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Non-symmetrical oligothiophenes with 'incompatible' substituents

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Abstract—The syntheses of oligothiophenes **1** and **2** comprising two different types of peripheral substituents, namely alkyl and perfluoroalkyl, is reported. The key synthetic step is the Pd-catalyzed cross-coupling of perfluoroalkylated bromide **3** with an appropriate boronate. This molecular design is expected to promote unusual two-layer packing, which is of interest for application in electronic devices. Quaterthiophene **1** forms smectic mesophase, though in the narrow temperature range, and is suitable for the fabrication of thin films by solution processing methods.

1. Introduction

Oligothiophenes have been receiving increasing attention in the field of organic electronics due to their interesting semiconducting properties. In particular, α,ω-dialkylthiophenes demonstrate high charge carrier mobility in liquid crystalline mesophases combined with the excellent chemical and electrochemical stability.[1,2] However, all such systems behave as p-type (hole transporting) semiconductors, presumably because of the electron-richness of the thiophene rings.

On the other hand, development of n-type (electron transporting) semiconducting materials would promote new applications such as ambipolar transistors or p–n junction diodes and contribute to a better fundamental understanding of charge transport in organic molecular semiconductors.[3] Recently, the synthesis of a series of α,ω-diperfluorohexyloligothiophene was reported.[4] Notably, α,ω-diperfluorohexylsexithiophene shows n-type semiconductivity in thin film transistors.[3] Apparently, electron transport in this molecule bearing polyfluoroalkyl substituents is facilitated by the stabilization of anion-radicals.

Here, we report the syntheses and characterization of the non-symmetric quaterthiophene **1** and sexithiophene **2**, comprising three 'incompatible' parts: a rigid aromatic core, a perfluoroalkyl chain and an alkyl chain. Several new features are anticipated from these rod-like molecules depicted in Figure 1: (i) the self-organization into a large variety of lyotropic mesophases as a function of concentration and the nature of solvent (alkanes, perfluoroalkanes, aromatics); (ii) formation of thin films with different morphologies depending on deposition conditions; and (iii) the packing into highly ordered smectic mesophases promoting fast ambipolar charge transport.

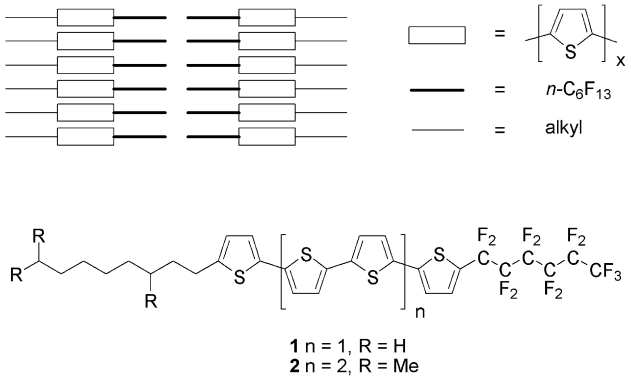

Figure 1. Molecular structure of oligothiophenes **1** and **2** (bottom) and their two-layer packing (top).

2. Results and discussion

The convergent syntheses of oligothiophenes **1** and **2** comprising alkyl and perfluoroalkyl substituents rely on Suzuki–Miyaura coupling[5] as a key step (Schemes 1 and 2). It should be noted here that only few examples of oligothiophenes with different substituents in one molecule are known to date. Thus, Funahashi and Hanna recently reported high charge

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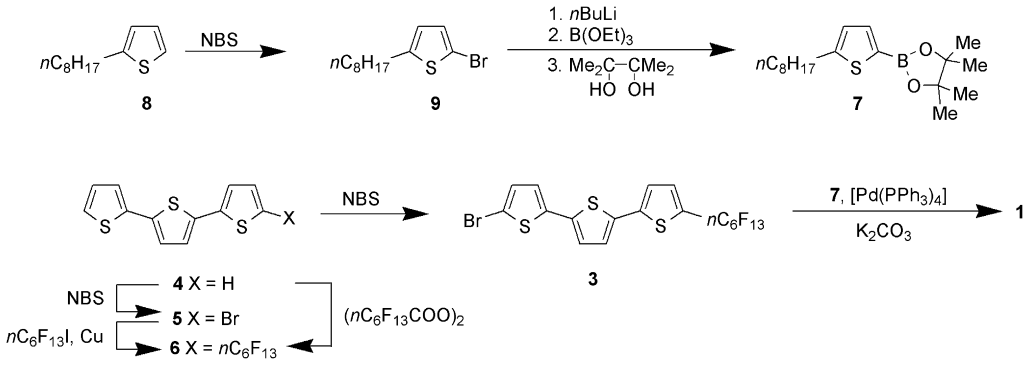


Scheme 1. Synthesis of quaterthiophene **1**.

carrier mobility in smectic phases of α-alkyl-α′-alkynyloligothiophenes, prepared by multi-step synthesis involving sequential Kumada couplings as key steps to assemble the oligothiophene core.[2] Although it appears clear that non-symmetrical oligothiophenes should be easily accessible by the Suzuki coupling of the correspondent building blocks, no successful attempt is mentioned in the literature. In addition, the synthetic approach based on Suzuki coupling is particularly attractive since a great number of arylboronate building blocks is either available commercially or can be easily prepared from commercial precursors.

