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Homologous series of regioregular alkylsubstituted oligothiophenes up to an 11-mer

Jens Krömer[†] and Peter Bäuerle[*]

Department of Organic Chemistry II (Organic Materials and Combinatorial Chemistry), University of Ulm, Albert-Einstein-Allee 11, D-89081 Ulm, Germany

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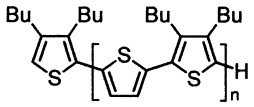
Abstract—A complete series of structurally well-defined butylated oligothiophenes up to an 11-mer was synthesized by a combination of aryl–aryl cross-coupling reactions and cyclization of 1,3-butadiyne precursors with sulfide anions. Palladium-catalyzed cross-coupling of halogenated thiophene units with trimethylsilylacetylene effectively yields ethynylated thiophenes which after deprotection are oxidatively coupled to the corresponding 1,3-butadiynes. © 2001 Published by Elsevier Science Ltd.

1. Introduction

Owing to their defined structure, chain and conjugation length, α-conjugated oligothiophenes represent the most frequently investigated model compounds for conducting polymers.[1] Various series of oligothiophenes which were preferably alkylated and therefore soluble, have been synthesized and the physical properties are well correlated to the (conjugated) chain length. Thus, structure–property relationships become available and valuable information can be deduced which is normally not obtainable from the corresponding polymers due to their polydisperse nature.[1,2] Moreover, the study on defined oligomers led to novel organic materials and α-conjugated oligothiophenes have recently successfully been used as active components in organic field-effect transistors,[3] light-emitting devices,[4] or photovoltaic solar cells.[5]

Several synthetic routes to linear α-conjugated oligothiophenes have recently been established, however, their syntheses by step-wise assembly of defined units are typically tedious with respect to (isomeric) purity and yield, particularly for longer oligomers.[1] Two different general routes are widely used, either transition metal-catalyzed aryl–aryl cross-coupling reactions of thiophene building blocks or ring closure reactions from acyclic precursors. Very recently, oligothiophenes comprising chain lengths exceeding the mean conjugation length of corresponding polymers by far were synthesized and characterized.[6] Interestingly, it was shown that conjugation along the one-dimensional chain is saturated after 20 repeating units.[6a] Our aim now was to evaluate synthetic routes to finally obtain a complete homologous series of linear β-alkyl-substituted α-conjugated oligothiophenes consisting of members in which the chain length only varies by bithiophene units (Scheme 1).



(n=0-5)

Scheme 1.

2. Results and discussion

2.1. Synthesis of alkylsubstituted oligothiophenes via nickel-catalyzed cross-coupling reactions

For the synthesis of the oligothiophene series 3,4-dibutylthiophene **1** was chosen as the key building block in order to provide sufficient solubility of particularly the longer oligomers in organic solvents. In contrast to the use of 3-alkylthiophene units, symmetric 3,4-dibutylthiophene **1** guarantees isomerically pure products, because regioirregular couplings are avoided.[7] Sterically demanding substituents in oligo- or polythiophenes typically lead to a distortion of the conjugated backbone and consequently to a reduced effective conjugation length. In particular, 3,3′-substituted bithiophene units result in a nearly perpendicular conformation of adjacent thiophene rings and give rise to higher redox potentials and optical band gaps.[1b] Therefore, in our oligomers each second thiophene ring

Keywords: conjugated oligomers; oligothiophenes; metal-catalyzed cross-coupling reactions.

* Corresponding author. Tel.: +49-731-502-2850; fax: +49-731-502-2840; e-mail: peter.baeuerle@chemie.uni-ulm.de

† Present address: Henkel KGaA, Henkelstr. 67, D-40191 Düsseldorf, Germany.

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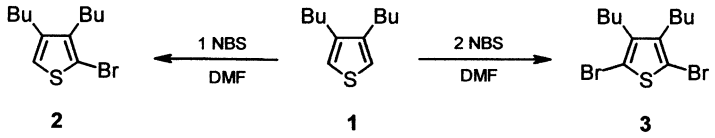


Scheme 2.

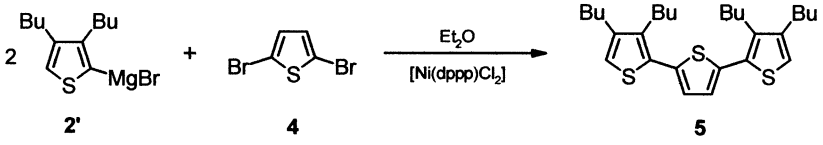
was not substituted. Owing to this alternating pattern, at the same time sufficient solubility and minimized steric interactions between individual thiophene rings is achieved which ideally provides structurally defined model compounds for polythiophenes.

3,4-Dibutylthiophene **1** was synthesized according several literature procedures in 29% overall yield starting from thiophene via tetrabromothiophene and 3,4-dibromothiophene. Bromination of **1** with one equivalent NBS in DMF[8] gave 2-bromo-3,4-dibutylthiophene **2** in 69% yield and with two equivalents 2,5-dibromo-3,4-dibutylthiophene **3** in 84% yield (Scheme 2). Nickel-catalyzed cross-coupling of the Grignard reagent of bromothiophene **2** and 2,5-dibromothiophene **4** resulted in the next higher homologue, tetrabutyl-terthiophene **5**, in 82% yield (Scheme 3). Similarly, 'Kumada-coupling' of 2-thienylmagnesium bromide **6′** and dibromothiophene **3** with $Ni(dppp)Cl_2$ as catalyst gave 3′,4′-dibutylterthiophene **7** (93% yield) which successively was brominated with the system NBS/DMF to yield the corresponding dibromo compound **8** (91% yield). In a further nickel-catalyzed coupling, the latter was reacted with the Grignard reagent of bromothiophene **2** to hexabutyl-quinquethiophene **9** in 76% yield (Scheme 4). Owing to homo-couplings, 3,3′,4,4′-tetrabutyl-2,2′-bithiophene was formed as a side product (7% yield) which was easily separated by chromatography. For the synthesis of the higher homologues, however, aryl–aryl coupling reactions proved to be less effective and face several problems, i.e. selective metallation of oligothiophenes and an increasing portion of homo-coupling products which become more difficult to separate and finally results in gradually decreased yields.

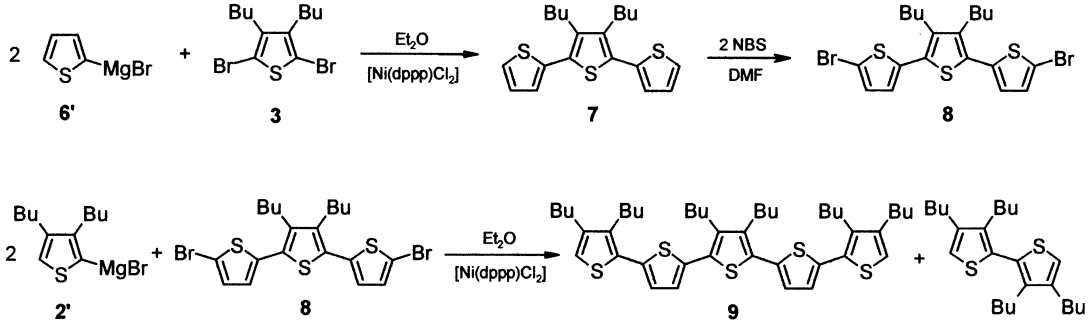
2.2. Introduction of ethynyl groups into the oligothiophene core

Besides transition metal-catalyzed aryl–aryl cross-coupling reactions, for the synthesis of oligothiophenes various methods starting from acyclic precursor molecules have been established. 1,4-Diketones can be cyclized by means of sulfur donors such as phosphorous pentasulfide or Lawesson's reagent to the corresponding thiophenes in good yields.[6i,9] However, as a side reaction, direct dehydratisation of the 1,4-diketone may lead to furans which are difficult to separate.[10] In contrast, cyclization of 1,3-butadiynes with sulfide anions to the corresponding thiophenes is more generally applicable.[11] In particular, longer oligothiophenes are accessible by this method via random oligomerization of bis- and mono-functionalized building blocks and their successive chromatographic separation.[6a,6b]

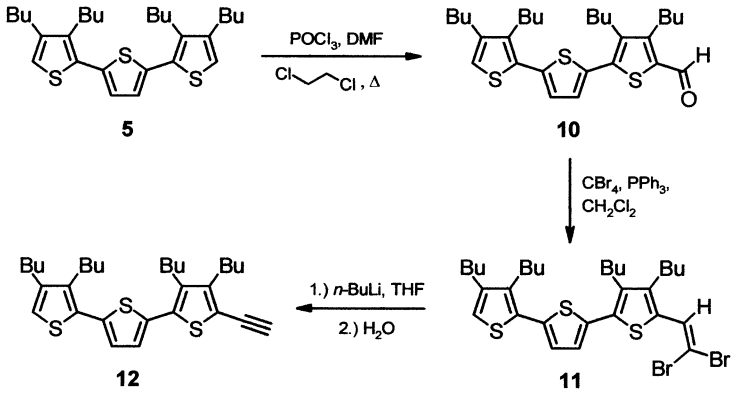
Thienyl-substituted 1,3-butadiynes are obtained by oxidative dimerization of thiophene-acetylenes.[6a,6b,12] We have evaluated the effective introduction of ethynyl groups at the oligothiophene core by using tetrabutyl-terthiophene **5** as an example. The Corey–Fuchs method for the preparation of 2-ethynylthiophenes combines Vilsmeier formylation and the Wittig reaction.[11,13] Terthiophene **5** was selectively formylated with $POCl_3$ and DMF in dichloroethane to give monoaldehyde **10** in 77% yield. Wittig reaction of the latter compound and a mixture of tetrabromomethane and triphenylphosphane effectively resulted in 1,1-dibromoethylene-terthiophene **11** (85% yield) which is by reaction with *n*-butyl lithium subsequently transformed to the monoethynylated terthiophene **12** (Scheme 5). Due to the inherent instability of these acetylene



Scheme 3.



