

Symmetrical and Nonsymmetrical Liquid Crystalline Oligothiophenes: Convenient Synthesis and Transition-Temperature Engineering

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Two approaches to transition-temperature engineering in liquid crystalline oligothiophenes are described: (i) substitution at the aromatic core with two identical branched alkyl chains and (ii) desymmetrization of the molecule with two alkyl substituents of different length or structure. Key steps in the synthesis of symmetrical and nonsymmetrical terthiophenes and quaterthiophenes involve Suzuki coupling

and carbanion alkylation. A well-adjusted balance between the π - π stacking of the aromatic core and the disorder caused by the peripheral alkyl chains is demonstrated to be important for the control of the thermotropic behavior of oligothiophene mesogens.

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Introduction

Oligothiophenes have been attracting increasing attention due to their high charge-carrier mobility (μ), which is a key feature for materials used in organic electronic devices such as organic field-effect transistors (OFETs).^[1] Among other oligothiophene derivatives, symmetrical α,α' -disubstituted oligothiophenes show enhanced chemical and electrochemical stability.^[2] In addition, a combination of a rigid aromatic core and flexible side chains in the structure of α,α' -dialkyloligothiophenes induces the formation of liquid crystalline mesophases.^[3] The practical application of polycrystalline materials in OFETs is often hampered by structural defects and grain-boundary effects, which dramatically decrease the charge-carrier mobility.^[4] In contrast, liquid crystals have been recognized as a new type of organic semiconductors, as they are capable of self-healing structural defects and of self-organization in large structurally homogeneous domains.^[5] Furthermore, it was shown that the influence of domain boundaries, if any, on carrier transport in liquid crystalline phases is very small.^[6] Funahashi and Hanna reported higher temperature-independent charge-carrier mobility ($\mu = 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) in the ordered SmG phase of dioctylterthiophene **1a** relative to that ($\mu = 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) in the crystalline phase.^[7] In addition, low-

molecular-weight liquid crystalline semiconductors are easily processible from solution and can therefore be considered as realistic candidates for large-area organic electronic devices.

Our current research aim is to design oligothiophenes with thermotropic properties suitable for OFET applications and to reach a better understanding of the relationship between their molecular structure and phase order. Fabrication of realistic organic electronic devices such as OFETs requires ambient-temperature liquid crystalline semiconductors. On the other hand, the stability of mesophases in a temperature range that is as broad as possible is also crucially important for device performance. However, the prediction of phase behavior from the chemical structure of oligothiophenes is still hardly possible. The major principle in the design of new mesogens consists of a compromise between the order caused by the π - π stacking of the flat aromatic cores and the disorder induced by the flexible peripheral substituents. The transition between the crystalline (Cr) and liquid crystalline (LC) phases involves the conformational disordering of the side chains, also referred to as "side-chain melting".^[8] In agreement with this simple model, symmetrical 5,5''-bis(*n*-alkyl)terthiophenes with six to nine carbon atoms in the alkyl chain demonstrate increasing Cr–LC transition temperatures with increasing chain length,^[3,9] i.e., the same tendency as that of the melting points of linear alkanes. On the other hand, it has been well documented that branching of peripheral substituents results in the lowering of the Cr–LC transition temperatures of discotic mesogens.^[8,10] Here, we explore two different possibilities of tuning the transition temperature in liquid crystalline terthiophenes and quaterthiophenes: substitution at the aromatic core with two identical

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branched alkyl chains and desymmetrization of the molecule with two alkyl substituents of different length or structure.

Results and Discussion

Synthesis

A four-step synthesis of symmetrical 2,5''-dialkylterthiophenes (such as **1a,b**) was reported earlier by Byron et al.^[3] Repeated Friedel–Crafts acylation with the corresponding acyl chloride followed by Wolff–Kishner–Huang–Minlon reduction afforded the target molecules in rather low yield (15–30% starting from terthiophene **3**). More recently, Kirchmeyer and co-workers reported on the large-scale synthesis of didecyl oligothiophenes from the appropriate thiophenes or bithiophenes by Ni- or Pd-catalyzed Kumada cross-coupling or Cu-catalyzed oxidative homocoupling.^[11] This approach provides fair-to-excellent yields but requires a relatively high number of synthetic steps. The commercial availability of terthiophene **3** and quaterthiophene **4** prompted us to examine their direct one-step functionalization to give **1** and **2**.

