Doped Polymers by Oxidative Polymerization. 4.[†] Oxidative Coupling of Methylated Oligothiophenes by $FeCl_3 \cdot 6H_2O$ as a Model Reaction for the Oxidative Polymerization of Thiophene Derivatives

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ABSTRACT: Methylated bi- and terthiophenes (monomers, **1**, **3**, **5**, **8**) with one free α-position can be oxidized with $FeCl_3 \cdot 6H_2O$. An irreversible dimerization reaction forms dimers of the expected structure. The radical cations of the monomers also react with free *β*-positions of the formed dimers (**6**, **9**) having two methylated α-positions. The products of these reactions show α,*β*′ linkages (**7**, **10**, **11**). Different *β*-positions in end-capped dimers show a graduated reactivity against radical cations of the monomers; the free *β*-position with the higher electron spin density can be attacked preferably by an α-position of a radical cation of a monomer molecule. No products with *β*,*β*′ linkages were found. Electrochemical investigations using fast-scan voltammetry show the formation of α,α′ linkages of methylated oligothiophenes. For bithiophene derivatives, rate constants of the dimerization process in the range of 10^9 $L \cdot mol^{-1} \cdot s^{-1}$ were determined. In comparison with a terthiophene derivative, it was found that the dimerization rates decrease with increasing chain length of the oligomers.

Introduction

Thiophene, its derivatives, and its oligomers can be oxidized either by oxidants (chemical oxidation) or electrochemically (electrochemical oxidation) to form polythiophenes.[1−3] Oxidants used for this reaction are AsF_5,[4,5] nitronium and nitrosonium salts,[6] or simply $FeCl_3$.[7] In the case of $FeCl_3$, the water free salt or the hexahydrate can be taken for such oxidative coupling reactions. It was found that $FeCl_3$ with water as ligand molecules acts smoother as a more selective oxidant[8] forming dimerization products of a controlled structure in a purer form and in higher yields than water free $FeCl_3$.

For polythiophene [poly(2,5-thiophenediyl)], the literature[1] claims that the linkages between the thiophene rings are preferably α,α′ linkages. It is obvious that during the first coupling steps the more reactive α-positions tend to undergo the formation of α,α′ bonds between thiophene rings. The question as to whether α,*β*′ linkages between thiophene rings are also formed during the first coupling steps of the oligomer formation is still unanswered by structural evidence.

In this paper, we wish to present our results on the graduated reactivity of α- and *β*-positions in various methylated bi- and terthiophenes in the oxidative coupling reaction with $FeCl_3 \cdot 6H_2O$.

Results and Discussion

Studying the reactivity of free *β*-positions beside α-positions in thiophene systems during the oxidative coupling reaction, **1**, **3** (each containing only one free α-position), **5** (with one free α- and one free *β*-position), and **8** (with one free α- and two different free *β*-positions) were oxidized with $FeCl_3 \cdot 6H_2O$ in acetonitrile (AN). Radical cations are the reactive species.[1] The oxidation products are formed in an oxidized state (as radical cation $FeCl_4$ salts) and must be reduced by the action of $Na_2S_2O_4$ in order to acquire the neutral methylated oligothiophenes for isolation and identification. In the expected dimers of the α-monomethylated monomers both outer α-positions are methylated. Therefore, no polymerization occurs. Solely free *β*-positions can react.

It is obvious that the oxidative coupling reaction of the *β* permethylated 3,3′,4,4′,5-pentamethyl-2,2′-bithiophene (**1**) with one free α-position gives its dimer 3,3′,3″,3‴,4,4′,4″,4‴,5,5‴-decamethyl-2,2′;5′,2″;5″,2‴-quaterthiophene (**2**) as the α,α′ coupling product, which can be isolated in a yield of 43% (Scheme 1). Analogously, the permethylated sexithiophene **4** was formed in a 65% yield as dimer from the heptamethylated terthiophene **3** having one free α-position. It can be seen that with a longer oligomer chain in the monomer a higher yield of the dimer results. The remaining material of the monomer was converted to undetectable products by unknown side reactions during the oxidation and reduction process. This behavior was found for all oxidation reactions.