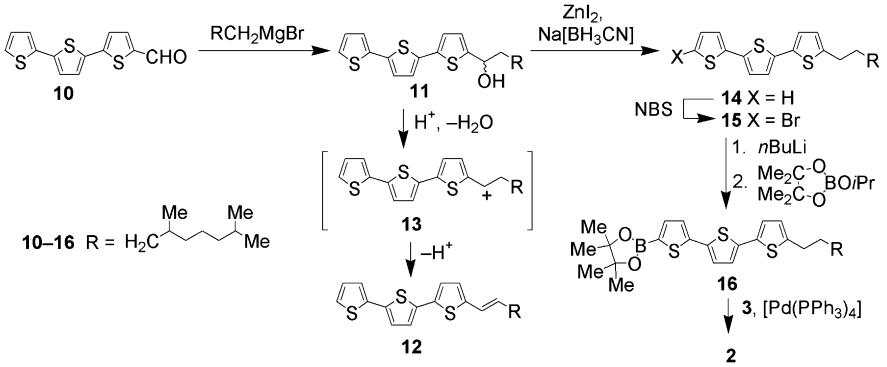
They key intermediate in the syntheses of **1** and **2** is the perfluorohexyl terthiophene **3**. Among known methods of perfluoroalkylation of aromatic molecules, a Cu-promoted cross-coupling between aryl bromides or iodides and perfluoroalkyl iodides in polar solvent (typically DMSO) is frequently used. This method was reported to give satisfactory results for a variety of aromatic substrates[6] including thiophenes and oligothiophenes.[4] The use of the Cu-promoted cross-coupling method requires the synthesis of the intermediate monobromide **5**, which was prepared from the commercial terthiophene (**4**) by slightly modified known methods.[4,7] We have found that the bromination with *N*-bromosuccinimide (NBS) in *N*,*N*-dimethylformamide (DMF) at the ambient temperature gives the best results (69% yield of **5** after crystallization) while reaction in CCl_4 produced considerable amounts of the corresponding dibromide.

The subsequent reaction of bromide **5** with *n*–$C_6F_{13}I$ and copper in DMSO at 125 °C furnished perfluoroalkylterthiophene **6** (Scheme 1). However, we found this reaction to be poorly reproducible: the yield of **6** varied between 14 and 68% while 53% was reported by Facchetti et al.[4] In addition, further unidentified side products were detected (TLC and ^{1}H NMR).

Due to encountered reproducibility problem, we decided to test an alternative synthesis of **6** by the mild radical perfluoroalkylation of terthiophene (**4**) with perfluorohexanoyl peroxide. This method was successfully employed in the synthesis of various perfluoroalkyl thiophenes and furans and demonstrated excellent regioselectivity and high yields.[8] However, its use for the perfluoroalkylation of oligothiophenes was not reported. Perfluorohexyl peroxide was generated in situ from the corresponding acyl chloride and H_2O_2/NaOH in water[9] and its concentration in solution was determined by the iodometric titration.[10] When terthiophene (**4**) was allowed to react with solution of perfluorohexanoyl peroxide at 40 °C, the product **6** with the perfluorohexyl substituent in the α-position of the terminal thiophene ring was isolated. No detectable amounts of regioisomeric side products or products resulting from the multiple substitution of hydrogen atoms by the C_6F_{13} radical were observed. On the other hand, the yield of **6** remained rather moderate (31%). In addition, the polyfluorinated diacyl peroxides are unstable at ambient conditions even in diluted solutions and require quick manipulations at low temperatures.

Finally, perfluorohexyl terthiophene **6** was brominated (NBS and DMF) to give bromide **3** in 68% yield.

Another intermediate in the synthesis of quaterthiophene **1** is boronate **7**. It was synthesized from the bromo thiophene **9**,



Scheme 2. Synthesis of sexithiophene **2**.

prepared by the bromination of commercial 2-octylthiophene (**8**) with NBS in 92% yield.[11] On the other hand, one-pot synthesis involving bromine–lithium exchange in **9** followed by the reaction of the lithium derivative with $B(OEt)_3$ and subsequent transesterification with pinacol (2,3-dimethylbutane-2,3-diol)[12] produced boronate **7** in 59% yield after purification by column chromatography.