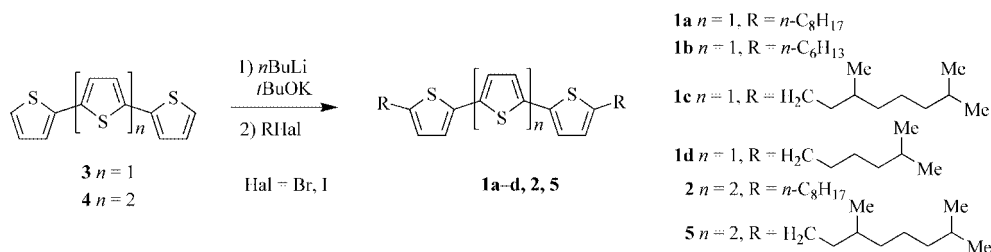
Very recently, we reported in a preliminary communication a practical and high-yield one-step synthesis of α,α' -bis(*n*-alkyl)oligothiophenes such as **1a,b** and **2** by lithiation of **3** and **4**, respectively, followed by alkylation with *n*-alkyl halides.^[9] The use of *t*BuOK to enhance the reactivity of dilithiated oligothiophene species towards alkylating agents was demonstrated to be of crucial importance. Without the addition of *t*BuOK, the reaction resulted in small amounts of mono- and disubstituted oligothiophenes, and up to 85% of unreacted starting material was recovered. Earlier, it was reported that the simple addition of *t*BuOK considerably enhanced the reactivity of various lithiated species, including 2-lithiated derivatives of furan, thiophene, and *N*-substituted pyrroles, toward alkylating agents such as haloalkanes and epoxides.^[12] The observed effect was attributed to the formation of an organopotassium compound, likely in equilibrium with a lithium derivative. The higher reactivity of the former towards alkyl halides is probably due to the lower aggregation, whereas organolithium compounds are well known to form associates in solution.^[13]

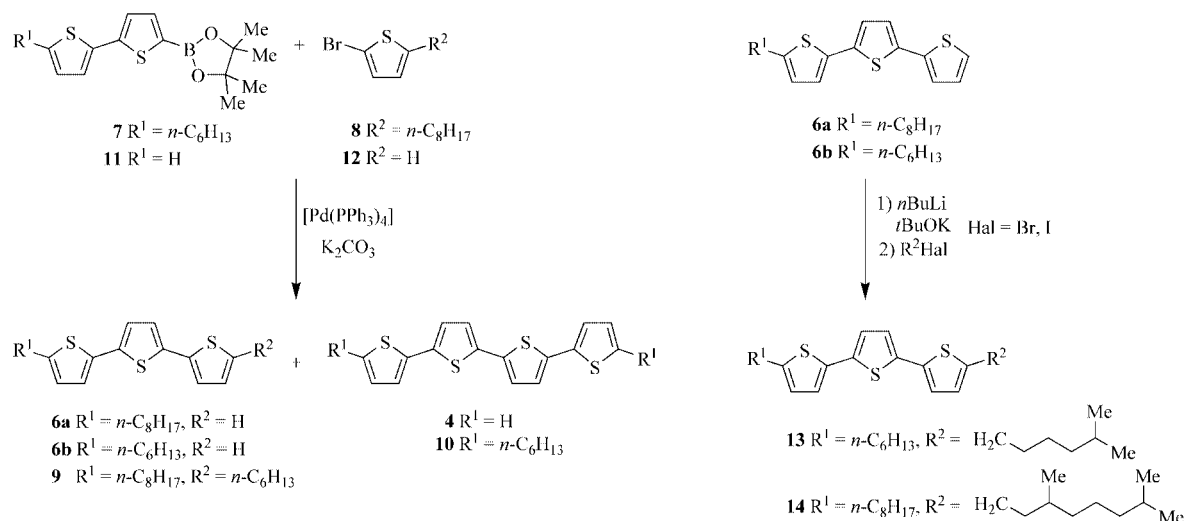
Using the same method, symmetrical dialkyl derivatives of terthiophene with branched 3,7-dimethyloctyl (compound **1c**) or 5-methylhexyl (compound **1d**) substituents

were prepared (Scheme 1). As expected, haloalkanes in which the branching site was remote from the halogen atom did not cause any changes in reactivity relative to that of their linear analogs: **1c** and **1d** were isolated in 88–90% yield. ¹H NMR spectra of the crude product indicated only traces of the starting material and no monoalkylterthiophenes. In addition, the symmetrical dialkylquaterthiophene **5** was prepared by the same method from quaterthiophene **4** in 85% yield.