Scheme 4.



Scheme 5.

derivatives and side reactions (alkylation at the 5-position with *n*-BuLi), only moderate yields were obtained (47%).

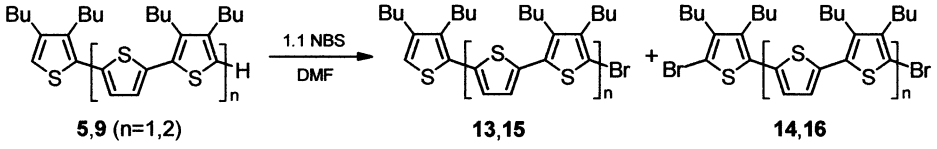
The Sonogashira–Hagihara coupling of acetylenes and halogenated (het)arenes is an interesting alternative for the synthesis of monoethynylated oligothiophenes.[6a,6b,14] Despite the general problem to selectively monobrominate oligothiophenes, terthiophene **5** was first reacted with the system NBS/DMF to give after chromatographic work-up and separation from dibromoterthiophene **14** 5-bromo derivative **13** in 52% yield (Scheme 6). Subsequent palladium-catalyzed reaction of bromoterthiophene **13** and trimethylsilylacetylene went very smoothly to result in TMS-protected 5-ethynylterthiophene **18** in 73% yield (Scheme 7).

If one compares both methods for the preparation of ethynylated terthiophenes **12** and **18** the latter method comprises minor advantages with respect to the overall yield (38% vs. 31%) and to practicality. Therefore, the same methodology was applied to bromothiophene **2** and bromoquinquethiophene **15** which was analogously synthesized from pentamer **9** and NBS/DMF in 42% yield. Palladium-catalyzed couplings of each compound and trimethylsilylacetylene gave coresponding TMS-protected 2-ethynylthiophene **17** in 66% and 5-ethynylquinquethiophene **19** in 69% yield (Scheme 7).

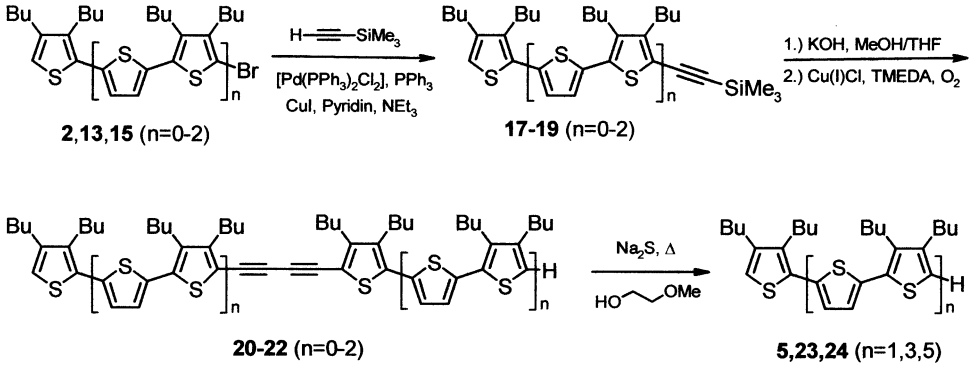
2.3. Copper-promoted coupling of ethynylated oligothiophenes to 1,3-butadiynes and their cyclization to oligothiophenes with sulfide anions

Symmetric 1,3-butadiynes are accessible in good yields through oxidative coupling of acetylenes with the aid of copper salts.[6a,6b,12] Pioneering work of Hay demonstrated that the system Cu(I)Cl/TMEDA in acetone or dichloromethane is very effective to couple ethynylated benzenes at moderate temperatures.[15] We used this methodology to dimerize ethynylated thiophenes **17**–**19** after deprotection by hydroxide in situ to the bis(oligo)thiophene-1,3-butadiynes **20**–**22** in 73, 77, and 65% yield, respectively, which represent stable crystalline solids (Scheme 7).

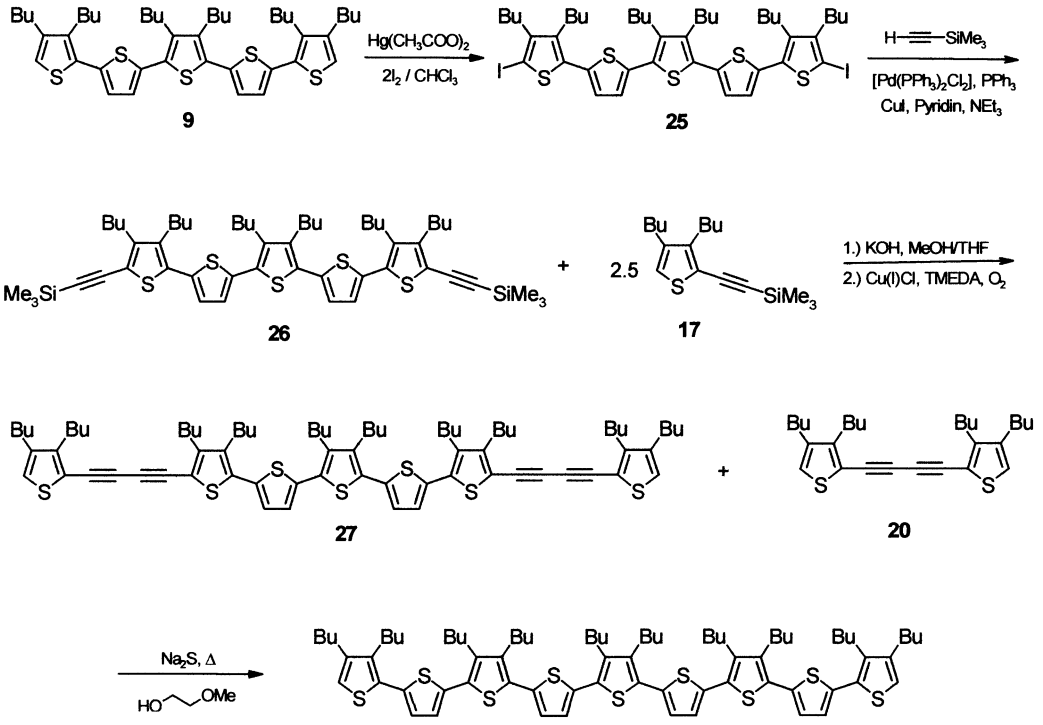
Kagan et al. reported that dithienylbutadiynes quantitatively react with sodium sulfide in boiling methanol to give the corresponding terthiophenes in excellent yields.[11,13] We



Scheme 6.



Scheme 7.



Scheme 8.

optimized this protocol for our (oligo)thiophenebutadiynes and found that the butyl side chains exert steric constraints on adjacent diyne units so that the temperature had to be raised. Analogous reaction of (oligo)thiophenebutadiynes **20**–**22** with sodium sulfide nonahydrate in boiling 2-methoxyethanol cleanly gave trimer **5** in 61%, heptamer **23** in 80%, and undecamer **24** in 73% yield, respectively (Scheme 7).

2.4. Synthesis of a nonamer—nonithiophene 28

By the procedures described above the whole homologous series of alkylated oligothiophenes except the nonamer could be synthesized. Therefore, quinquethiophene **9** was iodinated with elemental iodine in the presence of mercuric acetate to give diiodoquinquethiophene **25** in 87% yield, which was further reacted with TMS–acetylene under palladium catalysis to the twofold ethynylated pentamer **26** (70% yield). After deprotection, this bis-functionalized oligothiophene was coupled under 'Hay conditions' with monoethynylthiophene **17** as a 'capping reagent'. Besides dithienylbutadiyne **20** which is formed in 21% yield as a homo-coupling product and higher molecular weight products, oligomer **27** was isolated in 17% yield after chromatographic work-up. Final cyclization of the two diyne units with sodium sulfide in 2-methoxyethanol gave the desired nonithiophene **28** in 69% yield (Scheme 8).

In conclusion, a complete homologous series of butylated linear α-conjugated oligothiophenes (1T, 3T, 5T, 7T, 9T, 11T) was prepared. The new approach involves a combination of two basic synthetic routes. Oligothiophenes up to the corresponding quinquethiophene were synthesized on large scale (>10 g) by nickel-catalyzed 'Kumada' cross-coupling reactions; higher homologues were obtained by a sequence including 'Sonogashira–Hagihara' coupling and introduction of acetylene groups to the thiophene core, followed by an oxidative dimerization under 'Hay' conditions and final cyclization of the resulting butadiynes with sulfide to the various oligothiophenes. Due to their excellent solubility, the characterization of the physical properties in dependence of the chain length leads to excellent structure–property relationships. This will be reported elsewhere.

3. Experimental

$^1H/^{13}C$ NMR: AMX 500, ACF 250, AC 200; TMS internal standard. MS: Finnigan MAT 8200 and SSQ 7000 (EI: 70 eV), Finnigan MAT 95 (FAB), Bruker Daltonik Reflex III (MALDI–TOF). IR: Perkin–Elmer FTIR Spectrum 2000. Elemental analyses: Perkin–Elmer EA 240 and EA 2400 in the Division of Analytical Chemistry of the University of Ulm. Melting points (uncorrected): Büchi B-545. TLC: Macherey–Nagel SIL G/UV_{254}. Column chromatography (CC): Silica gel 60 (0.020–0.200 mm). Gas chromatography (GC): Carlo–Erba Auto-HRGC MFC 500, PS086 glass capillary column, 10 m and 20 m. HPLC: Shimadzu SCL-10AVP controller, LC-10AT pump, SPD-M10AVP detector, Macherey–Nagel nucleosil column NO_2 (4 mm×250 mm, corn diameter 5 μm). Preparative HPLC: Shimadzu LC-8A pump, SPD-10A detector, Macherey–Nagel nucleosil column NO_2 (40 mm×250 mm, corn diameter 100–10 μm). All solvents and reagents were purified and dried according to common procedures prior to use. All reactions were performed under an argon atmosphere.