In a key step, boronate **7** was reacted with bromide **3** in typical Suzuki coupling conditions with $[Pd(PPh_3)_4]$ as a catalyst.[13] After standard workup, quaterthiophene **1** (53% yield) was isolated by precipitation from CH_2Cl_2 and purified by two repetitive crystallizations from toluene.

Quaterthiophene **1** (yellow solid with limited solubility in common organic solvents) was characterized and its high purity was confirmed by ^1H, ^{19}F, and ^{13}C NMR, EIMS, and UV–vis spectroscopy. Thermotropic properties of **1** were investigated by differential scanning calorimetry (DSC). The DSC trace of **1** (Fig. 2) exhibits a distinct transition between crystalline (Cr) and liquid crystalline (LC) phases at 198 °C [enthalpy 23.1 kJ mol^{-1}] and a clearing point at 207 °C [2.8 kJ mol^{-1}]. The LC mesophase between 198 °C and 207 °C was preliminarily identified as a fluid smectic, probably SmA phase from the characteristic birefringent flowing texture obtained by the polarized optical microscopy (POM) study.[14] This tentative assignment is supported by the low value of the enthalpy of isotropization, which is consistent with moderately ordered structure of a mesophase.[15]

For the synthesis of non-symmetrical sexithiophene **2** we used a similar strategy involving Suzuki cross-coupling as a key step. It is well known that the expansion of the aromatic core dramatically reduces solubility of π-conjugated rod-like molecules. On the other hand, branching of side chains efficiently reduces π–π-stacking between aromatic cores of various mesogens and improves solubility.[16] Taking into account the modest solubility of quaterthiophene **1** in organic solvents, we decided to introduce branched alkyl substituents in the molecule of sexithiophene **2**. Addition of the Grignard reagent prepared from the racemic 1-bromo-3,7-dimethyloctane to aldehyde **10**[17] afforded the tertiary alcohol **11** as a mixture of diastereoisomers, which was used in the next synthetic step without separation. It should be noted that this addition was accompanied by the elimination of water from **11** to give olefin **12**. This elimination is likely catalyzed by traces of acid and proceeds extremely easily because of formation of the resonance-stabilized cation **13**. However, by a thorough control of reaction time the unwanted side reaction was completely avoided and the target alcohol **11** was isolated in 95% yield (Scheme 2).

The hydride transfer reduction of alcohol **11** to give **14** is non-trivial as many reducing agents provoke the above mentioned elimination of water from **11** to give olefin **12**. However, reduction with ZnI_2 and $Na[BH_3CN]$ in dry 1,2-dichloroethane at the ambient temperature according to the known general method[18] provided the target **14** (89% yield). Subsequent bromination of **14** with NBS in DMF did not represent any difficulty and afforded bromide **15** in nearly quantitative yield (97%). In the next step, **15** was converted to the boronate **16** via bromine–lithium exchange followed by reaction of the lithium intermediate with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.[19]

Finally, Suzuki coupling between bromide **3** and boronate **16** in the same conditions as in the synthesis of quaterthiophene **1** afforded sexithiophene **2** as an orange solid (55%), which precipitated from the reaction mixture. In spite of the sterically demanding branched alkyl chain, sexithiophene **2** is nearly insoluble in common organic solvents and was purified by washing with copious amounts of water and toluene and then dried in vacuum.

Sexithiophene **2** was characterized by ^1H NMR, UV–vis, and EIMS spectroscopy. ^1H NMR spectrum confirmed the substitution of the oligothiophene core with α-alkyl and α′-perfluoroalkyl groups (characteristic signals at ca. 6.65 and ca. 7.45 ppm, respectively, cf. spectrum of **1**). On the other hand, ^1H NMR spectrum revealed presence of impurities in the sample. In addition, broadening of the signals, presumably due to strong self-aggregation, was observed. Very low solubility of sexithiophene **2** renders its purification by chromatography or crystallization impossible. It should be noted that even the ^1H NMR measurement was very difficult and required long time due to very poor solubility of **2**. The DSC trace of **2** did not indicate any phase transitions before the apparent decomposition above 250 °C. Taking all this into account, we decide to focus our further studies on derivatives of quaterthiophene with 'incompatible' alkyl and