We also attempted to extend this method to the synthesis of nonsymmetrical dialkylterthiophenes by sequential alkylation with two different haloalkanes. However, alkylation of terthiophene **3** with 1 equiv. of 1-iodooctane resulted in a mixture of the mono-octylterthiophene **6a**, the dioctylterthiophene **1a**, and the starting material. We explain this by the higher solubility, and therefore higher reactivity, of the monoanion of **6a** compared with that of the dianion of **3**. Therefore, we decided to use an alternative synthetic strategy based on Suzuki–Miyaura coupling^[14] as a key step. It should be noted here that only limited examples of oligothiophenes with different substituents in one molecule have been reported. Funahashi and Hanna recently reported high charge-carrier mobility in smectic phases of α -alkyl- α' -alkynyloligothiophenes prepared by multistep synthesis involving sequential Kumada couplings as key steps in assembling the oligothiophene core.^[15] Although it appeared that nonsymmetrical oligothiophenes should be easily accessible by the Suzuki coupling of the corresponding building blocks, no successful attempts are mentioned in the literature. In addition, syntheses based on Suzuki coupling appeared particularly practical because of the great and constantly increasing variety of commercially available arylboronic reagents.

The reaction between commercially available *n*-hexyl-substituted bithiophenylboronate **7** and 2-bromo-5-octylthiophene (**8**) directly furnished the nonsymmetrical terthiophene **9** (60%) with linear alkyl chains of different length. Alternatively, Suzuki coupling of 2-bromo-5-alkylthiophene **8** with boronate **11** and that of 2-bromothiophene (**12**) with boronate **7** delivered monosubstituted 2-alkylterthiophenes **6a** and **6b**, respectively, in 47–50% yield. The second alkyl substituents were introduced by alkylation in the presence of *n*BuLi/*t*BuOK as described above (Scheme 2). In all Suzuki couplings to give **6a,b** or **9**, minor amounts (10% or less) of the quaterthiophenes **4** or **10** resulting from the homocoupling^[16] of the corresponding bithiophenylboronates **11** or **7**, respectively, were obtained.

Scheme 1. Synthesis of symmetrical dialkyloligothiophenes **1a–d**, **2**, and **5**.

Scheme 2. Synthesis of nonsymmetrical dialkyloligothiophenes **9**, **13**, and **14**.

Fortunately, these impurities were easy to separate by taking advantage of the much lower solubility of the quaterthiophenes relative to that of the terthiophenes.

Thermotropic Behavior and Structure of Mesophases

Thermotropic properties of the novel oligothiophenes as well as those of some previously synthesized symmetrical oligothiophenes with linear alkyl substituents are summarized in Table 1. Terthiophene **1c** with two double-branched 3,7-dimethyloctyl substituents is a low-melting crystalline solid that does not form liquid crystalline mesophases. The melting point of **1c** is much lower than the Cr–LC transition temperature of its straight-chain analog, dioctylterthiophene **1a** (Table 1, entries 1 and 3). This is probably due to both the conformational changes in the side chains and their stereoheterogeneity, as the synthesis of **1c** from the racemic 1-bromo-3,7-dimethyloctane gave a mixture of two diastereoisomers. However, because of the steric repulsion of the bulkier peripheral substituents, the π – π stacking of the cores is also disturbed. Accordingly, at the disordering temperature of the side chains, the aromatic cores are already unstacked, and the crystalline solid melts directly to the isotropic liquid. We reasoned that the thermotropic behavior of **1d**, which possesses less bulky 5-methylhexyl substituents and also lacks the center of chirality, may be an average between those of **1a** and **1c**. Unfortunately, **1d** does not form liquid crystalline phases either, and its melting point is unexpectedly high relative to the Cr–LC transition temperature of its straight-chain analog **1b** (Table 1, entries 2 and 4).

Unlike those in terthiophene **1c**, the two 3,7-dimethyloctyl substituents in quaterthiophene **5** stabilize the mesophase, and the Cr–LC transition temperature is lowered by 35 °C relative to that of the straight-chain dioctylquaterthiophene **2** (Table 1, entries 5 and 6). Undoubtedly, the major difference in thermotropic behavior between quaterthiophene **5** and terthiophene **1c**, both bearing identical

Table 1. Transition temperatures of dialkyloligothiophenes **1a-d**, **2**, **5**, **9**, **13**, and **14**.