3.1. Starting materials

Commercially available: [1,3-Bis(diphenylphosphino)propane]nickel(II)-chloride (Aldrich), bis(triphenylphosphine)-palladium(II)-chloride (Merck), *N*-bromosuccinimid (Aldrich), 2-bromothiophene (Aldrich), *n*-butyl lithium (1.6N in *n*-hexane, Merck), 2,5-dibromothiophene (ABCR), iodine (Merck), copper(I)-chloride (Merck), copper(II)-chloride (Merck), copper(I)-iodide (Aldrich), magnesium (Merck), magnesium sulfate (Merck), sodium sulfide nonahydrate (Fluka), thiophene (Merck). Prepared according to literature procedures: tetrabromothiophene (67%, mp 113–114°C),[16] 3,4-dibromothiophene (55%, bp 104–105°C/20 mbar),[17] 3,4-dibutylthiophene (**1**) (79%, bp 60–62°C; 10^{-2} mbar),[18] 3′,4′-dibutyl-2,2′:5′,2″-terthiophene (**7**) (93%, oil),[19] trimethylsilylacetylene (35%, bp 52–53°C).[20]

3.2. General procedure for the bromination of thiophenes with NBS in DMF (GP1)

In the absence of light and at 0°C, a solution of NBS in DMF was added dropwise over a period of several hours to a solution of the thiophene in DMF, and the mixture was stirred for several hours at ambient temperature, poured onto ice, and extracted with diethyl ether. The organic phases were combined, washed with water, and dried over sodium sulfate. Evaporation of the solvent and either distillation under reduced pressure or chromatographic work-up (phase; eluent) yielded the desired brominated thiophenes.

3.2.1. 2-Bromo-3,4-dibutylthiophene (2). According to GP1, NBS (27.10 g, 152.3 mmol) in 200 ml DMF, 3,4-dibutylthiophene (**1**) (29.90 g, 152.3 mmol) in 200 ml DMF, 4 h, 18 h, distillation, yield 28.92 g (69%), slightly yellow liquid, bp 84–86°C (10^{-2} mbar). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.97 (t, 6 H, $-CH_3$), 1.52 (m, 8 H, β,γ-CH_2), 2.54 (m, 4 H, α-CH_2), 6.86 (s, 1 H, H-5). ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.9 ($-CH_3$), 22.7, 22.5 (γ-CH_2), 29.3, 27.8 (α-CH_2), 31.6, 31.5 (β-CH_2), 109.2 (C-2), 119.9 (C-5), 141.0 (C-3), 141.9 (C-4). MS (EI) *m*/*z* (%): 276 (21) [M^+], 274 (20) [M^+], 234 (15) [$M^+-C_3H_6$], 232 (14) [$M^+-C_3H_6$], 191 (50) [$M^+-C_3H_6-C_3H_7$], 189 (47) [$M^+-C_3H_6-C_3H_7$], 153 (10) [$M^+-C_3H_6-$Br]. Anal. Calcd for $C_{12}H_{19}BrS$ (275.3): C, 52.36; H, 6.96; S, 11.65. Found C, 52.22; H, 6.99; S, 11.61.

3.2.2. 2,5-Dibromo-3,4-dibutylthiophene (3). According to GP1, NBS (13.10 g, 73.5 mmol) in 70 ml DMF, 3,4-dibutylthiophene (**1**) (6.0 g, 30.6 mmol) in 55 ml DMF, 1 h, 3 h, distillation, yield 9.9 g (29.7 mmol, 92%) yellow oil, bp 135–136°C (10^{-2} mbar). ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.95 (t, 6 H, $-CH_3$), 1.42 (m, 8 H, β,γ-CH_2), 2.45 (m, 4 H, α-CH_2). ^{13}C NMR (63 MHz, $CDCl_3$) δ 14.1 ($-CH_3$), 22.8 (γ-CH_2), 28.9 (α-CH_2), 31.9 (β-CH_2), 108.0 (C-2,5), 141.0 (C-3,4). Anal. Calcd for $C_{12}H_{18}Br_2S$ (354.14): C, 40.70; H, 5.12; S, 9.05. Found C, 40.55; H, 4.93; S, 8.89.

3.2.3. 5,5″-Dibromo-3′,4′-dibutyl-2,2′:5′,2″-terthiophene (8). According to GP1, NBS (3.26 g, 18.3 mmol) in 50 ml DMF, dibutylterthiophene (**7**) (3.30 g, 9.15 mmol) in 50 ml DMF, 1 h, 3 h, chromatographic work-up (SiO_2; petroleum ether/dichloromethane 9:1), yield 4.30 g (8.33 mmol, 91%) yellow solid, mp 38–39°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.96 (t, 6 H, $-CH_3$), 1.48 (m, 8 H, β,γ-CH_2), 2.66 (m, 4 H, α-CH_2), 6.87 (d, ^3J=3.1 Hz, 2 H, H-3,3″), 7.01 (d, ^3J=3.1 Hz, 2 H, H-4,4″). ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.8 ($-CH_3$), 22.9 (γ-CH_2), 27.8 (α-CH_2), 32.9 (β-CH_2), 112.0 (C-5,5″), 126.2 (C-3,3″), 129.4 (C-2′,5′), 130.2 (C-4,4″), 137.4 (C-2,2″), 140.5 (C-3′,4′). Anal. Calcd for $C_{20}H_{22}Br_2S_3$ (518.4): C, 46.34; H, 4.28; S, 18.55. Found C, 46.44; H, 4.27; S, 18.45.

3.2.4. 5-Bromo-3,3″,4,4″-tetrabutyl-2,2′:5′,2″-terthiophene (13). According to GP1, NBS (4.14 g, 23.3 mmol) in 150 ml DMF, tetrabutylterthiophene (**5**) (10.00 g, 21.1 mmol) in 300 ml DMF, 1 h, 6 h, chromatographic work-up (SiO_2; petroleum ether/dichloromethane 12:1), yield 6.05 g (11.0 mmol, 52%) yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.94 (t, 12 H, $-CH_3$), 1.52 (m, 16 H, β,γ-CH_2), 2.55 (m, 4 H, α-CH_2), 2.72 (m, 4 H, α-CH_2), 6.87 (s, 1H, H-5″), 7.00 [d, ^3J=3.8 Hz, 1 H, H-4′ (or 3′)], 7.03 [d, ^3J=3.8 Hz, 1 H, H-3′ (or 4′)]. ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.97, 13.87, 13.81 ($-CH_3$), 22.95, 22.88, 22.81, 22.67 (γ-CH_2), 28.90, 28.42, 28.21, 27.50 (α-CH_2), 32.93, 32.69, 31.90, 31.80 (β-CH_2), 108.5 (C-5), 119.2 (C-5″), 143.6, 142.6, 139.0, 138.8, 137.2, 135.1, 131.0, 130.6, 126.3, 125.8 (C-2,3,4,2′,3′,4′,5′,2″,3″,4″). MS (EI) *m*/*z* (%): 554 (15) [M^+], 553 (30) [M^+], 552 (100) [M^+], 551 (28) [M^+], 550 (87) [M^+]. Anal. Calcd for $C_{28}H_{39}BrS_3$ (551.7): C, 60.96; H, 7.13; S, 17.43. Found C, 61.02; H, 7.23; S, 17.21.

3.2.5. 5,5″-Dibromo-3,3″,4,4″-tetrabutyl-2,2′:5′,2″-terthiophene (14). According to GP1, NBS (7.48 g, 42 mmol) in 200 ml DMF, tetrabutylterthiophene (**5**) (9.45 g, 20 mmol) in 100 ml DMF, 1 h, 3 h, chromatographic work-up (SiO_2; *n*-hexane/dichloromethane 10:1), yield 10.7 g (16.8 mmol, 84%) yellow solid, mp 35–36°C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.96 (m, 12 H, $-CH_3$), 1.48 (m, 16 H, β,γ-CH_2), 2.55 (t, 4 H, α-CH_2), 2.71 (t, 4 H, α-CH_2), 6.89 (s, 2 H, H-3′,4′). ^{13}C NMR (63 MHz, $CDCl_3$) δ 13.89, 13.95 ($-CH_3$), 22.85, 22.94 (γ-CH_2), 28.24, 28.44 (α-CH_2), 31.84, 32.97 (β-CH_2), 108.7 (C-5,5″), 126.3 (C-3′,4′), 130.7, 135.7, 139.0, 142.6 (C-2,3,4,2′,5′,2″,3″,4″). MS (EI) *m*/*z* (%):632 (63) [M^+], 630 (100) [M^+], 628 (50) [M^+]. Anal. Calcd for $C_{28}H_{38}Br_2S_3$ (630.6): C, 53.33; H, 6.07; S, 15.25. Found C, 53.23; H, 5.95; S, 15.05.