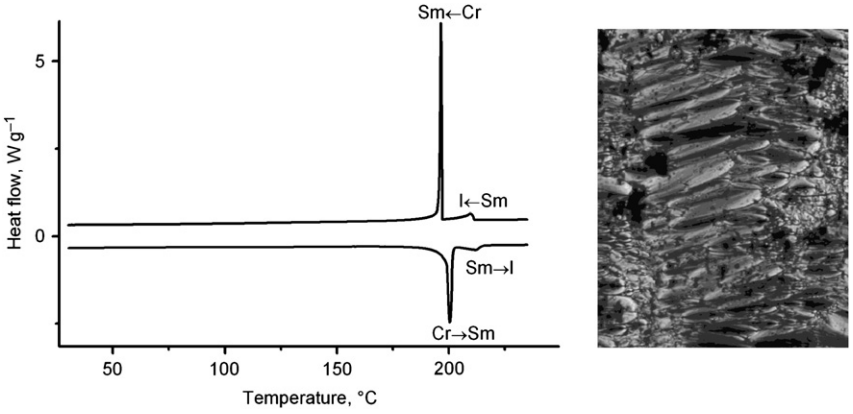


Figure 2. Left: DSC traces of quaterthiophene **1** upon heating and cooling, 10 °C min^{-1}; right: POM images of **1** obtained after cooling from 220 °C (isotropic liquid) to 200 °C (smectic liquid crystalline phase).

perfluoroalkyl substituents such as **1**. On the other hand, we planned to study the possibility of purification and processing of **2** by vacuum techniques such as gradient sublimation and vapor deposition.

3. Conclusion

We have described the syntheses of quaterthiophene **1** and sexithiophene **2** bearing 'incompatible' peripheral substituents. This is, to the best of our knowledge, the first example of such design of the rod-like molecules with potential semiconducting properties. Although quaterthiophene **1** is relatively poorly soluble in organic solvents, it can be easily purified by crystallization. Solubility of **1** in some solvents such as CH_2Cl_2/CS_2 is sufficient for the processing of thin films by solution methods. On the contrary, thorough purification of the nearly insoluble sexithiophene **2** is hardly possible.

We are currently investigating fabrication of thin films of **1** by spin coating and their morphology by STM and X-ray diffraction techniques. The fact that quaterthiophene **1** forms a smectic liquid crystalline mesophase, though in narrow temperature range, is quite encouraging. Our further research efforts are directed to the tuning of the thermotropic behavior and improvement of solubility of the novel quaterthiophene mesogens. Further objectives involve studies of their semiconducting properties in organic field effect transistors.

4. Experimental section

4.1. 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 distilled directly into the reaction flask. Commercially available solution of *n*–BuLi in hexane was titrated with $Ph_2CHCOOH$ immediately before use. Column chromatography: SiO_2 Kieselgel 60 (Macherey–Nagel, particle size 0.04–0.063 mm). TLC: precoated SiO_2 plates Kieselgel $60F_{254}$ (Merck). ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded in $CDCl_3$ on a Brucker Avance 300 spectrometer; chemical shifts (δ) are given in parts per million relative to Me_4Si; coupling constants (J) are given in Hertz. ^{19}F NMR (376 MHz) spectra were recorded in $CDCl_3$ on a Varian VNMR System 400 spectrometer; chemical shifts (δ) are given in parts per million relative to $CFCl_3$. EIMS (70 eV) and CIMS (NH_3) spectra were recorded on a VG Micromass 7070F instrument; *m/z* with the lowest isotopic mass is reported. Phase transition temperatures were measured by differential scanning spectroscopy (Mettler Toledo DSC 821); heating and cooling rates 10 °C min^{-1}; phase transitions were determined from the onset of the second heating curve. Optical textures of mesophases were observed with polarizing microscope (Nikon Eclipse 80i).

4.1.1. 5-Bromo-2,2′:5′,2″-terthiophene (5). NBS (694 mg, 3.90 mmol) was added to a solution of terthiophene **4** (0.966 g, 3.89 mmol) in DMF (55 mL). The reaction mixture was stirred for 24 h at room temperature and filtered. Water (100 mL) and CH_2Cl_2 (50 mL) were added to the filtrate, the organic layer was washed with water, dried over $MgSO_4$, and concentrated in vacuum. Crystallization from hexane/toluene afforded compound **5** (882 mg, 69%). Yellow solid; mp 135–136 °C; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ=7.22 (dd, $^3J_{H,H}$=5.1 Hz, $^4J_{H,H}$=1.2 Hz, 1H), 7.16 (dd, $^3J_{H,H}$=3.6 Hz, $^4J_{H,H}$=1.2 Hz, 1H), 7.05 (d, $^3J_{H,H}$=3.9 Hz, 1H), 7.01 (dd, $^3J_{H,H}$=3.6, 5.1 Hz, 1H), 6.99 (d, $^3J_{H,H}$=3.9 Hz, 1H), 6.96 (d, $^3J_{H,H}$=3.9 Hz, 1H), 6.89 (d, $^3J_{H,H}$=3.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ=138.6, 136.8, 136.7, 135.0, 130.6, 127.9, 124.7, 124.5, 124.3, 123.9, 123.7, 111.0; HREIMS: *m/z*: calcd for $C_{12}H_7{}^{79}BrS_3$ ($[M]^+$): 325.8893; found 325.8944; CIMS (NH_3): *m/z* (%)=326 (58, $[M]^+$), 249 (32), 203 (49); UV (MeOH): λ_{max} (ε)=387 nm (2.16×10^4 L mol^{-1} cm^{-1}).