En- try	Com- pound	Transition temperatures/°C [enthalpy /kJ mol ⁻¹] ^[a,b]
1	1a ^[c]	Cr 62 [21.7] SmG 68 [3.2] SmF 84 [0.8] SmC 87 [6.8] I
2	1b ^[c]	Cr 48 [13.6] SmG 75 [11.3] I
3	1c	Cr 45 [25.2] I
4	1d	Cr 85 [13.7] I
5	2 ^[c]	Cr 77 [4.3] LC 140 [6.0] I
6	5	Cr 42 [1.5] (LC ₁ 58 [3.9]) (LC ₂ 65 [0.2]) LC ₃ 127 [29.1] I
7	9	Cr 52 [15.6] LC 65 [7.1] I
8	13	Cr ₁ 32 [4.3] Cr ₂ 41 [0.7] Sm G/H 79 [19.2] I
9	14	Cr 20 [5.1] (LC ₁ 33 [0.3]) LC ₂ 43[5.5] I

[a] Determined from the onset of the second heating curve (DSC); Cr: crystalline phase; Sm: smectic phase; Sm G/H: smectic G or H phase; LC: undefined liquid crystalline phase of unknown nature; I: isotropic liquid. [b] The transitions in brackets are monotropic transitions (observed only during the heating). [c] Data from ref.^[9] are given for the sake of discussion.

alkyl substituents, must be explained by the more efficient π - π stacking between the longer quaterthiophene moieties. Comparison of the thermotropic behavior of **1c** and **5** clearly demonstrates the importance of the well-adjusted balance between the stacking of the aromatic core and the disorder caused by the peripheral alkyl chains.

Another approach to the tuning of thermotropic properties involves the introduction of two different substituents at the oligothiophene core. Thus, the above-mentioned combination of *n*-alkyl and *n*-alkynyl substituents resulted in few examples of oligothiophenes that are liquid crystalline at ambient temperature.^[15] We studied the influence of two alkyl substituents that differ in length or in branching sites on the thermotropic behavior of oligothiophenes. Terthiophene **9** with two linear alkyl substituents of different length (*n*-hexyl and *n*-octyl) has nearly the same Cr–LC transition temperature as that of the symmetrical dihexyl analog **1b** but a lower clearing point (Table 1, entries 2 and

7). A more pronounced effect was observed when a branched chain and a linear chain were combined in the same molecule. In the design of the nonsymmetrical terthiophenes **13** and **14**, we kept the length of the two alkyl substituents in the molecule the same but introduced additional branching sites (methyl groups) in one of them. An additional methyl substituent on one of the hexyl chains of the nonsymmetrical molecule **13** essentially stabilizes the mesophase: the temperature of the Cr–LC transition decreases relative to that of the symmetrical analog **1b**, while the clearing point remains nearly unchanged (Table 1, entries 2 and 8). As expected, a bulkier 3,7-dimethyloctyl substituent in **14** causes more pronounced changes in the thermotropic behavior, and both the temperature of Cr–LC transition and the isotropization point are remarkably lower than those of dioctylterthiophene **1a** (Table 1, entries 1 and 9). Notably, the nonsymmetrical terthiophene **14** is liquid crystalline at ambient temperature (between 23 and 49 °C). For all liquid crystalline mesophases of the oligothiophenes, birefringent flowing textures were obtained by polarized optical microscopy (POM) (see Supporting Information).