3.2.6. 5-Bromo-3,3‴,3⁗,4,4″,4‴-hexabutyl-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophene (15). According to GP1, NBS (0.52 g, 2.9 mmol) in 100 ml DMF, hexabutylquinquethiophene (**9**) (2.02 g, 2.7 mmol) in 100 ml DMF, 1 h, 12 h, chromatographic work-up (SiO_2; petroleum ether/dichloromethane 15:1, R_f=0.52), yield 0.92 g (1.1 mmol, 42%) yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.97 (t, 18 H, $-CH_3$), 1.54 (m, 24 H, β,γ-CH_2), 2.56 (m, 4 H, α-CH_2), 2.74 (m, 8 H, α-CH_2), 6.87 (s, 1 H, H-5⁗), 7.02 (d, ^3J=3.8 Hz, 1 H, βH–Th), 7.06 (d, ^3J=3.8 Hz, 1 H, βH–Th), 7.08 (d, ^3J=3.8 Hz, 1 H, βH–Th), 7.09 (d, ^3J=3.8 Hz, 1 H, βH–Th). ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.85 ($-CH_3$), 22.68, 22.81, 22.90, 22.98, 23.03 (γ-CH_2), 28.91, 28.42, 28.22, 27.96, 27.52 (α-CH_2), 32.90, 32.69, 31.91, 31.80 (β-CH_2), 108.6 (C-5), 119.2 (C-5⁗), 143.6, 142.6, 140.3, 140.1, 138.9, 138.9, 136.9, 136.4, 135.7, 135.3, 130.9, 130.8, 130.1, 129.6, 126.3, 126.0, 125.9,

125.9 (C-2,3,4,2′,3′,4′,5′,2″,3″,4″,5″,2‴,3‴,4‴,5‴,2⁗,3⁗,4⁗). MS (EI) *m/z* (%): 828 (100) [M^+], 414 (6) [M^{2+}]. Anal. Calcd for $C_{44}H_{59}BrS_5$ (828.2): C, 63.81; H, 7.18; S, 19.36. Found C, 63.60; H, 6.99; S, 19.64.

3.2.7. 5,5⁗-Dibromo-3,3″,3⁗,4,4″,4⁗-hexabutyl-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophene (16). This compound was isolated as a second fraction from the chromatographic work-up (R_f=0.68) of the corresponding monobromo derivative **15**, yield 0.25 g (0.27 mmol, 10%) orange solid, mp 70–71°C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.99 (m, 18 H, $-CH_3$), 1.52 (m, 24 H, β,γ-CH_2), 2.56 (t, 4 H, α-CH_2), 2.76 (m, 8 H, α-CH_2), 7.03 (d, ^3J=3.6 Hz, 2 H, βH–Th), 7.09 (d, ^3J=3.6 Hz, 2 H, βH–Th). ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.85, 13.90 ($-CH_3$), 22.80, 22.91, 23.04 (γ-CH_2), 27.94, 28.21, 28.37 (α-CH_2), 31.79, 32.87, 32.91 (β-CH_2), 108.6 (C-5,5⁗), 125.89, 126.22, 129.71, 130.87, 135.28, 136.14, 138.74, 140.16, 142.55 (C-2,3,4,2′,3′,4′,5′,2″,3″,4″,5″, 2‴,3‴,4‴,5‴,2⁗,3⁗,4⁗). MS (EI) *m/z* (%): 906 (100) [M^+], 826 (15) [M^+–Br]. Anal. Calcd for $C_{44}H_{58}Br_2S_5$ (907.1): C, 58.26; H, 6.45; S, 17.67. Found C, 58.35; H, 6.29; S, 17.76.

3.3. General procedure for the nickel-catalyzed cross-coupling ('Kumada' coupling) of halogenated thiophenes and metallated thiophenes (GP2)

A solution of the bromothiophene in diethyl ether was added dropwise to magnesium chips in boiling diethyl ether. The resulting mixture was heated at reflux for several hours, allowed to cool to room temperature, and transferred by means of a syringe to the dropping funnel of a second apparatus. The Grignard solution was added dropwise to a solution or suspension of the dibrominated thiophene and 1,3-bis(diphenylphosphino)propane nickel(II) chloride in diethyl ether. The resulting mixture was heated at reflux for several hours, cooled to 0°C, acidified with 1N HCl, and was extracted with dichloromethane. The organic phase was washed with water and was dried with magnesium sulfate. Evaporation of the solvent and purification of the raw material by chromatography (phase; eluent) or recrystallization (solvent) yielded the desired oligothiophene.

3.3.1. 3,3″,4,4″-Tetrabutyl-2,2′:5′,2″-terthiophene (5). According to GP2, bromothiophene (**2**) (32.65 g, 118.7 mmol) in 90 ml diethyl ether, magnesium (2.90 g, 118.7 mmol) in 30 ml diethyl ether, 4 h; 2,5-dibromothiophene (**4**) (13.04 g, 53.9 mmol), Ni(dppp)Cl_2 (135 mg, 250 μmol) in 150 ml diethyl ether, 24 h; recrystallization (2-propanol), yield 20.8 g (44.2 mmol, 82%), yellow crystals, mp 49–50°C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.98 (m, 12 H, $-CH_3$), 1.59 (m, 16 H, β,γ-CH_2), 2.56 (t, 4 H, α-CH_2), 2.75 (t, 4 H, α-CH_2), 6.88 (s, 2H, H-5,5″), 7.07 (s, 2 H, H-3′,4′). ^{13}C NMR (63 MHz, $CDCl_3$) δ 13.9, 14.0 ($-CH_3$), 22.7, 23.0 (γ-CH_2), 27.5, 28.9 (α-CH_2), 31.8, 32.7 (β-CH_2), 119.0 (C-5,5″), 125.8 (C-3′,4′), 130.8 (C-2,2″), 136.5 (C-3,3″), 138.8 (C-4,4″), 143.5 (C-2′,5′). MS (EI) *m/z* (%): 474 (16) [M^+], 473 (31) [M^+], 472 (100) [M^+], 430 (13), 429 (20) [M^+–C_3H_7]. Anal. Calcd for $C_{28}H_{40}S_3$ (472.8): C, 71.15; H, 8.54; S, 20.31. Found C, 70.91; H, 8.44; S, 20.42.

3.3.2. 3,3″,3⁗,4,4″,4⁗-Hexabutyl-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophene (9). According to GP2, bromothiophene (**2**) (8.06 g, 29.3 mmol) in 15 ml diethyl ether, magnesium (0.71 g, 29.3 mmol) in 15 ml diethyl ether, 4 h; dibromoterthiophene (**8**) (3.80 g, 7.3 mmol), Ni(dppp)Cl_2 (80 mg, 146 μmol) in 30 ml diethyl ether, 24 h; chromatographic work-up (SiO_2; *n*-hexane/dichloromethane 9:1, second fraction of chromatography), yield 4.17 g (5.5 mmol, 76%), orange crystals, mp 60–61°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.95 (m, 18 H, $-CH_3$), 1.59 (m, 24 H, β,γ-CH_2), 2.56 (t, 4 H, α-CH_2), 2.75 (t, 8 H, α-CH_2), 6.89 (s, 2H, H-5,5″), 7.08 (d, ^3J=3.5 Hz, 2 H, βH–Th), 7.10 (d, ^3J=3.5 Hz, 2 H, βH–Th). ^{13}C NMR (63 MHz, $CDCl_3$) δ 13.87, 14.00 ($-CH_3$), 22.68, 22.98, 23.04 (γ-CH_2), 27.52, 27.96, 28.90 (α-CH_2), 31.88, 32.70, 32.91 (β-CH_2), 119.1 (C-5,5″), 125.88, 125.90, 129.8, 130.8, 135.8, 136.7, 138.9, 140.1, 143.6 (C-2,3,4,2′,3′,4′,5′,2″,3″,4″,5″, 2‴,3‴,4‴,5‴, 2⁗,3⁗,4⁗). HRMS (EI) *m/z*: $C_{44}H_{60}S_5$: 748.32986. Found 748.33029 [M^+]. Anal. Calcd for $C_{44}H_{60}S_5$ (749.3): C, 70.53; H, 8.07; S, 21.39. Found C, 70.65; H, 8.22; S, 21.12.

As a side product 0.80 g (2.0 mmol, 7%) 3,3′,4,4′-tetrabutyl-2,2′-bithiophene was isolated as a yellow oil (first fraction of chromatography). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87 (t, 6 H, $-CH_3$), 1.01 (t, 6 H, $-CH_3$), 1.50 (m, 16 H, β,γ-CH_2), 2.50 (t, 4 H, α-CH_2), 2.59 (t, 4 H, α-CH_2), 6.87 (s, 2 H, H-5,5″). ^{13}C NMR (63 MHz, $CDCl_3$) δ 13.77, 13.98 ($-CH_3$), 22.68, 22.78 (γ-CH_2), 27.25, 29.00 (α-CH_2), 32.66, 31.91 (β-CH_2), 120.1 (C-5,5″), 129.9 (C-2,2′), 141.3, 142.2 (C-3,3′,4,4′).

3.4. General procedure for the palladium-catalyzed cross-coupling ('Sonogashira–Hagihara' coupling) of halogenated thiophenes and trimethylsilylacetylene (GP3)

A suspension of the halogenothiophene, bis(triphenylphosphino) palladium(II) chloride, triphenylphosphine, copper(I) iodide, pyridine, and triethylamine was purged with argon for 20 min and subsequently heated to 60°C. Trimethylsilylacetylene was added by means of a syringe and the resulting mixture stirred for several hours at 60°C, cooled to 0°C, and filtered. Evaporation of the solvent and purification of the raw material by chromatography (phase; eluent) yielded the desired protected ethynylated oligothiophene.

3.4.1. 3,4-Dibutyl-2-(trimethylsilylethynyl)thiophene (17). According to GP3, bromothiophene (**2**) (4.10 g, 14.9 mmol), $Pd[PPh_3]_2Cl_2$ (520 mg, 0.74 mmol), triphenylphosphine (390 mg, 1.48 mmol), copper(I) iodide (282 mg, 1.48 mmol), 10 ml pyridine, 10 ml triethylamin, trimethylsilylacetylene (2.92 g, 29.8 mmol), 12 h; chromatographic work-up (SiO_2; petroleum ether), yield 2.87 g (9.8 mmol, 66%), yellow liquid, bp 103–104°C (1×10^{-2} mbar). ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.26 (s, 9 H, $Si(CH_3)_3$), 0.95 (m, 6 H, $-CH_3$), 1.49 (m, 8 H, β,γ-CH_2), 2.50 (t, 2 H, α-CH_2), 2.66 (t, 2 H, α-CH_2), 6.80 (s, 1H, H-5). ^{13}C NMR (50 MHz, $CDCl_3$) δ −0.04 ($Si(CH_3)_3$), 13.88, 13.93 ($-CH_3$), 22.51, 22.62 (γ-CH_2), 27.82, 28.65 (α-CH_2), 31.90, 31.95 (β-CH_2), 98.4 (Th–C≡C–), 100.0 (Th–C≡C–), 118.4 (C-2); 121.2 (C-5), 141.8 (C-4), 147.9 (C-3). MS (EI) *m/z* (%): 293 (23) [M^+], 292 (100) [M^+], 277

(40) [M^+-CH_3], 250 (42) [$M^+-C_3H_7$], 235 (32) [$M^+-C_3H_7-CH_3$], 207 (34) [$M^+-2C_3H_7$], 177 (28) [$M^+-2C_3H_7-2CH_3$]. Anal. Calcd for $C_{17}H_{28}SSi$ (292.6): C, 69.79; H, 9.65; S, 10.96. Found C, 69.56; H, 9.55; S, 10.73.