4.1.2. 5-Tridecafluorohexyl-2,2′:5′,2″-terthiophene (6). *Procedure 1*. A mixture of bromide **5** (206 mg, 0.631 mmol), Cu powder (217 mg, 3.42 mmol), $C_6F_{13}I$ (340 μL, 1.58 mmol), and dry DMSO (2.5 mL) was placed in a Schlenk tube. The mixture was degassed by three freeze-pump-thaw cycles and then heated for 18 h at 125 °C (bath temperature). After cooling to room temperature, Et_2O (20 mL) was added and the reaction mixture was filtered over Celite. The organic phase was washed with water, dried over $MgSO_4$, and concentrated in vacuum. Column chromatography (hexane) afforded **6** as a yellow solid. Yield 163 mg (46%); mp 127 °C; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ=7.32–7.36 (m, 1H), 7.26 (dd, $^3J_{H,H}$=3.6 Hz, $^4J_{H,H}$=1.2 Hz, 1H), 7.20 (dd, $^3J_{H,H}$=5.1 Hz, $^4J_{H,H}$=1.2 Hz, 1H), 7.13–7.17 (m, 2H), 7.11 (d, $^3J_{H,H}$=3.9 Hz, 1H), 7.04 (dd, $^3J_{H,H}$=3.6, 5.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ=142.4, 138.3, 136.6, 134.0, 131.2, 128.1, 127.3, 126.0, 125.2, 124.5, 124.2, 123.4, 117.3, 114.7, 111.1, 110.5, 110.3, 108.5; ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ=−81.2 (3F), −101.7 (2F), −121.9 (4F), −123.3 (2F), −126.6 (2F); HREIMS: *m/z*: calcd for $C_{18}H_7F_{13}S_3$ ($[M]^+$): 565.9502; found 565.9635; CIMS (NH_3): *m/z* (%)=567 (100, $[M+H]^+$), 565 (39), 547 (46, $[M-F]^+$), 297 (34, $[M-C_5F_{11}-H]^+$); UV(MeOH): λ_{max} (ε)=361 nm (2.32×10^4 L mol^{-1} cm^{-1}).

Procedure 2. Solutions of NaOH (3.03 M in H_2O, 2.60 mL) and H_2O_2 (30% in H_2O, 0.40 mL) were added to 1,1,2-trichlorotrifluoroethane (5 mL) at −6 °C. Precooled $C_6F_{13}COCl$ (1.3 mL, 7.84 mmol) was added at the same temperature, after 2 min the solution was allowed to reach 0 °C and stirred for further 5 min. The organic layer was quickly washed with an ice-cold saturated aqueous $NaHCO_3$ solution and water, dried over Na_2SO_4, and kept at −78 °C. The concentration of acylperoxide solution was determined by iodometric titration of an aliquot (1 mL).[10]

In a Schlenk tube, a solution of terthiophene **4** (249 mg, 1.00 mmol) in CH_2Cl_2 (5 mL) was added to a solution containing 0.5 mmol of acylperoxide. The mixture was degassed by three freeze-pump-thaw cycles and then heated for 3 h at 40 °C. The mixture was cooled to the room temperature, the organic phase was separated, washed with water, dried over $MgSO_4$, and concentrated in vacuum. Column chromatography (hexane) afforded **6** (174 mg, 31%) as a yellow solid. All analytical data were identical to those for compound **6** prepared by the *Procedure 1*.

4.1.3. 5″-Bromo-5-tridecafluorohexyl-2,2′:5′,2″-terthiophene (3). Prepared similarly to **5** from NBS (50 mg, 0.282 mmol) and **6** (160 mg, 0.282 mmol) in DMF (7 mL). Crystallization from CH_2Cl_2 afforded pure **3** (124 mg, 68%). Yellow solid; mp 116 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ=7.32–7.35 (m, 1H), 7.13–7.16 (m, 2H), 7.04 (d, $^3J_{H,H}$=3.9 Hz, 1H), 6.99 (d, $^3J_{H,H}$=3.9 Hz, 1H), 6.94 (d, $^3J_{H,H}$=3.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ=142.0, 138.0, 137.0, 134.4, 131.2, 130.8, 127.1, 125.9, 124.7, 124.3, 123.5, 111.8; HREIMS: *m/z*: calcd for $C_{18}H_6{}^{79}BrF_{13}S_3$ ([M]$^+$): 643.8601; found 643.8561; EIMS: *m/z* (%)=644 (50), 376 (48), 374 (44), 126 (100).

