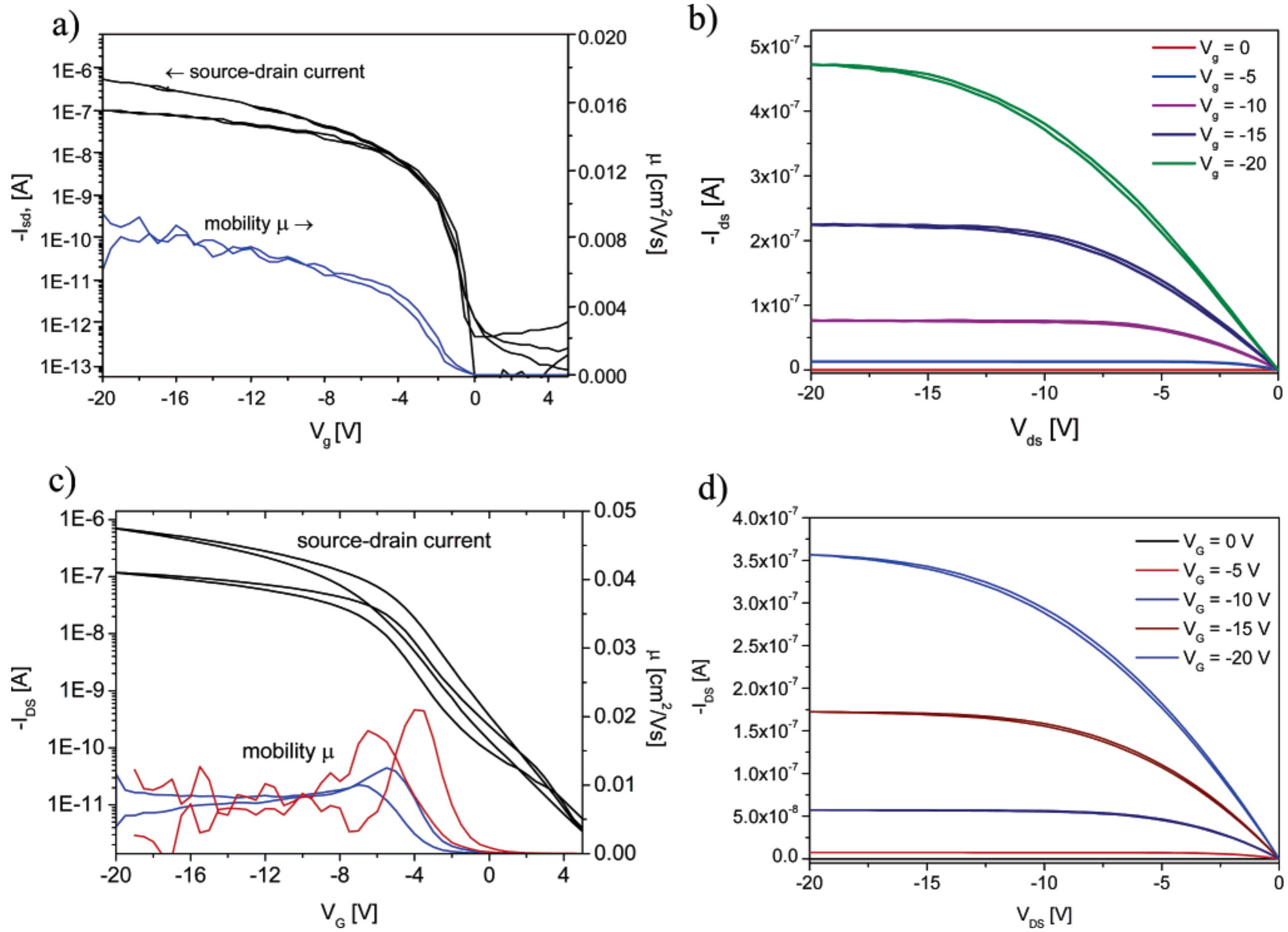

Figure 6. Transfer (a,c) and output (b,d) characteristics of OFETs made by spin-coating of compound **1** from toluene (a,b) and xylene (c,d) solutions on a hot substrate, annealed at 70 °C. The drain potentials were −2 and −20 V in the upper and lower traces of drain current vs gate bias in plot (a). Forward and backward curves are shown; no remarkable hysteresis is seen. Linear mobility is shown in blue color (a, c), saturated mobility in red.

Table 1. Influence of Solvent, Concentration, and Primer on the Field-Effect Mobility of Compound 1

solvent	substrate primer[a]	concentration (mg/mL)	linear mobility (cm²/Vs × 10⁻³)
toluene	HMDS	1	1−10
xylenes	HMDS	0.5	1
xylenes	HMDS	1	3−4
mesitylene	HMDS	0.5	0.01
mesitylene	HMDS	1	4−6
mesitylene	HMDS	2	3−5
toluene	ODMCS	1	2−3
xylenes	ODMCS	1	6−12
mesitylene	ODMCS	1	0.5−0.7
mesitylene	ODMCS	2	1

[a] HMDS is hexamethyldisilazane, ODMCS is octyldimethylchlorosilane.

on HDMS-treated substrates, but are not as good for ODMCS-treated substrates. The best results were obtained for transistors prepared from 1 mg/mL xylene solutions spin-coated onto the substrate with ODMCS primer. The linear mobility reaches a value of 1.2×10^{-2} cm²/Vs with an on/off ratio of 1×10^{5}, whereas the saturated mobility was 2×10^{-2} cm²/Vs (Figure 6c). Output characteristics of this transistor are presented in Figure 6d. It should be noted that all transistors reported upon herein were produced under normal atmospheric conditions and that no further vacuuming or annealing was required.

The field-effect mobilities obtained are close to those reported for α,α′-didecylquaterthiophene on the same substrate,[8] although compound **1** is lower in concentration of functional quaterthiophene group than the corresponding dialkylquaterthiophenes. Therefore, we can conclude that this new approach to solution-processing organic semiconductors allows for improvement of the film-forming properties of quaterthiophene derivatives without sacrificing mobility.

Conclusions

In summary, we have successfully designed, synthesized, and investigated a new type of organic semiconducting solution-processible material based on a quaterthiophene linked through flexible aliphatic spacers to a carbosilane branching core. The structure of this new class of four-arm molecules, exemplified by compound **1** reported upon here, allowed us to strike a reasonable compromise between the high crystallinity of quaterthiophene, good solubility, and improved film-forming properties imparted by the carbosilane core and aliphatic spacers. Compound **1** not only forms smooth films on large substrate surfaces but also shows better monolayer formation compared to **Hex-4T-Hex**. Its processability properties in combination with high field-effect mobility and good transistor characteristics make compound **1** and similar molecules part of a promising new class of semiconducting materials for use in flexible organic electronics. Further optimization to solubility, film-forming properties, and mobility characteristics may be accomplished by varying the length of the aliphatic spacer between the oligothiophenes and the branching core, or by variations in the functionality of the carbosilane core itself, in the length of the oligothiophene group, or in the length of the oligothiophene end-capping group. Furthermore, the synthetic route presented here could be used to attach alternative types of semiconducting oligomers to any branching core via flexible aliphatic spacers. Synthesis and investigation of higher-generation carbosilane dendrimers with terminal quaterthiophene groups are currently underway and will be the focus of our next publication in this field.

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Supporting Information Available: NMR spectra, GPC, UV−vis and MALDI-TOF data, DSC curve, field-effect mobility calculation details, discussion on the film structure of compound 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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