The oxidation of 3,4,4′,5′-tetramethyl-2,2′-bithiophene (**5**) with one free α- and one free *β*-position gives by α,α′ coupling reaction as main product (41%) 3′,3″,4,4′,4″,4‴,5,5‴-octamethyl-2,2′;5′,2″;5″,2‴-quaterthiophene (**6**) (Scheme 2). Further reaction leads to the dodecamethylated sexithiophene **7** (trimer) with one α,*β*′ linkage between thiophene rings in a yield of 6% as a reaction product of **5** in its α-position and **6** in one of its *β*-positions. Despite one free *β*-position in the trimer **7**, no tetramer (an octithiophene derivative) could be

[†] For part 3, see ref 15.

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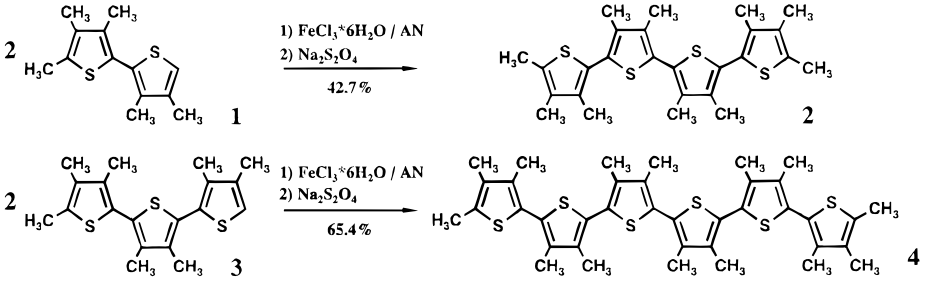
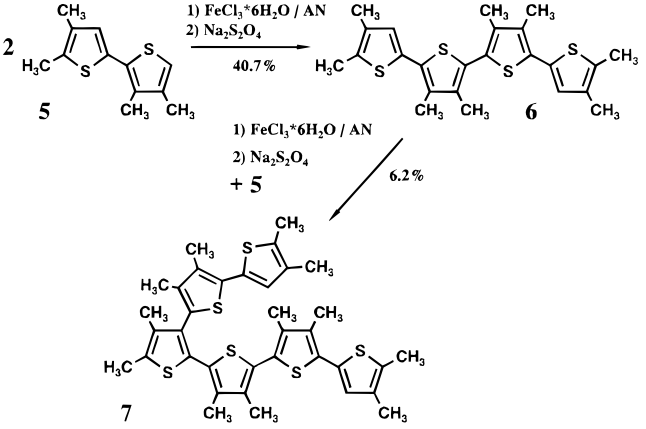
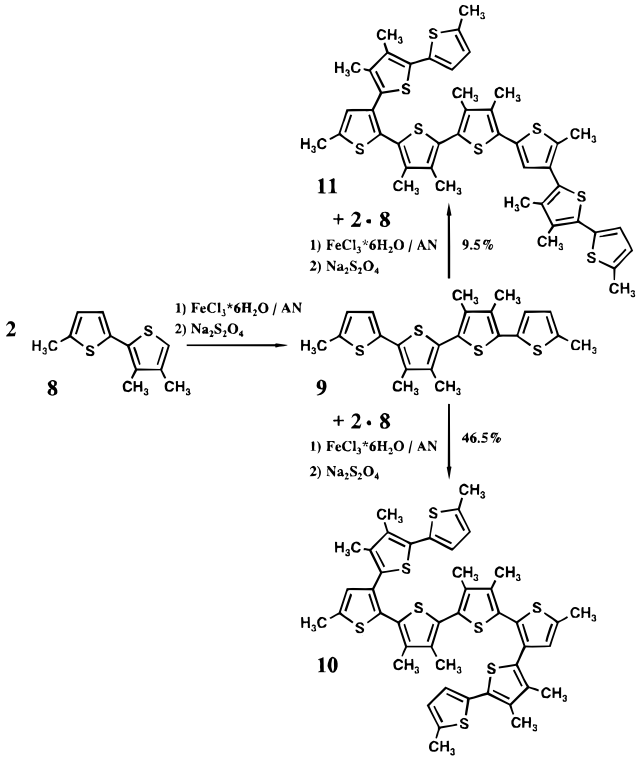
Scheme 1



Scheme 2



Scheme 3



reliably identified. This fact may be explained by sterical effects.