3.4.2. 3,3″,4,4″-Tetrabutyl-5-(trimethylsilylethynyl)-2,2′:5′,2″-terthiophene (18). According to GP3, bromoterthiophene (**13**) (1.60 g, 2.9 mmol), $Pd[PPh_3]_2Cl_2$ (98 mg, 0.14 mmol), triphenylphosphine (76 mg, 0.29 mmol), copper(I) iodide (55 mg, 0.29 mmol), 20 ml pyridine, 20 ml triethylamin, trimethylsilylacetylene (865 mg, 8.8 mmol), 18 h; chromatographic work-up (SiO_2; petrol ether / dichloromethane 8:1), yield 1.21 g (2.1 mmol, 73%), yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.26 (s, 9 H, Si(CH_3)$_3$), 0.96 (t, 12 H, –CH_3), 1.54 (m, 16 H, β,γ-CH_2), 2.54 (t, 4 H, α-CH_2), 2.68 (m, 4 H, α-CH_2), 6.87 (s, 1H, H-5″), 7.04 (d, ^3J=3.8 Hz, 1 H, H-4′(or 3′)), 7.06 [d, ^3J=3.8 Hz, 1 H, H-3′ (or 4′)]. ^{13}C NMR (126 MHz, $CDCl_3$) δ −0.05 (Si(CH_3)$_3$), 13.85, 13.89, 13.98 (–CH_3), 22.67, 22.78, 22.89, 22.96 (γ-CH_2), 27.51, 27.73, 28.41, 28.89 (α-CH_2), 31.89, 32.26, 32.69, 32.76 (β-CH_2), 97.8 (Th–C≡C–), 101.8 (Th–C≡C–), 117.1 (C-5), 119.2 (C-5″), 125.9, 126.2, 130.6, 131.8, 135.4, 137.1, 138.3, 139.0, 143.6, 149.5 (C-2,3,4,2′,3′,4′,5′,2″,3″,4″). HRMS (EI) *m/z*: $C_{33}H_{48}S_3Si$: 568.26875. Found 568.26922 [M^+]. Anal. Calcd for $C_{33}H_{48}S_3Si$ (569.0): C, 69.66; H, 8.50; S, 16.90. Found C, 69.68; H, 8.46; S, 17.05.

3.4.3. 3,3″,3‴,4,4″,4‴-Hexabutyl-5-(trimethylsilylethynyl)-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophene (19). According to GP3, bromoquinquethiophene (**15**) (0.91 g, 1.1 mmol), $Pd[PPh_3]_2Cl_2$ (39 mg, 0.055 mmol), triphenylphosphine (29 mg, 0.11 mmol), copper(I) iodide (21 mg, 0.11 mmol), 5 ml pyridine, 5 ml triethylamin, trimethylsilylacetylene (324 mg, 3.3 mmol), 18 h; chromatographic work-up (SiO_2; petroleum ether/dichloromethane 8:1), yield 0.64 g (0.76 mmol, 69%), orange solid, mp 61–62°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.27 (s, 9 H, Si(CH_3)$_3$), 0.98 (m, 18 H, –CH_3), 1.56 (m, 24 H, β,γ-CH_2), 2.56 (t, 2 H, α-CH_2), 2.67 (t, 2 H, α-CH_2), 2.74 (t, 8 H, α-CH_2), 6.88 (s, 2 H, H-5,5″), 7.07 (d, ^3J=3.7 Hz, 1 H, βH–Th), 7.08 (d, ^3J=3.7 Hz, 1 H, βH–Th), 7.09 (d, ^3J=3.7 Hz, 1 H, βH–Th), 7.10 (d, ^3J=3.5 Hz, 1 H, βH–Th). ^{13}C NMR (63 MHz, $CDCl_3$) δ −0.06 (Si(CH_3)$_3$), 13.85, 13.89, 13.97 (–CH_3), 22.68, 22.79, 22.91, 22.97, 23.03, 23.04 (γ-CH_2), 27.53, 27.76, 27.96, 27.99, 28.44, 28.91 (α-CH_2), 31.91, 32.26, 32.71, 32.76, 32.91 (β-CH_2), 97.9 (Th–C≡C–), 101.9 (Th–C≡C–), 119.1 (C-5,5″), 117.3 (C-5), 119.1 (C-5⁗), 125.90, 125.96, 125.98, 126.30, 129.61, 130.09, 130.79, 131.72, 135.69, 135.70, 136.34, 136.87, 138.40, 138.93, 140.10, 140.26, 143.6, 149.5 (C-2,3,4,2′,3′,4′,5′,2″,3″, 4″,5″,2‴, 3‴,4‴,5‴,2⁗,3⁗,4⁗). HRMS (FAB, NBA) *m/z*: $C_{49}H_{68}S_5Si$: 844.3694. Found 844.3696 [M^+]. Anal. Calcd for $C_{49}H_{68}S_5Si$ (845.4):C, 69.61; H, 8.11; S, 18.96. Found C, 69.55; H, 8.13; S, 19.07.

3.4.4. 5,5⁗-Bis(trimethylsilylethynyl)-3,3″,3⁗,4,4″,4⁗-hexabutyl-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophene (26). According to GP3, diiodoquinquethiophene (**25**) (5.0 g, 5.0 mmol), $Pd[PPh_3]_2Cl_2$ (350 mg, 0.5 mmol), triphenylphosphine (262 mg, 1.0 mmol), copper(I) iodide (190 mg, 1.0 mmol), 20 ml pyridine, 20 ml triethylamin, trimethylsilylacetylene (1.47 g, 15.0 mmol), 18 h; chromatographic work-up (SiO_2; petroleum ether/dichloromethane 12:1), yield 3.3 g (3.5 mmol, 70%), orange solid, mp 112–113°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.27 (s, 18 H, Si(CH_3)$_3$), 0.97 (m, 18 H, –CH_3), 1.52 (m, 24 H, β,γ-CH_2), 2.66 (t, 4 H, α-CH_2), 2.73 (t, 8 H, α-CH_2), 7.07 (d, ^3J=3.9 Hz, 2 H, βH–Th), 7.09 (d, ^3J=3.9 Hz, 2 H, βH–Th). ^{13}C NMR (63 MHz, $CDCl_3$) δ −0.06 (Si(CH_3)$_3$), 13.80 (–CH_3), 22.79, 22.91, 23.04 (γ-CH_2), 27.76, 27.97, 28.43 (α-CH_2), 32.26, 32.75, 32.89 (β-CH_2), 97.8 (Th–C≡C–), 101.9 (Th–C≡C–), 117.3 (C-5,5⁗), 126.02, 126.29, 129.80, 131.70, 135.80, 136.20, 138.40, 140.30, 149.6 (C-2–C-2⁗,C-3–C-3⁗,C-4–C-4⁗,C-5′-5⁗). MS (EI) *m/z* (%): 943 (23) [M^+], 942 (50) [M^+], 941 (66) [M^+], 940 (100) [M^+], 470 (12) [M^{2+}]. Anal. Calcd for $C_{54}H_{76}S_5Si_2$ (941.7): C, 68.88; H, 8.13; S, 17.02. Found C, 68.92; H, 8.37; S, 16.88.

3.5. General procedure for the copper-promoted dimerization ('Hay' coupling) of ethynylated thiophenes (GP4)

An aqueous solution of potassium hydroxide is dropped to the protected ethynylthiophene dissolved in aqueous tetrahydrofuran and methanol. After stirring for 1 h ice is added to the reaction mixture which subsequently is extracted with dichloromethane. The organic phase is washed with water and dried over magnesium sulfate. Under cooling the solution is concentrated to a small volume. The deprotected ethynylthiophene is then added to a stirred solution of copper(I) chloride and TMEDA in dichloromethane, chloroform, or acetone. During several hours a stream of oxygen is purged through the solution which is simultaneously heated at reflux. For work-up ice is added to the reaction mixture, the organic phase washed with water and dried over magnesium sulfate. Evaporation of the solvent and purification of the raw material by chromatography (phase; eluent) and subsequent recrystallization (solvent) yielded the desired butadiyne.

3.5.1. 1,4-Bis(3,4-dibutylthien-2-yl)-1,3-butadiyne (20). According to GP4, potassium hydroxide (498 mg, 8.9 mmol) in 2 ml water, protected ethynylthiophene (**17**) (2.37 g, 8.1 mmol) in 10 ml THF, 10 ml methanol; copper(I) chloride (198 mg, 2 mmol) and TMEDA (348 mg, 3 mmol) in 25 ml dichloromethane, 3 h; chromatographic work-up (SiO_2; petroleum ether/dichloromethane 4:1), recrystallization (methanol) yield 1.30 g (5.9 mmol, 73%) bright yellow crystals, mp 60–61°C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.95 (m, 12 H, –CH_3), 1.49 (m, 16 H, β,γ-CH_2), 2.49 (t, 4 H, α-CH_2), 2.68 (t, 4 H, α-CH_2), 6.87 (s, 2 H, H-5). ^{13}C NMR (63 MHz, $CDCl_3$) δ 13.90, 13.94 (–CH_3), 22.55, 22.58 (γ-CH_2), 28.09, 28.62 (α-CH_2), 31.84, 32.29 (β-CH_2), 77.3 (Th–C≡C–), 79.7 (Th–C≡C–), 117.6 (C-2), 122.9 (C-5), 142.1 (C-3), 149.8 (C-4). MS (EI) *m/z* (%): 439 (29) [M^+], 438 (100) [M^+], 353 (13) [$M^+-2C_3H_7$]. Anal. Calcd for $C_{28}H_{38}S_2$ (438.7): C, 76.65; H, 8.73; S, 14.62. Found C, 76.75; H, 8.97; S, 14.76.