The supramolecular structure of the nonsymmetrical terthiophene **13** has been studied in detail. We paid particular attention to this compound because of its very low enthalpy of transition between the LC and crystalline phases, which could enable us to obtain also single-crystalline aligned films for OFET applications.^[17] At lower temperatures, two different crystalline phases exist, and the transition between them is at 32 °C (Figure 1). The mosaic texture (POM) of the phase between 41 °C and 79 °C (clearing point) suggests its smectic liquid crystalline nature.^[18] This was corroborated by powder X-ray diffraction. The diffractogram of **13** at 65 °C displays an intense reflection at $q = 0.26 \text{ \AA}^{-1}$ (Figure 2). This peak is indexed as (001) and corresponds to the interplanar spacing (smectic layer thickness) of 24.3 Å. From the comparison of the thickness of the smectic layer with the length of the molecule (ca. 28 Å, estimated from the AM1 molecular geometry optimization), it can be concluded that the long axes of the molecules are tilted at ca. 30° relative to the normal of the smectic plane. Higher-order reflection peaks are observed at $q = 0.52 \text{ \AA}^{-1}$ (002), $0.78 \text{ \AA}^{-1}$ (003), and $1.03 \text{ \AA}^{-1}$ (004). They indicate long-range order in the direction perpendicular to the smectic plane. Peaks at $q = 1.48 \text{ \AA}^{-1}$, $1.68 \text{ \AA}^{-1}$, and $1.90 \text{ \AA}^{-1}$ are indexed as (020), (110), and (–120), respectively, and correspond to interplanar distances. Peaks at $q = 1.31 \text{ \AA}^{-1}$ and $1.38 \text{ \AA}^{-1}$ are assigned to intermolecular distances between the sulfur atoms (4.80 Å and 4.57 Å, respectively).^[1,19] The reflections at high q values arises from the packing of the molecules within the smectic layers. A hexatic structure and a monoclinic cell are derived with the following calculated parameters: $a = 4.60 \text{ \AA}$, $b = 8.54 \text{ \AA}$, $c = 24.3 \text{ \AA}$, $\gamma = 96^\circ$. Together, the tilt of the long axis of molecules relative to the normal of the smectic plane and the reflections at high q values are consistent with a highly ordered smectic G or H phase. This conclusion is supported by the low enthalpy of the Cr₂–Sm transition (1.0 kJ mol^{–1}) and the high enthalpy of isotropi-

zation (28.0 kJ mol^{–1}). It is, however, not possible to distinguish between these two phases on the basis of our X-ray diffraction data.^[20]

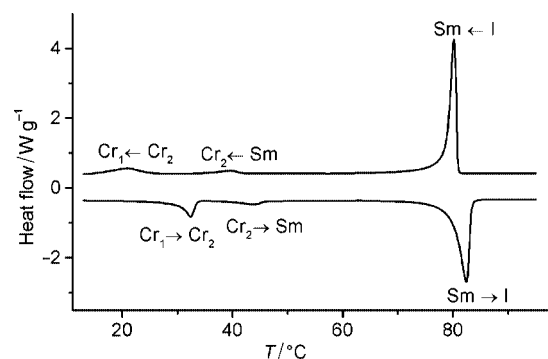


Figure 1. DSC curve of the nonsymmetrical terthiophene **13**, 10 °C min^{–1}; Cr: crystalline phase, Sm G/H: smectic G or H phase, I: isotropic liquid. Temperatures and enthalpies of the phase transitions are given in Table 1.

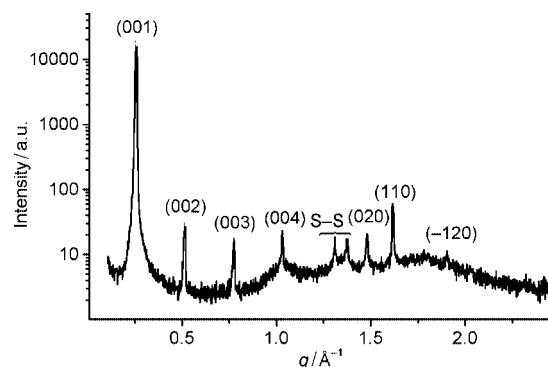


Figure 2. X-ray diffractogram of **13** at 65 °C; S–S is used for distances between sulfur atoms.

Conclusions

We have described a practical synthesis of symmetrical and nonsymmetrical terthiophenes and quaterthiophenes involving Suzuki coupling and carbanion alkylation as key steps. The branching of the side chains and desymmetrization of the molecule are two efficient tools for tailoring thermotropic properties of rodlike mesogens. A balance between the order caused by the stacking of the aromatic cores and the disorder caused by the alkyl chains should be carefully optimized to obtain desirable thermotropic properties. Using different approaches, we achieved a wide mesophase temperature range and liquid crystallinity at room temperature, two important properties for the fabrication of organic semiconducting devices. Studies of the performance of novel liquid crystalline oligothiophenes in field-effect transistors are in progress.