The oxidation of 3,4,5′-trimethyl-2,2′-bithiophene (**8**) with two unoccupied differing β-positions in one thiophene ring, as well as one free reactive α-position in the other thiophene ring with $FeCl_3 \cdot 6H_2O$, forms two octithiophene derivatives (tetramers). The coupling product tetramer **10** with two α,β'(3) linkages was isolated in a yield of 47%, and tetramer **11** with one α,β'-(3) and one α,β'(4) linkage was isolated in a yield of only 9.5%. A product with two α,β'(4) linkages was not observed. No products with β,β' linkages could be isolated, demonstrating the lower reactivity of these β-positions in contrast to the α-positions. Based on the previous experimental results (see Scheme 2) it was assumed that at first the radical cations of monomer **8** would dimerize at the free reactive α-positions to form the dimer **9**. Because compound **9** was not detectable, a consequent reaction of this substance with radical cations of monomer **8** obviously took place because of the higher degree of free β-positions in **9** than in **6**. We assume that the steady state concentration of **9** arising from forming and consequent reaction is so low that it was impossible to isolate this compound. The preferable attack of the radical cations of monomer **8** at the marked 3,3‴-positions in compound **9** (Scheme 3) was surprising. For a better understanding of these reactions, compound **9** was synthesized by cross-coupling reaction after Kumada.

The X-ray structure[9] of dimer **9** (Figure 1) shows that there are no sterical reasons for the favored attack of radical cations of monomer **8** in the 3- and 3‴-positions, in contrast to the 4- and 4‴-positions of dimer **9**. If **9** is treated with $FeCl_3 \cdot 6H_2O$, radical cations are formed, which, being stable under these conditions, therefore do not form a dimerization product (tetramer of the octathiophene type). It is remarkable that a graduated regioselectivity exists for both types of β-positions following the different electron spin densities, as can be seen by EPR studies.[10]

With regard to the graduated reactivity of the β-positions, we refer to our EPR studies of 5,5‴-dimethyl-2,2′;5′,2″;5″,2‴-quaterthiophene.[10] Here, we found remarkably higher electron spin densities for the 3- and 3‴-positions in relation to the 4- and 4‴-positions. Additional methyl groups in the molecule do not essentially change the hyperfine coupling constants;[10] therefore, the same ratios of electron spin density distributions may also be valid for its 3′,3″,4′,4″-tetramethyl derivative **9**. Quantum mechanical calculations (PM3) demonstrated the electron spin density of the radical cation of dimer **9** (Figure 2).

Therefore, it is clear that two radical cations of monomer **8** with their reactive α-positions (high electron spin density) react preferably with the β(3) positions of dimer **9**, having the higher electron spin density in relation to the β(4)-positions. Therefore, tetramer **10** arises in a higher yield than tetramer **11**.

The coupling of the radical cations can also be observed by means of cyclic voltammetry. For conventional scan rates the bithiophene derivatives **1**, **5**, and **8** and the terthiophene derivative **3** undergo irreversible oxidation and show anodic peaks at potentials of 1.11, 1.05, 1.14, and 1.07 V vs SCE, respectively. However, with increasing scan rate, the reversibility of the monomer oxidation could be achieved. The rate constant for the irreversible chemical coupling step was