3.5.2. 1,4-Bis(3,3″,4,4″-tetrabutyl-2,2′:5′,2″-terthien-2-yl)-1,3-butadyine (21). According to GP4, potassium hydroxide (162 mg, 2.9 mmol) in 2 ml water, protected ethynylterthiophene (**18**) (1.48 g, 2.6 mmol) in 20 ml THF, 20 ml

methanol; copper(I) chloride (100 mg, 1 mmol) and TMEDA (232 mg, 2 mmol) in 35 ml dichloromethane, 5 h; chromatographic work-up (SiO_2; petroleum ether/dichloromethane 9:1), recrystallization (2-propanol) yield 1.0 g (2.0 mmol, 77%) orange solid, mp 72–73°C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.95 (t, 24 H, –CH_3), 1.51 (m, 32 H, β,γ-CH_2), 2.52 (t, 4 H, α-CH_2), 2.68 (m, 12 H, α-CH_2), 6.86 (s, 2 H, H-5″), 7.05 [d, ^3J=3.7 Hz, 2 H, H-4′ (or 3′)], 7.10 [d, ^3J=3.7 Hz, 2 H, H-3′ (or 4′)]. ^{13}C NMR (63 MHz, $CDCl_3$) δ 13.85, 13.91, 14.00 (–CH_3), 22.67, 22.72, 22.94, 22.98 (γ-CH_2), 27.52, 27.75, 28.66, 28.87 (α-CH_2), 31.86, 32.63, 32.68 (β-CH_2), 77.2 (Th–C≡*C*–), 81.2 (Th–*C*≡C–), 116.0 (C-5), 119.3 (C-5″), 125.9, 126.5, 130.5, 133.6, 135.1, 137.4, 138.5, 139.1, 143.7, 151.6 (C-2,3,4,2′,3′,4′,5′,2″,3″,4″). MS (EI), *m/z* (%): 993 (22) [M^+], 992 (47) [M^+], 991 (63) [M^+], 990 (100) [M^+]. Anal. Calcd for $C_{60}H_{78}S_6$ (991.6): C, 72.67; H, 7.93; S, 19.40. Found C, 72.46; H, 7.89; S, 19.12.

3.5.3. 1,4-Bis(3,3‴,3⁗,4,4″,4⁗,4‴-hexabutyl-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2‴′-quinquethien-5-yl)-1,3-butadyine (22). According to GP4, potassium hydroxide (35 mg, 0.63 mmol) in 1 ml water, protected ethynylquinquethiophene (**19**) (465 mg, 0.55 mmol) in 15 ml THF, 10 ml methanol; copper(I) chloride (50 mg, 0.5 mmol) and TMEDA (232 mg, 2 mmol) in 40 ml dichloromethane, 4 h; chromatographic work-up (SiO_2; petroleum ether/dichloromethane 9:1) yield: 276 mg (0.36 mmol, 65%) red solid, mp 85–87°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.96 (m, 36 H, –CH_3), 1.57 (m, 48 H, β,γ-CH_2), 2.56 (t, 4 H, α-CH_2), 2.75 (m, 20 H, α-CH_2), 6.88 (s, 2H, H-5⁗), 7.07 (d, ^3J=3.7 Hz, 2 H, β*H*–Th), 7.10 (d, ^3J=3.7 Hz, 2 H, β*H*–Th), 7.11 (d, ^3J=3.7 Hz, 2 H, β*H*–Th), 7.13 (d, ^3J=3.5 Hz, 2 H, β*H*–Th). ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.84, 13.88, 13.97 (–CH_3), 22.67, 22.72, 22.94, 22.97, 23.03 (γ-CH_2), 27.52, 27.79, 27.96, 28.00, 28.69, 28.91 (α-CH_2), 31.91, 32.62, 32.67, 32.69, 32.89 (β-CH_2), 77.8 (Th–C≡*C*–), 81.3 (Th–*C*≡C–), 116.3 (C-5), 119.2 (C-5⁗), 125.90, 125.99, 126.02, 126.61, 129.50, 130.22, 130.77, 133.6, 135.33, 135.64, 136.74, 136.927, 138.61, 138.94, 140.14, 140.38, 143.6, 151.6 (C-2,3,4,2′,3′,4′,5′,2″,3″,4″,5″,2‴,3‴,4‴,5‴,2⁗,3⁗,4⁗). HRMS (FAB, NBA) *m/z*: $C_{92}H_{118}S_{10}$: 1542.6441. Found 1542.638 [M^+]. Anal. Calcd for $C_{92}H_{118}S_{10}$ (1544.6): C, 71.54; H, 7.70; S, 20.76. Found C, 71.39; H, 7.80; S, 20.52.

3.5.4. 5,5⁗-Bis[4-(3,4-dibutylthien-2-yl)-buta-1,3-diynyl]-3,3‴,3⁗,4,4″,4⁗-hexabutyl-2,2′:5′, 2″:5″,2‴:5‴,2⁗-quinquethiophene (27). According to GP4, potassium hydroxide (442 mg, 7.9 mmol) in 2 ml water, protected bisethynylquinquethiophene (**26**) (1.50 g, 1.6 mmol) and ethynyl-protected thiophene (**17**) (1.17 g, 4.0 mmol) in 25 ml THF, 20 ml methanol; copper(I) chloride (150 mg, 1.5 mmol) and TMEDA (696 mg, 6 mmol) in 75 ml dichloromethane, 6 h; chromatographic work-up (SiO_2; petroleum ether/dichloromethane 10:1), yield bisthienyl-butadiyne (**20**) 450 mg (1.0 mmol, 50%), bright yellow solid, mp 60–61°C. Analytical data are identical to the material obtained by coupling of thiophene (**17**). Subsequent preparative HPLC of the residue (SiO_2–nitrophenyl; dichloromethane), yield quinquethiophene (**27**): 375 mg (0.3 mmol, 15%) orange-red oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.03 (m, 30 H, –CH_3), 1.54 (m, 40 H, β,γ-CH_2), 2.55 (t, 4 H, α-CH_2), 2.77 (m, 16 H, α-CH_2), 6.90 (s, 2 H, α*H*-Th), 7.13 (s, 4 H, β*H*–Th). ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.84, 13.88 (–CH_3), 22.53, 22.58, 22.70, 22.94, 23.03 (γ-CH_2), 27.76, 27.97, 28.09, 28.61 (α-CH_2), 31.87, 32.27, 32.59, 32.63, 32.83 (β-CH_2), 76.9, 78.2, 79.8, 81.3 (Th–C≡*C*–, Th–*C*≡C–), 116.3, 117.6 (C-2‴,5″), 123.1 (C-5‴), 126.01, 126.53, 129.80, 133.40, 135.40, 136.50, 138.50, 140.30, 142.10, 149.80, 151.40 (C-2,3,2′,3′,4′,5′,2″,3″,4″,3‴,4‴). HRMS (FAB, NBA) *m/z*: $C_{76}H_{96}S_7$: 1232.5557. Found 1232.556 [M^+]. Anal. Calcd for $C_{76}H_{96}S_7$ (1234.0): C, 73.97; H, 7.84. Found C, C 74.10; H, 7.94.

3.6. General procedure for the ring closure of diacetylenes with sulfide anions to thiophenes (GP5)

Under inert gas, a solution of the butadiyne and sodium sulfide nonahydrate in 2-methoxyethanol is heated at reflux for several hours. After evaporation of the solvent, water and dichloromethane were added. The organic phase was washed several times with water and dried over magnesium sulfate. Evaporation of the solvent and purification of the raw material by chromatography (phase; eluent) yielded the desired oligothiophene.

3.6.1. 3,3″,4,4″-Tetrabutyl-2,2′:5′,2″-terthiophene (5). According to GP5, thiophene-butadiyne (**20**) (1.00 g, 2.28 mmol) and sodium sulfide nonahydrate (3.20 g, 13.22 mmol) in 200 ml 2-methoxyethanol, 24 h; chromatographic work-up (SiO_2; *n*-hexane), yield: 0.68 g (1.44 mmol, 63%). The analytical data of terthiophene **5** are identical to the material obtained by Grignard cross-coupling.

3.6.2. 3,3″,3‴,3⁗,4,4″,4‴,4⁗,4‴′-Octabutyl-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2‴′:5‴′,2⁗′:5⁗′-septithiophene (23). According to GP5, terthiophene-butadiyne (**21**) (218 mg, 0.22 mmol) and sodium sulfide nonahydrate (528 mg, 2.2 mmol) in 30 ml 2-methoxyethanol, 12 h; chromatographic work-up (SiO_2; petrol ether/dichloromethane 9:1) yield: 181 mg (0.18 mmol, 80%) red solid, mp 73–74°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.97 (m, 24 H, –CH_3), 1.58 (m, 32 H, β,γ-CH_2), 2.57 (t, 4 H, α-CH_2), 2.78 (m, 12 H, α-CH_2), 6.89 (s, 2 H, H-5⁗′), 7.09 (d, ^3J=3.7 Hz, 2 H, β*H*–Th), 7.12 (d, ^3J=3.7 Hz, 2 H, β*H*–Th), 7.13 (d, ^3J=3.7 Hz, 2 H, β*H*–Th). ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.87, 13.90, 13.99 (–CH_3), 22.68, 22.98, 23.05 (γ-CH_2), 27.52, 27.96, 27.99, 28.98 (α-CH_2), 31.88, 32.70, 32.90 (β-CH_2), 119.1 (C-5,5⁗′), 125.89, 125.91, 125.94, 129.75, 129.94, 130.80, 135.71, 135.94, 136.80, 138.90, 140.06, 140.11, 143.60 (C-2–C2⁗′, C3–C3⁗′, C4–C4⁗′, C-5′– C5⁗′). HRMS (FAB, NBA) *m/z*: $C_{60}H_{80}S_7$: 1024.43051. Found 1024.4303 [M^+]. Anal. Calcd for $C_{60}H_{80}S_7$ (1025.7): C, 70.28; H, 7.87; S, 21.85. Found C, 70.34; H, 7.85; S, 21.81.