4.1.4. 2-Bromo-5-octyl-thiophene (9). A solution of NBS (4.53 g, 0.0255 mol) in DMF (20 mL) was added dropwise at 0 °C to a solution of 2-octylthiophene **8** (5.00 g, 0.0255 mol) in DMF (5 mL). The mixture was stirred for 16 h at room temperature and then partitioned between water (10 mL) and hexane (50 mL). The organic layer was washed with water, dried over $MgSO_4$, and concentrated in vacuum. Column chromatography (hexane) afforded **9** (6.46 g, 92%). Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ=6.82 (d, $^3J_{H,H}$=3.7 Hz, 1H), 6.52 (d, $^3J_{H,H}$=3.7 Hz, 1H), 2.72 (t, $^3J_{H,H}$=7.2 Hz, 2H), 1.62 (quint, $^3J_{H,H}$=7.2 Hz, 2H), 1.20–1.40 (m, 10H), 0.88 (t, $^3J_{H,H}$=6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ=147.6, 129.3, 124.3, 108.5, 31.8, 31.4, 30.3, 29.3, 29.2, 29.0, 22.6, 14.1.

4.1.5. 4,4,5,5-Tetramethyl-2-(5-octylthiophen-2-yl)-1,3,2-dioxaborolane (7). A solution of bromide **9** (462 mg, 1.68 mmol) in THF (14 mL) was cooled to −70 °C, and a 1.43 M solution of *n*–BuLi in hexane (1.44 mL, 2.057 mmol) was added. The mixture was allowed to reach room temperature, stirred for 1 h, and cooled again to −70 °C. Triethylborate (1.91 mL, 11.22 mmol) was added, the mixture was allowed to reach room temperature and stirred for 1 h. Pinacol (1.436 g, 12.16 mmol) was added and stirring was continued for further 16 h, then the mixture was partitioned between CH_2Cl_2 (15 mL) and water (60 mL). The organic phase was washed with water (3×60 mL), dried over $MgSO_4$, and concentrated in vacuum. Column chromatography (hexane, then CH_2Cl_2/AcOEt 1:1) afforded **7** (0.320 g, 59%) as an orange oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ=7.47 (d, $^3J_{H,H}$=3.3 Hz, 1H), 6.86 (d, $^3J_{H,H}$=3.3 Hz, 1H), 2.84 (t, $^3J_{H,H}$=7.5 Hz, 2H), 1.68 (quint, $^3J_{H,H}$=7.6 Hz, 2H), 1.33 (s, 12H), 1.18–1.40 (m, 10H), 0.82–0.92 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ=153.7, 137.3, 125.7, 83.8, 31.8, 31.6, 30.1, 29.3, 29.2, 29.0, 24.7, 22.6, 14.0; HREIMS: *m/z*: calcd for $C_{18}H_{31}BO_2S$ ([M]$^+$): 322.2138; found: 322.2132; EIMS: *m/z* (%)=322 (100), 320 (17), 307 (14), 236 (11), 224 (30), 223 (79), 222 (14).

4.1.6. 5-Octyl-5‴-tridecafluorohexyl-2,2′:5′,2″:5″,2‴-quaterthiophene (1). Boronate **7** (227 mg, 0.704 mmol) in EtOH (2 mL) and K_2CO_3 (390 mg, 2.82 mmol) in water (1 mL) were added to a solution of bromide **3** (0.303 mg, 0.470 mmol) and [$Pd(PPh_3)_4$] (55 mg, 0.0475 mmol) in toluene (10 mL). The mixture was heated at 80 °C for 5 h, cooled to room temperature and diluted with CH_2Cl_2. The organic layer was filtered through the sintered glass filter and the yellow solid was washed with CH_2Cl_2. Combined organic phases were washed with water (3×20 mL), dried over $MgSO_4$, and concentrated in vacuum. Addition of a small amount of CH_2Cl_2 caused precipitation of a yellow crystalline solid, which was filtered. Both solids were combined and dried in vacuum. Crude **1** was then crystallized twice from toluene and finally washed with MeOH to give 188 mg (53%) of a yellow solid. DSC: Cr 200 °C LC 213 °C I; ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ=7.33 (d, $^3J_{H,H}$=3.6 Hz, 1H), 7.14 (d, $^3J_{H,H}$=4.2 Hz, 2H), 7.04–7.08 (m, 2H), 6.97 (d, $^3J_{H,H}$=4.2 Hz, 1H), 6.95 (d, $^3J_{H,H}$=4.2 Hz, 1H), 6.67 (d, $^3J_{H,H}$=3.6 Hz, 1H), 2.81 (t, $^3J_{H,H}$=7.8 Hz, 2H), 1.70 (q, $^3J_{H,H}$=7.8 Hz, 2H), 1.20–1.40 (m, 10H), 0.90 (t, $^3J_{H,H}$=6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ=145.7, 134.3, 125.9, 124.9, 124.8, 124.0, 123.6, 123.5, 123.1, 32.0, 31.7, 30.3, 29.5, 29.4, 29.2, 22.9, 14.2 (signals of *C*–F and of some aromatic C were not observed because of the ^{19}F–^{13}C coupling resulting in the low intensity of signals); ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ=−81.1 (3F), −101.4 (2F), −121.7 (4F), −123.7 (2F), −126.4 (2F). HREIMS: *m/z*: calcd for $C_{30}H_{25}F_{13}S_4$ ([M]$^+$): 760.0631; found 760.0590; EIMS: *m/z* (%)=760 (100), 661 (30), 392 (14); UV (hexane): λ_{max} (ε)=398 nm (2.97×10^4 L mol^{-1} cm^{-1}).