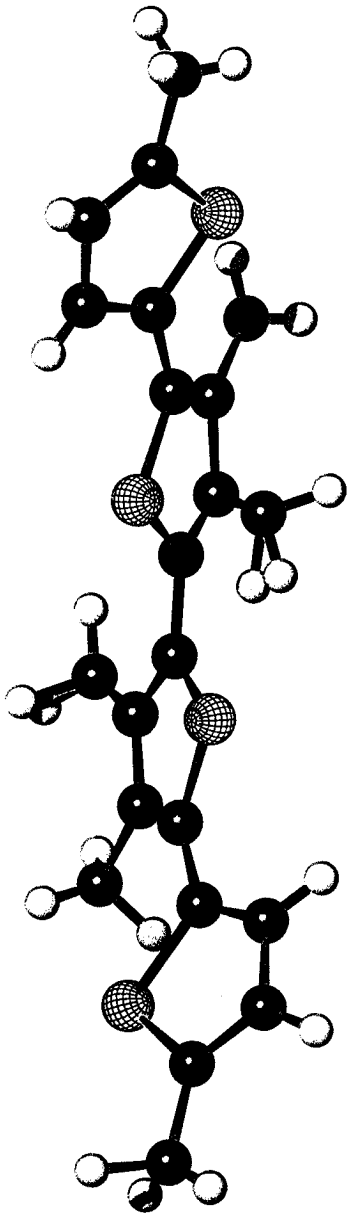


Figure 1.

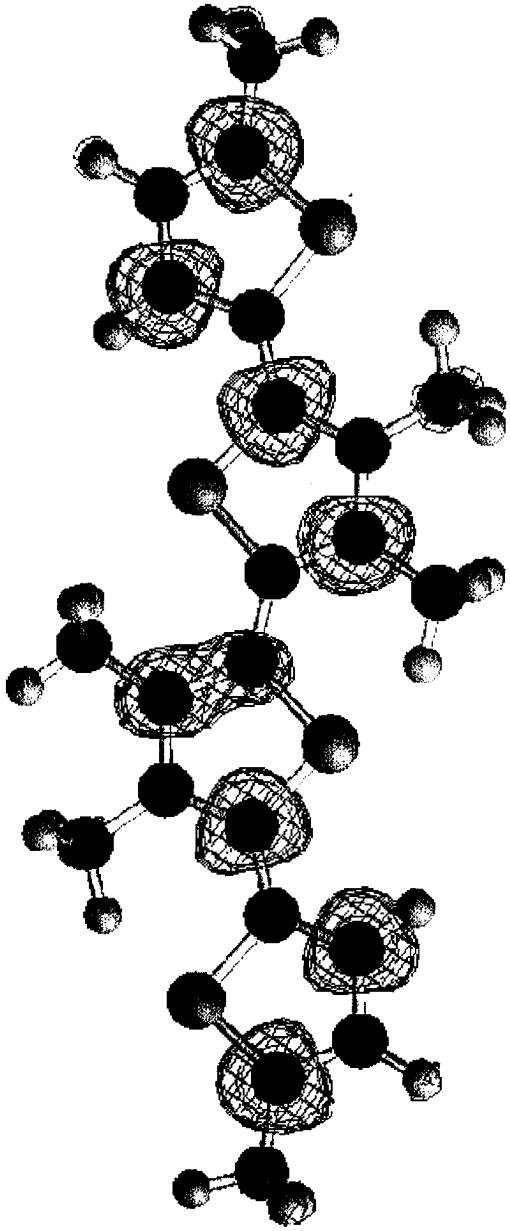


Figure 2.

determined by the powerful fast-scan cyclovoltammetry from the peak current ratio in the forward and reverse scan of the first oxidation peak (v = 32.000 V/s; $i^{l}{}_{p}{}^{c}/i^{l}{}_{p}{}^{a}$ = 0.6) with the help of working curves.[11] Compound **1** showed a rate constant of 2×10^9 L·mol^{-1}·s^{-1}. In the case of substances **3**, **5**, and **8**, the corresponding rate constant could not be determined because the redox potentials of the coupling products have approximately the same peak potential values as the monomers. Therefore, an exact determination of the peak currents of these monomers was not possible.