Experimental Section

General: All chemicals were purchased from Aldrich or Acros and used without further purification unless stated otherwise. THF was

refluxed over sodium and benzophenone until a blue-violet color persisted, and it was distilled directly into the reaction flask. A commercially available solution of *n*BuLi in hexane was titrated with Ph₂CHCOOH immediately before use. *t*BuOK was used as a 1-M solution in THF. Dialkyloligothiophenes **1a**, **1b**, and **2** were synthesized as described by us earlier.^[9] 1-Iodo-5-methylhexane was prepared by the Finkelstein reaction: a mixture of 1-bromo-5-methylhexane (1 mmol) and NaI (1.5 mmol) in acetone (10 mL) was heated at reflux overnight; after filtration and careful evaporation of the solvent, the crude product (judged to be >95% pure by ¹H NMR) was used without further purification. 2-Bromo-5-octylthiophene (**8**) was synthesized according to a published procedure.^[21] Column chromatography: SiO₂ Kieselgel 60 (Macherey–Nagel, particle size 0.04–0.063 mm). TLC: precoated SiO₂ plates Kieselgel 60F₂₅₄ (Merck). ¹H NMR (300 MHz) and ¹³C NMR (75 MHz) spectra were recorded in CDCl₃ with a Bruker Avance 300 spectrometer; chemical shifts (δ) are given in ppm relative to Me₄Si (internal standard); coupling constants (*J*) are given in Hz. EI-MS (70 eV) spectra were recorded with a VG Micromass 7070F instrument. Phase transition temperatures were measured by differential scanning spectroscopy (Mettler Toledo DSC 821) at heating and cooling rates of 10 °C min⁻¹. Optical textures of mesophases were observed with a polarizing microscope (Nikon Eclipse 80i). Powder X-ray diffraction measurements were carried out with a Bruker D8-diffractometer (Cu-K α radiation).

General Procedure 1: Alkylation of 2,2':5',2''-Terthiophene (3): A solution of terthiophene **3** (500 mg, 2.12 mmol) in dry THF (10 mL) was cooled to -78 °C, and a solution of *n*BuLi (ca. 1.6 M in hexane, 6.04 mmol) was added dropwise by cannula. The reaction mixture was stirred for 10 min at -78 °C, then a solution of *t*BuOK (1.0 M in THF, 8.05 mmol) was added. The stirring was continued for 15 min at -78 °C, then the 1-haloalkane (5 mmol) was added. The reaction mixture was allowed to slowly reach room temperature, stirred overnight, quenched by the slow addition of water (10 mL), and extracted with hexane (3 × 10 mL). After evaporation of the solvent, the residue was purified by column chromatography or crystallized from methanol/toluene to give pure **1**.

General Procedure 2: Synthesis of Terthiophenes 6 and 9 by Suzuki Coupling: A suspension of pinacolborane ester **7** or **11** (7.5 mmol) in EtOH (10 mL) and a solution of K₂CO₃ (3.43 g, 24.8 mmol) in H₂O (15 mL) were added to a solution of bromide **8** or **12** (5.0 mmol) and [Pd(PPh₃)₄] (61 mg, 0.05 mmol) in toluene (100 mL). The mixture was heated at 75 °C for 45 min, then cooled to room temperature and diluted with hexane (100 mL). The organic layer was dried with MgSO₄ and concentrated in vacuo. The residue was purified by column chromatography to give pure **6** or **9**.

(±)-(S,S/R,R)- and meso-5,5''-Bis(3,7-dimethyloctyl)-2,2':5',2''-terthiophene (1c), Mixture of Diastereoisomers: Prepared according to General Procedure 1 from (±)-1-bromo-3,7-dimethyloctane (0.860 mL). Crystallization from methanol/toluene afforded pure **1c**. Yellow solid; yield 0.986 g (88%); m.p. 45 °C. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 6.96 (s, 2 H), 6.95 (d, *J* = 3.6 Hz, 2 H), 6.67 (d, *J* = 3.6 Hz, 2 H), 2.70–2.90 (m, 4 H), 1.63–1.72 (m, 2 H), 1.44–1.56 (m, 4 H), 1.08–1.35 (m, 14 H), 0.92 (d, *J* = 2.5 Hz, 6 H), 0.88 (d, *J* = 2.5 Hz, 12 H) ppm. ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ = 145.6, 136.1, 134.6, 124.6, 123.4, 123.1, 39.3, 38.7, 37.0, 32.3, 27.9, 27.8, 24.7, 22.7, 22.6, 19.5 ppm. HR-EI-MS: calcd. for C₃₂H₄₈S₃ [M]⁺ 528.2918; found 528.2919.