3.6.3. 3,3″,3⁗,3⁗′,3⁗′′,3⁗′′′,4,4″,4⁗,4⁗′,4⁗′′,4⁗′′′-Dodecabutyl-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2⁗′:5⁗′,2⁗′′:5⁗′′,2⁗′′′:5⁗′′′, 2⁗′′′′:5⁗′′′′,2⁗′′′′′:5⁗′′′′′,2⁗′′′′′′,5⁗′′′′′,2⁗′′′′′′-undecithiophene (24). According to GP5, quinquethiophene-butadiyne (**22**) (120 mg, 0.078 mmol) and sodium sulfide nonahydrate (186 mg, 0.78 mmol) in 30 ml 2-methoxyethanol and 2 ml *p*-xylene, 6 h; chromatographic work-up (SiO_2; petroleum ether/dichloromethane 9:1), yield: 89 mg (56.7 μmol, 73%) red solid, mp 83–84°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.97

(m, 36 H, $-CH_3$), 1.57 (m, 48 H, β,γ-CH_2), 2.55 (t, 4 H, α-CH_2), 2.75 (m, 20 H, α-CH_2), 6.87 (s, 2H, H-5$''''''''$), 7.06 (d, ^3J=3.7 Hz, 2 H, βH–Th), 7.09 (d, ^3J=3.7 Hz, 2 H, βH–Th), 7.11 (m, ^3J=3.7 Hz, 6 H, βH–Th). ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.86, 13.97 ($-CH_3$), 22.67, 22.97, 23.04, 23.06 (γ-CH_2), 27.52, 27.96, 27.99, 28.90 (α-CH_2), 31.89, 32.69, 32.89 (β-CH_2), 119.1 (C-5,5$''''''''$), 125.87, 125.92, 125.95, 125.98, 129.76, 129.87, 129.90, 129.97, 130.80, 135.72, 135.92, 135.96, 136.01, 136.80, 138.90, 140.07, 140.12, 140.15, 143.50 (C-2–C2$''''''''$, C3–C3$''''''''$, C4–C4$''''''''$, C-5′– C5$''''''''$). HRMS (FAB, NBA) *m/z*: $C_{92}H_{120}S_{11}$: 1576.6318. Found 1576.633 [M^+]. Anal. Calcd for $C_{92}H_{120}S_{11}$ (1578.6): C, 70.00; H, 7.66; S, 22.34. Found C, 70.27; H, 7.78; S, 22.28.

3.6.4. 3,3″,3‴,3⁗,3⁗′,4,4″,4‴,4⁗,4⁗′,4⁗′′-Decabutyl-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2⁗′:5⁗′,2⁗′′:5⁗′′,2⁗′′′:5⁗′′′,2⁗′′′′-nonithiophene (28). According to GP5, bisbutadiyne (**27**) (300 mg, 0.24 mmol) and sodium sulfide nonahydrate (583 mg, 2.43 mmol) in 30 ml 2-methoxyethanol, 4 h; chromatographic work-up (SiO_2; petrol ether/dichloromethane 8:1), yield: 220 mg (0.17 mmol, 69%) red solid, mp 77–78°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.02 (m, 30 H, $-CH_3$), 1.57 (m, 40 H, β,γ-CH_2), 2.59 (t, 4 H, α-CH_2), 2.78 (m, 16 H, α-CH_2), 6.90 (s, 2H, H-5$''''''''$), 7.10 (d, ^3J=3.7 Hz, 2 H, βH–Th), 7.14 (d, ^3J=3.7 Hz, 2 H, βH–Th), 7.15 (m, ^3J=3.7 Hz, 6 H, βH–Th). ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.87, 13.97 ($-CH_3$), 22.67, 22.97, 23.05 (γ-CH_2), 27.51, 27.98, 28.88 (α-CH_2), 31.85, 32.67, 32.88 (β-CH_2), 119.1 (C-5,5$''''''''$), 125.83, 125.88, 125.91, 125.93, 129.73, 129.85, 129.93, 130.79, 135.67, 135.87, 135.95, 136.74, 138.80, 140.01, 140.06, 140.09, 143.50 (C-2–C2$''''''''$, C3–C3$''''''''$, C4–C4$''''''''$, C-5′– C5$''''''''$). HRMS (FAB, NBA) *m/z*: $C_{76}H_{100}S_9$: 1300.5312. Found 1300.5319 [M^+]. Anal. Calcd for $C_{76}H_{100}S_9$ (1302.2): C, 70.10; H, 7.74; S, 22.16. Found C, 69.96; H, 7.69; S, 22.39.

3.6.5. 3,3″,4,4″-Tetrabutyl-2,2′:5′,2″-terthiophene-5-carbaldehyde (10). To a solution of terthiophene (**5**) (5.7 g, 12 mmol) and DMF (0.95 g, 13 mmol) in 20 ml 1,2-dichloroethane at 0°C freshly distilled phosphorous oxychloride is slowly added by means of a syringe and the mixture heated at 60°C for 4 h. After cooling to 0°C saturated sodium hydrogen carbonate solution and dichloromethane were added. The separated organic phase was washed several times with saturated sodium hydrogen carbonate solution and water and dried over magnesium sulfate. Evaporation of the solvent and chromatography (SiO_2, dichloromethane) yielded 4.7 g (9.3 mmol, 77%) terthiophene (**10**) as a red oily solid. ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.97 (m, 12 H, $-CH_3$), 1.47 (m, 16 H, β,γ-CH_2), 2.54 (t, 2 H, α-CH_2), 2.73 (t, 4 H, α-CH_2), 2.90 (t, 2 H, α-CH_2), 6.89 (s, 1H, H-5″), 7.08 (d, ^3J=4.0 Hz, 1 H, βH–Th), 7.23 (d, ^3J=4.0 Hz, 1 H, βH–Th), 10.01 (s, 1 H, C*H*O). ^{13}C NMR (63 MHz, $CDCl_3$) δ 13.78, 13.86, 13.95 ($-CH_3$), 22.62, 22.79, 22.92 (γ-CH_2), 27.03, 27.11, 27.50, 28.81 (α-CH_2), 31.80, 32.58, 34.60 (β-CH_2), 119.5 (C-5″), 126.0, 127.6, 130.2, 134.56, 135.70, 138.85, 139.33, 140.00, 141.2, 143.7, 153.0 (C-2,3,4,5,2′,3′,4′,5′,2″,3″,4″), 181.9 (*C*HO). MS (EI) *m/z* (%):501 (36) [M^+], 500 (100) [M^+], 472 (12) [M^+–CO], 457 (17) [M^+–CH_3–CO], 415 (11) [M^+–CO–CH_3–C_3H_6]. Anal. Calcd for $C_{29}H_{40}OS_3$ (500.8): C, 69.55; H, 8.05; S, 19.20. Found C, 69.22; H, 8.37; S, 18.92.

3.6.6. 1,1-Dibrom-2-(3,3″,4,4″-tetrabutyl-2,2′:5′,2″-terthien-5-yl)-ethylene (11). Tetrabromomethane (3.62 g, 10.91 mmol) and triphenylphosphine (5.72 g, 21.82 mmol) were dissolved in 120 ml dichlormethane. The solution is cooled to 0°C and terthiophene aldehyde (**10**) (4.28 g, 8.55 mmol) dissolved in 40 ml dichloromethane was slowly added and the mixture stirred for 2 h at room temperature. To the reaction mixture *n*-hexane was added, the resulting precipitate filtered, and the remaining solution evaporated. The raw product was purified by chromatography (SiO_2, cyclohexane/dichloromethane 4:1) to yield 4.79 g (7.27 mmol, 85%) terthiophene (**11**) as a red oil. ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.97 (m, 12 H, $-CH_3$), 1.50 (m, 16 H, β,γ-CH_2), 2.56 (m, 4 H, α-CH_2), 2.73 (t, 4 H, α-CH_2), 6.88 (s, 1 H, H-5″), 7.05 (d, ^3J=3.7 Hz, 1 H, βH–Th), 7.13 (d, ^3J=3.7 Hz, 1 H, βH–Th), 7.62 (s, 1 H, H_{olef}). ^{13}C NMR (63 MHz, $CDCl_3$) δ 13.86, 13.90, 14.01 ($-CH_3$), 22.67, 22.82, 22.96 (γ-CH_2), 27.40, 27.47, 28.87 (α-CH_2), 31.83, 32.65, 32.87, 33.47 (β-CH_2), 86.10 (–CH=*C*<), 119.2 (C-5″), 125.90, 126.28, 129.33, 130.46, 130.63, 132.30, 135.50, 137.26, 138.20, 138.95, 143.61, 144.91 (C-2,3,4,5,2′,3′,4′,5′,2″,3″,4″, –*C*H=C<). MS (EI) *m/z* (%):658 (63) [M^+], 656 (100) [M^+], 654 (47) [M^+], 576 (24) [M^+–Br], 574 (21) [M^+–Br], 496 (21) [M^+–2Br]. Anal. Calcd for $C_{30}H_{40}Br_2S_3$ (656.6): C, 54.88; H, 6.14; S, 14.65. Found C, 54.73; H, 6.26; S, 14.40.