More information about the kinetic of the oxidative α,α′ coupling was possible by related compounds. The question for the correlation between the length of the heteroaromatic system and the rate constant for the electrochemical oxidation could be answered by measuring the kinetic constants with fast-scan cyclovoltammetry. We refer to the values for 5-methyl-2,2′-bithiophene (v = 190.000 V/s; $i^{l}{}_{p}{}^{c}/i^{l}{}_{p}{}^{a}$ = 0.7; $k = 6 \times 10^8$ L·mol^{-1}·s^{-1} and 5-methyl-2,2′;5′,2″-terthiophene (v = 6000 V/s; $i^{l}{}_{p}{}^{c}/i^{l}{}_{p}{}^{a}$ = 0.7; $k = 2 \times 10^7$ L·mol^{-1}·s^{-1}), demonstrating that longer heteroaromatic systems are more stabilized and therefore have lower reactivity.

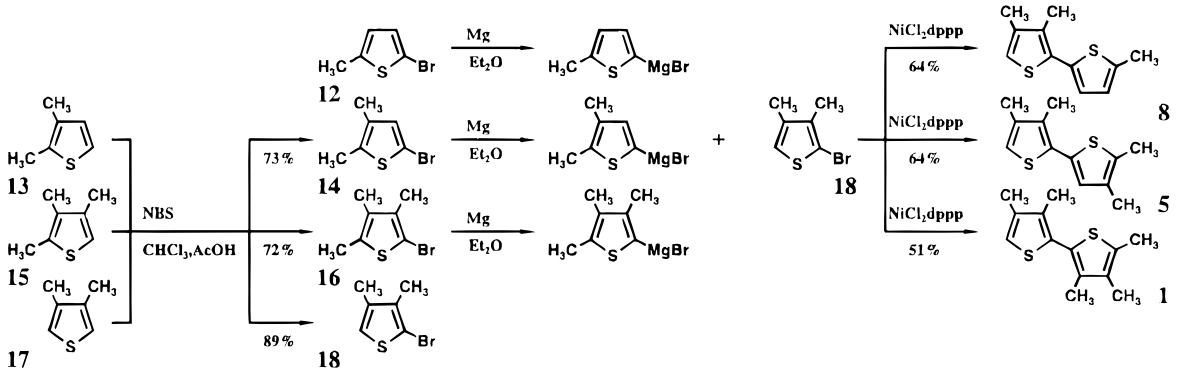
The starting compounds **1**, **3**, **5**, and **8** have been synthesized according to Schemes 4 and 5.

The structures of all compounds have been characterized by IR, ^{1}H-NMR, ^{13}C-NMR, MS, and elemental analyses (see Experimental Section).

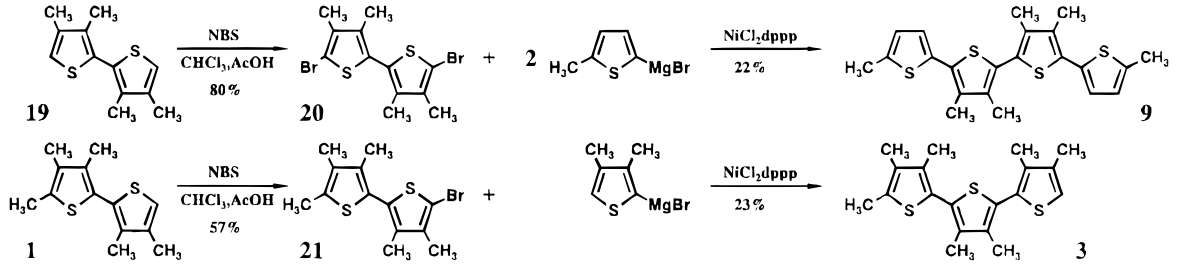
Conclusion

This paper describes the oxidation of oligothiophene derivatives and clears up for the first time by isolation of the reaction products the evidence for α,α′ and α,β′ coupling by structure analysis of the chromatographically purified compounds. This was only possible by using α-monomethylated bi- and terthiophenes with methyl groups in different β-positions. The more reactive free α-positions react at first by α,α′ coupling and build up dimers with two methylated α-positions (end-capped oligothiophenes). Therefore, these compounds cannot polymerize, giving the assumption for isolating pure compounds with detectable structures. If the dimers (end-capped oligothiophenes) have free β-positions, an α,β′ coupling with monomer radical cations occurs in a different manner. The β-positions with the

Scheme 4



Scheme 5



higher electron spin densities show the higher reactivity. This conclusion was supported by EPR investigation and quantum chemical calculations. No oxidation products with β,β' linkages were found. These results underline likewise the higher reactivity of α-positions in contrast to β-positions. A further confirmation therefore is the very high rate constant of 2×10^9 $L \cdot mol^{-1} \cdot s^{-1}$ for α,α′ coupling of the radical cations of monomer **1** estimated with the fast-scan cyclovoltammetry. The rate of ring coupling decreases with increasing chain length of the oligothiophenes.