5,5''-Bis(5-methylhexyl)-2,2':5',2''-terthiophene (1d): Prepared according to General Procedure 1 from 1-iodo-5-methylhexane (1.13 g). Column chromatography (hexane) afforded analytically

pure **1d**. Yellow solid; yield 0.847 g (90%); m.p. 85 °C. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 6.97 (s, 2 H), 6.96 (d, *J* = 4.5 Hz, 2 H), 6.68 (d, *J* = 3.5 Hz, 2 H), 2.80 (t, *J* = 7.5 Hz, 4 H), 1.67 (quint, *J* = 7.5 Hz, 4 H), 1.50–1.58 (m, 2 H), 1.36–1.50 (m, 4 H), 1.20–1.30 (m, 4 H), 0.88 (d, *J* = 7 Hz, 12 H) ppm. ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ = 145.4, 136.1, 134.6, 124.8, 123.4, 123.2, 38.7, 31.8, 30.2, 27.9, 26.9, 22.6 ppm. HR-EI-MS: calcd. for C₂₆H₃₆S₃ [M]⁺ 444.1979; found 444.1968.

(±)-(S,S/R,R)- and meso-5,5''-Bis(3,7-dimethyloctyl)-2,2':5',2''-5',2''-quaterthiophene (5), Mixture of Diastereoisomers: Prepared according to General Procedure 1 with the following amendment: quaterthiophene **4** (500 mg, 1.5 mmol) was dissolved in dry THF (50 mL) and treated with *n*BuLi (4.5 mmol), *t*BuOK (6 mmol), and (±)-1-bromo-3,7-methyloctane (3.75 mmol, 0.78 mL). Column chromatography (hexane/toluene 90:10) afforded analytically pure **5**. Yellow solid; yield 0.778 g (85%). ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 6.99–7.07 (m, 6 H), 6.71 (d, *J* = 3.4 Hz, 2 H), 2.70–2.90 (m, 4 H), 1.65–1.75 (m, 2 H), 1.07–1.55 (m, 18 H), 0.93 (d, *J* = 6.2 Hz, 6 H), 0.87 (d, *J* = 8.1, 12 H) ppm. ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ = 145.9, 136.7, 135.4, 134.4, 124.7, 124.0, 123.5, 123.4, 39.3, 38.9, 37.0, 32.3, 27.9, 27.8, 24.7, 22.7, 22.6, 19.5 ppm. HR-EI-MS: calcd. for C₃₆H₅₀S₄ [M]⁺ 610.2801; found 610.2795.

5-Octyl-2,2':5',2''-terthiophene (6a): Prepared according to General Procedure 2 from boronate **11** (1.17 g, 3.0 mmol) and bromide **8** (540 mg, 2.0 mmol). Column chromatography (hexane) followed by crystallization from methanol/toluene afforded analytically pure **6a**. Yellow solid; yield 0.360 g (50%); m.p. 69 °C. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 7.20 (dd, *J* = 5.1, 1.1 Hz, 1 H), 7.17 (dd, *J* = 3.6, 1.1 Hz, 1 H), 7.05 (d, *J* = 3.6 Hz, 1 H), 6.99–7.03 (m, 3 H), 6.68 (d, *J* = 3.6 Hz, 1 H), 2.79 (t, *J* = 7.5 Hz, 2 H), 1.68 (quint, *J* = 7.5 Hz, 2 H), 1.27–1.44 (m, 10 H), 0.88 (t, *J* = 6.6 Hz, 3 H) ppm. ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ = 145.6, 137.3, 136.8, 135.5, 134.4, 127.8, 124.8, 124.3, 124.2, 123.5, 123.4, 31.9, 31.6, 30.2, 29.3, 29.2, 29.1, 22.7, 14.1 ppm (1 signal of aromatic C is missing due to overlap). HR-EI-MS: calcd. for C₂₀H₂₄S₃ [M]⁺ 360.1040; found 360.1025.

5-Hexyl-2,2':5',2''-terthiophene (6b): Prepared according to General Procedure 2 from boronate **7** (1.00 g, 3.0 mmol) and bromide **12** (0.2 mL, 2.0 mmol). Column chromatography (hexane) followed by crystallization from methanol/toluene afforded analytically pure **6b**. Yellow solid; yield 0.312 g (47%); m.p. 57 °C. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 7.20 (dd, *J* = 5.1, 1.1 Hz, 1 H), 7.15 (dd, *J* = 3.3, 1.1 Hz, 1 H), 7.06 (d, *J* = 3.6 Hz, 1 H), 6.98–7.03 (m, 3 H), 6.69 (d, *J* = 3.6 Hz, 1 H), 2.80 (t, *J* = 7.5 Hz, 2 H), 1.69 (quint, *J* = 7.5 Hz, 2 H), 1.27–1.44 (m, 6 H), 0.90 (t, *J* = 6.6 Hz, 3 H) ppm. ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ = 145.6, 137.3, 136.8, 135.5, 134.4, 127.8, 124.8, 124.3, 123.5, 123.4, 31.6 (2C), 30.2, 28.7, 22.6, 14.1 ppm (2 signals of aromatic C are missing due to overlap). HR-EI-MS: calcd. for C₁₈H₂₀S₃ [M]⁺ 332.0727; found 332.0711.