3.6.7. 5-Ethynyl-3,3″,4,4″-tetrabutyl-2,2′:5′,2″-terthiophene (12). To a solution of terthiophene (**11**) (4.58 g, 6.98 mmol) in 80 ml THF, at −78°C *n*-butyllithium (9.5 ml 1.6N in *n*-hexane, 15 mmol) was added, stirred for 2 h at −78°C and 1 h at room temperature. The reaction mixture was poured onto 150 ml ice water, extracted with dichloromethane, dried over magnesium sulfate, and evaporated. The crude product was purified by chromatography (SiO_2, cyclohexane) to yield 1.63 g (3.28 mmol, 47%) ethynylterthiophene (**12**) as a colourless oil which is only stable in solution and immediately used for further reactions. ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.95 (m, 12 H, $-CH_3$), 1.52 (m, 16 H, β,γ-CH_2), 2.52 (m, 2 H, α-CH_2), 2.65 (m, 6 H, α-CH_2), 3.49 (s, 1 H, C≡C—*H*), 6.87 (s, 1H, H-5″), 7.04 (d, ^3J=3.8 Hz, 1 H, βH–Th), 7.06 (d, ^3J= 3.8 Hz, 1 H, βH–Th).

3.6.8. 5,5⁗′-Diiodo-3,3″,3⁗′,4,4″,4⁗′-hexabutyl-2,2′:5′,2″:5″,2‴:5‴,2⁗′-quinquethiophene (25). At 0°C, iodine (3.47 g, 13.67 mmol) in 150 ml chloroform was slowly added to a well-stirred suspension of quinquethiophene (**9**) (5.0 g, 6.67 mmol) and mercury(II) acetate (4.35 g, 13.67 mmol) in 100 ml chloroform and stirred for 2 h. The reaction mixture is filtered, washed with 1N HCl, aqeuous sodium thiosulfate solution, dried over magnesium sulfate, and evaporated. The crude product was purified by chromatography (SiO_2, petroleum ether/dichloromethane 12:1) to yield 5.78 g (5.8 mmol, 87%) quinquethiophene (**25**) as a yellow solid, mp 51–52°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.97 (m, 18 H, $-CH_3$), 1.51 (m, 24 H, β,γ-CH_2), 2.57 (m, 4 H, α-CH_2), 2.78 (m, 8 H, α-CH_2), 7.03 (d, ^3J=3.7 Hz, 2 H, βH–Th), 7.09 (d, ^3J=3.7 Hz, 2 H, βH–Th). ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.84, 13.86, 13.91 ($-CH_3$), 22.86, 22.90, 23.03 (γ-CH_2), 27.96, 28.29, 31.01 (α-CH_2), 32.08, 32.88, 32.96 (β-CH_2), 74.1 (C-5,5⁗′), 125.90, 126.30, 129.80, 135.49, 135.97, 136.26, 138.60, 140.20, 147.50

(C-2,3,4,2′,3′,4′,5′,2″,3″,4″,5″,2‴,3‴,4‴,5‴,2⁗,3⁗,4⁗). MS (MALDI–TOF) *m/z* (%):1003 (14) [M^+], 1002 (36) [M^+], 1001 (54) [M^+], 1000 (100) [M^+]. Anal. Calcd for $C_{44}H_{58}I_2S_5$ (1001.1): C, 52.79; H, 5.84; I, 25.35; S 16.01. Found C, 52.73; H, 5.89; I, 25.13; S, 15.84.

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References

1. (a) *Handbook of Oligo- and Polythiophenes*, Fichou, D., Ed.; Wiley-VCH: Weinheim, 1999. (b) Bäuerle, P. In *Oligothiophenes in Electronic Materials: The Oligomer Approach*, Müllen, K., Wegner, G., Eds.; Wiley-VCH: Weinheim, 1998; pp 105–197. (c) Roncali, J. *Acc. Chem. Res.* **2000**, *33*, 147–156. (d) Roncali, J. *Chem. Rev.* **1997**, *97*, 173–205.
2. (a) Martin, R. E.; Diederich, F. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1350–1377. (b) Tour, J. M. *Chem. Rev.* **1996**, *96*, 537–553. (c) Meier, H.; Stalmach, U.; Kolshorn, H. *Acta Polymer.* **1997**, *48*, 379–384.
3. (a) Bao, Z. *Adv. Mater.* **2000**, *12*, 227–230. (b) Horowitz, G. *Adv. Mater.* **1998**, *10*, 365–377. (c) Garnier, F. In *Field-Effect Transistors Based on Conjugated Materials in Electronic Materials: The Oligomer Approach*, Müllen, K., Wegner, G., Eds.; Wiley-VCH: Weinheim, 1998; pp 559–584. (d) Torsi, L.; Dodabalapur, A.; Rothberg, L. J.; Fung, A. W. P.; Katz, H. E. *Science* **1996**, *272*, 1462–1464.
4. (a) Mitschke, U.; Bäuerle, P. *J. Mater. Chem.* **2000**, *10*, 1471–1507. (b) Geiger, F.; Stoldt, M.; Bäuerle, P.; Schweizer, H.; Umbach, E. *Adv. Mater.* **1993**, *5*, 922–925.
5. Noma, N.; Tsuzuki, T.; Shirota, Y. *Adv. Mater.* **1995**, *7*, 647–648.
6. (a) Sumi, N., Nakanishi, H., Takimiya, K., Aso, Y., Otsubo, T. *Synth. Met.*, in print (48-mer). (b) Nakanishi, H.; Sumi, N.; Aso, Y.; Otsubo, T. *J. Org. Chem.* **1998**, *63*, 8632–8633 (27-mer). (c) Mustafa, A. H.; Shepherd, M. K. *Chem. Commun.* **1998**, 2743–2744 (24-mer). (d) Malenfrant, P. R. L.; Groenendaal, L.; Fréchet, J. M. *J. Am. Chem. Soc.* **1998**, *120*, 10990–10991 (17-mer). (e) Bäuerle, P.; Fischer, T.; Bidlingmeier, B.; Stabel, A.; Rabe, J. P. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 303–307 (16-mer). (f) Sato, M.; Hiroi, M. *Polymer* **1996**, *37*, 1685–1689 (15-mer). (g) Kirschbaum, T.; Briehn, C. A.; Bäuerle, P. *J. Chem. Soc., Perkin Trans. 1* **2000**, 1211–1216 (12-mer). (h) Yassar, A.; Delabouglise, D.; Hmyene, M.; Nessak, B.; Horowitz, G.; Garnier, F. *Adv. Mater.* **1992**, *4*, 490–494 (12-mer). (i) de Leeuw, D. M. *Synth. Met.* **1993**, *57*, 3597–3602 (12-mer). (j) ten Hoeve, W.; Wynberg, H.; Havinga, E. E.; Meijer, E. W. *J. Am. Chem. Soc.* **1991**, *113*, 5887–5889 (11-mer). (k) Zotti, G.; Schiavon, G.; Berlin, A.; Pagani, G. *Chem. Mater.* **1993**, *5*, 430–436 (10-mer).
7. McCullough, R. D. *Adv. Mater.* **1998**, *10*, 93–116.
8. Bäuerle, P.; Würthner, F.; Götz, G.; Effenberger, F. *Synthesis* **1993**, 1099–1103.
9. (a) Wynberg, H.; Metselaar, J. *Synth. Commun.* **1984**, *14*, 1–9. (b) Roncali, J.; Thobie-Gautier, C. *Adv. Mater.* **1994**, *6*, 846–848.
10. Mitschke, U.; Mena-Osteritz, E.; Debaerdemaeker, T.; Sokolowski, M.; Bäuerle, P. *Chem. Eur. J.* **1998**, *4*, 2211–2224.
11. Kagan, J.; Arora, S. K. *J. Org. Chem.* **1983**, *48*, 4317–4320.
12. (a) Perrine, D. M.; Kagan, J. *Heterocycles* **1986**, *24*, 365–368. (b) Kumada, M.; Zembayas, M. *Tetrahedron Lett.* **1977**, 4089–4092.
13. (a) Beny, J.-P.; Dhawan, S. N.; Kagan, J.; Sundlass, S. *J. Org. Chem.* **1982**, *47*, 2201–2204. (b) Perrine, D. M.; Kagan, J. *Heterocycles* **1986**, *24*, 365–368. (c) McKellar, B. R.; Feld, W. A. *Polym. Prepr.* **1993**, *34*, 380–381. (d) Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, *13*, 3769–3772.
14. (a) Neenan, T. X.; Whitesides, G. M. *J. Org. Chem.* **1988**, *53*, 2489–2496. (b) Hayashi, H.; Yamamoto, T. *Macromolecules* **1997**, *30*, 330–332. (c) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627–630. (d) Thorand, S.; Krause, N. *J. Org. Chem.* **1998**, *63*, 8551–8553.
15. (a) Hay, A. S. *J. Org. Chem.* **1960**, *25*, 1275–1276. (b) Hay, A. S. *J. Org. Chem.* **1962**, *27*, 3320–3321.
16. Gronowitz, S. *Ark. Kemi* **1960**, *16*, 267–285.
17. Gronowitz, S. *Acta Chem. Scand.* **1959**, *13*, 1045–1046.
18. Spangler, C. W.; He, M. *J. Chem. Soc., Perkin Trans. 1* **1995**, 715–720.
19. Wang, C.; Benz, M. E.; LeGoff, E.; Schindler, J. L.; Kannewurf, C. R.; Kanatzidis, M. G. *Polymer Preprints* **1993**, *34*, 422.
20. Jones, G. E.; Kendrick, D. A.; Holmes, A. B.; Sporikou, C. N. *Org. Synth.* **1987**, *65*, 61–67.