Experimental Section

3,3′,4,4′,5-Pentamethyl-2,2′-bithiophene (1). In a 250 mL three necked flask, fitted with a reflux condenser, drying tube, dropping funnel and gas inlet, 1.54 g (63.6 mmol) of Mg cuttings in 5 mL of dry diethyl ether and several iodine crystals were deposited. In an inert gas atmosphere 8.68 g (42.4 mmol) of 2-bromo-3,4,5-trimethylthiophene (**16**) in 20 mL of dry ether was slowly added dropwise. After completition, the reaction mixture was refluxed for 2 h under stirring, and afterward the resulting mixture was transferred into a dropping funnel through pressing with inert gas and separating from the unreacted Mg.

This Grignard solution was dropped into a 500 mL three-necked flask, fitted with a reflux condenser, drying tube, and gas inlet containing 8.09 g (42.4 mmol) of 2-bromo-3,4-dimethylthiophene (**18**) in 50 mL of dry ether and 459 mg (0.848 mmol) of $NiCl_2$dppp [bis-1,3(diphenylphosphino)propane nickel(II) chloride] in such a way that a controlled reflux took place. After 2 h refluxing while under stirring, the mixture was poured into 3 M HCl at 0 °C. This was followed by 3-fold extraction with 100 mL of ether; the combined organic phases were then washed three times with 100 mL of water and dried with $CaCl_2$, the solvent was distilled off in vacuo, and the crude product was purified chromatographically on silica gel (40−63 μm) with hexane. Colorless crystals, mp 83 °C (MeOH/$CHCl_3$). Yield: 5.12 g (51.2%).

IR (KBr) ν/cm^{-1}: 2971, 2938 (m); 2912 (st); 2852 (m); 1441 (st); 985 (st); 916 (m); 859 (m); 739 (st). ^{1}H-NMR ($CDCl_3$, TMS, 250 MHz) δ/ppm: 6.92 (s, 1H) [H5′]; 2.4 (s, 3H) [CH_3-5]; 2.22 (s, 3H); 2.088 (s, 3H); 2.072 (s, 3H); 2.06 (s, 3H) [CH_3-3,3′,4,4′]. ^{13}C-NMR ($CDCl_3$, TMS, 250 MHz) δ/ppm: 137.737; 136.431; 135.793; 133.329; 132.565; 130.195; 125.423; 120.281; 15.378; 14.023; 13.345; 13.251; 12.665. MS *m/e* (I_{rel}/%): 236 (100.0) [M^+]; 221 (25.7) [$(M - CH_3)^+$]; 203 (5.6) [$(M - SH)^+$]; 118 (6.4) [M^{2+}]. Anal. Calcd for $C_{13}H_{16}S_2$ (236.4): C, 66.05; H, 6.82; S, 27.13. Found: C, 66.03; H, 6.64; S, 26.92.

3,3′,3″,4,4′,4″,5-Heptamethyl-2,2′;5′,2″-terthiophene (3). Analogously to the preparation of **1**, the reaction was carried out of 2.88 g (15.1 mmol) of 2-bromo-3,4-dimethylthiophene (**18**) in 20 mL of dry ether, 0.55 g of Mg cuttings in 10 mL of dry ether, and some iodine crystals, followed by coupling with 4.75 g (15.1 mmol) of 5-bromo-3,3′,4,4′,5′-pentamethyl-2,2′-bithiophene (**21**) in 100 mL of dry ether and 82 mg (0.151 mmol) of $NiCl_2$dppp, and purification by column chromatography on silica gel with hexane and HPLC (reverse phase/MeOH). Colorless crystals, mp 124 °C (THF/MeOH). Yield: 1.2 g (23%).