4.1.7. (±)-(*S*,*S*/*R*,*R*)- and (±)-(*S*,*R*/*R*,*S*)-4,8-Dimethyl-1-(2,2′:5′,2″-terthiophen-5-yl)-nonan-1-ol (11), mixture of diastereoisomers. 1,2-Dibromoethane (0.067 mL, 0.078 mmol) was added to the suspension of Mg turnings (162 mg, 6.66 mmol) in dry Et_2O (8 mL). The solution was heated until continuous gas evolution was observed, then (±)-1-bromo-3,7-dimethyloctane (0.945 mL, 4.44 mmol) was added and the mixture was heated to reflux for 1 h. A suspension of aldehyde **10** (307 mg, 1.11 mmol) in dry Et_2O (2.5 mL) was added and the heating was continued for 1 h. The mixture was cooled to room temperature and water (20 mL) was added. The resulting mixture was stirred for 30 min, the organic phase was separated and the aqueous phase was extracted with Et_2O/hexane (1:1). Combined organic phases were washed with water, dried over Na_2SO_4, and concentrated in vacuum. Column chromatography (hexane/CH_2Cl_2 9:1) afforded **11** (443 mg, 95%) as an amorphous brown solid; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ=7.26 (dd, $^3J_{H,H}$=5.1 Hz, $^4J_{H,H}$=1.2 Hz, 1H), 7.21 (dd, $^3J_{H,H}$=3.6 Hz, $^4J_{H,H}$=1.2 Hz, 1H), 6.96–7.09 (m, 4H), 6.87 (d, $^3J_{H,H}$=3.6 Hz, 1H), 4.39 (t, $^3J_{H,H}$=6.9 Hz, 1H), 1.10–2.00 (m, 12H), 0.8–0.92 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ=147.19, 147.10, 136.10, 135.28, 135.24, 135.20, 135.12, 126.85, 123.55, 123.47, 123.44, 123.28, 123.09, 122.65, 122.07, 122.06, 69.90, 69.82, 38.26, 36.06, 35.73, 35.68, 31.86, 31.64, 26.94, 23.73, 23.68, 21.69, 21.59, 18.62, 18.59; HREIMS: *m/z*: calcd for $C_{23}H_{30}OS_3$ ([M]$^+$): 418.1458; found 418.1510; EIMS: *m/z* (%)=418 (65, [M]$^+$), 400 (27, [M−H_2O]$^+$), 287 (48), 277 (100), 261 (53), 57 (37); UV(MeOH): λ_{max} (ε)=357 nm (1.72×10^4 L mol^{-1} cm^{-1}).

4.1.8. (±)-5-(4,8-Dimethylnonyl)-2,2′:5′,2″-terthiophene (14). ZnI_2 (437 mg, 1.369 mmol) and Na[BH_3CN] (446 mg, 7.097 mmol) were added to a solution of alcohol **11** (424 mg, 1.01 mmol) in dry 1,2-dichloroethane (30 mL). The reaction mixture was stirred for 72 h at room temperature and filtered through Celite. The Celite cake was washed with CH_2Cl_2 (50 mL) and combined filtrates were evaporated. Column chromatography (hexane) afforded **14** (364 mg, 89%). Amorphous yellow solid; ^{1}H NMR

(300 MHz, $CDCl_3$, 25 °C): δ=7.20 (dd, $^3J_{H,H}$=5.1 Hz, $^4J_{H,H}$=1.2 Hz, 1H), 7.15 (dd, $^3J_{H,H}$=3.6 Hz, $^4J_{H,H}$=1.2 Hz, 1H), 7.05 (d, $^3J_{H,H}$=3.9 Hz, 1H), 6.96–7.03 (m, 3H), 6.68 (d, $^3J_{H,H}$=3.6 Hz, 1H), 2.77 (t, $^3J_{H,H}$=7.5 Hz, 2H), 1.00–1.80 (m, 12H), 0.80–0.90 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ=145.5, 137.3, 136.8, 135.4, 134.4, 127.8, 124.8, 124.28, 124.22, 123.43, 123.40, 123.3, 39.3, 37.2, 36.4, 32.6, 30.5, 29.1, 28.0, 24.8, 22.7, 22.6, 19.6; HREIMS: *m/z*: calcd for $C_{23}H_{30}S_3$ ($[M]^+$): 402.1509; found: 402.1489; EIMS: *m/z* (%)=402 (88, $[M]^+$), 261 (100); UV (MeOH): λ_{max} (ε)=358 nm (2.20×10^4 L mol^{-1} cm^{-1}).