5-Hexyl-5''-octyl-2,2':5',2''-terthiophene (9): Prepared according to General Procedure 2 from boronate **7** (1.03 g, 2.8 mmol) and bromide **8** (500 mg, 1.82 mmol). Crystallization from methanol/toluene gave analytically pure **9**. Yellow solid; yield 0.485 g (60%). ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 6.96 (s, 2 H), 6.95 (d, *J* = 4.1 Hz, 2 H), 6.67 (d, *J* = 4.1 Hz, 2 H), 2.78 (t, *J* = 7.5 Hz, 4 H), 1.68 (quint, *J* = 7.5 Hz, 4 H), 1.28–1.40 (m, 16 H), 0.86–0.92 (m, 6 H) ppm. ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ = 145.4, 136.1, 134.6, 124.7, 123.4, 123.1, 31.8, 31.6, 31.5, 30.2, 29.3, 29.2, 29.1, 28.7, 22.6, 22.5, 14.1, 14.0 ppm (2 signals of aliphatic C are missing

due to overlap). HR-EI-MS: calcd. for $C_{26}H_{36}S_3$ $[M]^+$ 444.1979; found 444.1998.

5-Hexyl-5''-(5-methylhexyl)-2,2':5',2''-terthiophene (13): Prepared according to General Procedure 1 with the following amendment: 5-hexylterthiophene **6b** (250 mg, 0.75 mmol) was dissolved in THF (10 mL) and treated with *n*BuLi (1.1 mmol), *t*BuOK (1.5 mmol), and 1-iodo-5-methylhexane (0.25 mL, 1.5 mmol). Column chromatography (hexane/toluene, 9:1) followed by crystallization from methanol/toluene afforded analytically pure **13**. Yellow solid; yield 0.194 g (60%). 1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 6.96 (s, 2 H), 6.95 (d, J = 4.1 Hz, 2 H), 6.67 (d, J = 4.1 Hz, 2 H), 2.78 (t, J = 7.5 Hz, 4 H), 1.22–1.77 (m, 15 H), 0.88–0.96 (m, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 145.4, 136.1, 134.6, 124.7, 123.4, 123.2, 38.7, 31.8, 31.6, 30.2, 30.2, 28.7, 27.9, 26.9, 22.6, 22.5, 14.1 ppm (2 signals of aliphatic C are missing due to overlap). HR-EI-MS: calcd. for $C_{25}H_{34}S_3$ $[M]^+$ 430.1823; found 430.1819.

(±)-5-(3,7-Dimethyloctyl)-5''-octyl-2,2':5',2''-terthiophene (14): Prepared according to General Procedure 1 with the following amendment: 5-octylterthiophene **6a** (250 mg, 0.69 mmol) was dissolved in THF (10 mL) and treated with *n*BuLi (1.05 mmol), *t*BuOK (1.4 mmol), and (±)-1-bromo-3,7-dimethyloctane (0.22 mL, 1.4 mmol). Column chromatography (hexane/toluene, 9:1) followed by crystallization from methanol/toluene afforded analytically pure **14**. Yellow solid; yield 0.207 g (60%). 1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 6.96 (s, 2 H), 6.95 (d, J = 4.1 Hz, 2 H), 6.67 (d, J = 4.1 Hz, 2 H), 2.78 (t, J = 7.5 Hz, 4 H), 1.10–1.80 (m, 22 H), 0.80–0.96 (m, 12 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 145.4, 145.6, 136.1, 134.6, 134.6, 124.8, 124.6, 123.4, 123.1, 39.3, 38.9, 37.0, 32.3, 31.8, 31.6, 30.2, 29.3, 29.2, 29.1, 27.9, 27.8, 24.7, 22.7, 22.6, 19.5, 14.1 ppm (3 signals of aromatic C are missing due to overlap). HR-EI-MS: calcd. for $C_{30}H_{44}S_3$ $[M]^+$ 500.2605; found 500.2613.

Supporting Information (see footnote on the first page of this article): POM textures of **5**, **9**, **13**, and **14**; powder X-ray diffraction data of **13**.

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