IR (KBr) ν/cm^{-1}: 2972 (m); 2936, 2911, 2851 (st); 1442 (st); 1387, 1372 (m); 1025, 1003 (m); 981 (st); 889, 859 (st); 732 (st). ^{1}H-NMR ($CDCl_3$, TMS, 250 MHz) δ/ppm: 6.92 (s, 1H) [H5″]; 2.36 (s, 3H) [CH_3-5]; 2.2 (s, 3H); 2.08 (s, 15H) [CH_3-3,3′,3″,4,4′,4″]. ^{13}C-NMR ($CDCl_3$, TMS, 250 MHz) δ/ppm: 137.829; 136.493; 136.314; 136.096; 133.42; 132.703; 130.131; 129.745; 124.918; 120.608 15.347; 14.175; 14.081; 13.475; 13.274; 12.667. MS *m/e* (I_{rel}/%): 346 (100.0) [M^+]; 331 (4.0) [$(M - CH_3)^+$]; 313 (2.1) [$(M - SH)^+$]; 173 (13.8) [M^{2+}]; 158 (3.4) [$(M - 2CH_3)^{2+}$]. Anal. Calcd for $C_{19}H_{22}S_3$ (346.6): C, 65.85; H, 6.40; S, 27.75. Found: C, 65.29; H, 6.28; S, 27.54.

3,4,4′,5′-Tetramethyl-2,2′-bithiophene (5). Analogously to the preparation of **1**, the reaction was carried out of 3.44 g (18 mmol) 2-bromo-3,4-dimethylthiophene (**18**) in 20 mL of dry ether, 0.66 g (27 mmol) of Mg cuttings in 10 mL of dry ether, and some iodine crystals, followed by coupling with 3.44 g (18 mmol) of 2-bromo-3,4-dimethylthiophene (**18**) in 50 mL of dry ether and 98 mg (0.18 mmol) of $NiCl_2$ dppp, and purification by column chromatography on silica gel with hexane. Colorless crystals, mp 46 °C. Yield: 2.54 g (64%).

IR (KBr) ν/cm^{-1}: 3065 (schw); 2971 (schw); 2944 (schw); 2910 (m); 2853 (m); 1546 (m); 1436 (st); 1368 (m); 1200 (schw); 863 (m); 838 (st); 824 (st); 732 (st). ^{1}H-NMR ($CDCl_3$, TMS, 250 MHz) δ/ppm: 6.9 (s, 1H) [H5]; 6.88 (s, 1H) [H3′]; 2.46 (s, 3H) [CH_3-5′]; 2.36 (s, 3H); 2.24 (s, 3H); 2.22 (s, 3H) [CH_3-3,4,4′]. ^{13}C-NMR ($CDCl_3$, TMS, 250 MHz) δ/ppm: 138.588; 133.307; 132.995; 132.702; 132.047; 131.437; 128.433; 118.556; 15.417; 13.471; 12.88. MS *m/e* (I_{rel}/%): 222 (100.0) [M^+]; 221 (26.0) [$(M - H)^+$]; 207 (19.6) [$(M - CH_3)^+$]; 189 (8.2) [$(M - SH)^+$]; 111 (6.5) [M^{2+}]. Anal. Calcd for $C_{12}H_{14}S_2$ (222.4): C, 64.82;

H, 6.35; S, 28.83. Found: C, 64.72; H, 6.31; S, 28.97.

3,4,5′-Trimethyl-2,2′-bithiophene (8). Analogously to the preparation of **1**, the reaction was carried out of 3.67 g (19.2 mmol) of 2-bromo-3,4-dimethylthiophene (**18**) in 20 mL of dry ether, 0.7 g (828.8 mmol) of Mg cuttings in 10 mL of dry ether, and some crystals of iodine, followed by coupling with 3.4 g (19.2 mmol) of 2-bromo-5-methylthiophene (**12**)[12] in 50 mL of dry ether and 104 mg (0.192 mmol) of $NiCl_2$dppp, and column chromatography on silica gel with hexane. Colorless liquid, bp >270 °C, n_D^{20}: 1.6289. Yield: 2.55 g (64%).