4.1.9. (±)-5″-Bromo-5-(4,8-dimethylnonyl)-2,2′:5′,2″-terthiophene (15). Prepared similarly to **5** from NBS (40 mg, 0.223 mmol) and **14** (89.7 mg, 0.223 mmol) in DMF (5 mL). Crystallization from CH_2Cl_2 afforded pure **15** (104 mg, 97%). Brown solid; mp 107–109 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ=6.95–6.99 (m, 4H), 6.88 (d, $^3J_{H,H}$=3.9 Hz, 1H), 6.68 (d, $^3J_{H,H}$=3.6 Hz, 1H), 2.77 (t, $^3J_{H,H}$=7.2 Hz, 2H), 1.00–1.80 (m, 12H), 0.80–0.92 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ=145.9, 138.8, 137.3, 134.3, 134.2, 130.6, 124.9, 124.5, 123.6, 123.5 (2C), 110.8, 39.3, 37.2, 36.6, 32.6, 30.5, 29.1, 28.0, 24.8, 22.7, 22.6, 19.6; HREIMS: *m/z*: calcd for $C_{23}H_{29}{}^{79}BrS_3$ ($[M]^+$): 480.0615; found 480.0635; EIMS: *m/z* (%)=480 (100, $[M]^+$), 340 (97), 338 (90); UV(MeOH): λ_{max} (ε)=363 nm (2.52×10^4 L mol^{-1} cm^{-1}).

4.1.10. (±)-2-[5″-(4,8-Dimethylnonyl)-2,2′:5′,2″-terthiophen-5-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (16). *n*–BuLi (1.66 M in hexane, 0.190 mL, 0.315 mmol) was added to dry THF (1.6 mL) at −78 °C, then a solution of bromide **15** (150 mg, 0.311 mmol) in dry THF (2.6 mL) was added dropwise and the mixture was stirred for 1 h at −78 °C. Then the mixture was allowed to reach 10 °C, cooled again to −78 °C and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.08 mL, 0.404 mmol) was added in one portion via syringe. The resulting mixture was stirred for 30 min at −78 °C, then allowed to reach room temperature and stirred for further 3 h. The mixture was poured into 15 mL of Et_2O, and a mixture of HCl (1 M in H_2O, 0.40 mL) and ice-cold water (15 mL) was added. The organic phase was separated, washed with water, dried over Na_2SO_4, and concentrated in vacuum to afford **16** as a green solid (120 mg, 72%), which was used without further purification. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ=7.52 (d, $^3J_{H,H}$=3.60 Hz, 1H), 7.21 (d, $^3J_{H,H}$=3.60 Hz, 1H), 7.11 (d, $^3J_{H,H}$=3.90 Hz, 1H), 6.97–7.01 (m, 2H), 6.68 (d, $^3J_{H,H}$=3.30 Hz, 1H), 2.77 (t, $^3J_{H,H}$=7.6 Hz, 2H), 1.35 (s, 12H), 1.10–1.70 (m, 12H), 0.80–0.92 (m, 9H).

4.1.11. 5-(4,8-Dimethylnonyl)-5‴″-tridecafluorohexyl-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2⁗′-sexithiophene (2). A solution of boronate **16** (103 mg, 0.195 mmol) in dry toluene (2.5 mL), a solution of Na_2CO_3 in water (2 M, 0.580 mL), bromide **3** (90 mg, 0.139 mmol), and $[Pd(PPh_3)_4]$ (10 mg, 0.008 mmol) was mixed in the Schlenk tube, Ar atmosphere was secured and the mixture was heated to reflux for 16 h. After cooling to the room temperature, the mixture was partitioned between toluene (50 mL) and water (25 mL) and then filtered through the glass filter. The solid on the filter was excessively washed with water and toluene and dried in vacuum. Orange solid; yield 74 mg (55%); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ=7.42–7.50 (m, 1H), 6.92–7.12 (m, 10H), 6.60–6.68 (m, 1H), 2.76–2.82 (m, 2H), 1.10–1.80 (m, 12H), 0.80–0.96 (m, 9H). HRCIMS (NH_3): *m/z*: calcd for $C_{41}H_{35}F_{13}S_6$ ($[M]^+$): 966.0855; found 966.1140; CIMS (NH_3): *m/z* (%)=966 (100, $[M]^+$), 826 (12); UV (CH_2Cl_2): λ_{max} (ε)=432 nm (1.31×10^4 L mol^{-1} cm^{-1}).

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