IR (KBr) ν/cm^{-1}: 3066 (m); 2970 (st); 2917 (st); 2857 (st); 1538 (m); 1440 (st); 1246 (m); 1216, 1202 (m); 1163 (m); 1048 (m); 988 (m); 861 (st); 794 (st); 730 (st). ^{1}H-NMR ($CDCl_3$, TMS, 250 MHz) δ/ppm: 6.86 (d, 1H, J = 3.75 Hz) [H3′]; 6.78 (s, 1H) [H5]; 6.68 (d, 1H, J = 3.75 Hz) [H4′]; 2.46 (s, 3H) [CH_3-5′]; 2.24 (s, 3H); 2.14 (s, 3H) [CH_3-3,4]. ^{13}C-NMR ($CDCl_3$, TMS, 250 MHz) δ/ppm: 139.558; 138.564; 134.685; 133.242; 131.344; 125.48; 125.444; 118.769; 15.385; 15.152; 13.436. MS *m/e* (I_{rel}/%): 208 (100.0) [M$^+$]; 207 (29.6) [(M − H)$^+$]; 193 (17.2) [(M − CH_3)$^+$]; 175 (11.4) [(M − SH)$^+$]; 147 (4.8) [(M − SH − 2CH_2)$^+$]; 104 (4.8) [M^{2+}]. Anal. Calcd for $C_{11}H_{12}S_2$ (208.3): C, 63.41; H, 5.81; S, 30.78. Found: C, 63.32; H, 5.79; S, 30.89.

Oxidation of 1, 3, 5, and 8 with $FeCl_3$·6H_2O. The educt (0.5 g) was dissolved in approximately 40 mL of acetonitrile or acetonitrile/CH_2Cl_2 mixtures. After bubbling with Ar for 10 min, 5 equiv of powdered $FeCl_3$·6H_2O was added at room temperature, the mixture was stirred for 30 min, and then 200 mL of CH_2Cl_2 was added and shaken with a saturated aqueous solution of $Na_2S_2O_4$; a yellow color indicated the completion of the reduction. This was followed up by extraction with three times 100 mL of water, separation of the organic phase, and drying with Na_2SO_4. The solvent was evaporated and the crude product purified by column chromatography (110 g silica gel, 40−63 μm) from a concentrated solution in CH_2Cl_2. The elution was started with hexane (for separating the educt) the elution time being shortened by pressing the hexane through the column at a pressure of around 100 kPa. A mixture of CH_2Cl_2/hexane (first 1:20, then 1:10) was used as an eluent for the product. The given yields are calculated from the real amount of oxidized educt. The remaining material of the monomer was converted to undetectable products by unknown side reactions during the oxidation and reduction process. This behavior was found for all oxidation reactions.

3,3′,3″,3‴,4,4′,4″,4‴,5,5‴-Decamethyl-2,2′;5′,2″;5″,2‴-quaterthiophene (2). (a) From 0.5 g (2.1 mmol) of **1** and 2.86 g (10.6 mmol) of $FeCl_3$·6H_2O in 40 mL of acetonitrile. Yield: 170 mg (42.7%).

(b) 2-Bromo-3,4,5-trimethylthiophene (**16**) (2.00 g, 9.5 mmol) in 20 mL of dry ether was added dropwise to 0.36 g (24.6 mmol) of Mg turnings in 5 mL of dry ether containing a small quantity of iodine. The formed Grignard solution was dropped into a boiling solution of 1.80 g (4.7 mmol) of 5,5′-dibromo-3,3′,4,4′-tetramethyl-2,2′-bithiophene (**20**) and 103 mg (0.19 mmol) of $NiCl_2$dppp in 50 mL of dry ether, followed by purification of the crude product by column chromatography on silica gel with hexane. Pale yellow powder, mp 147−153 °C. Yield: 0.3 g (6.2%).

IR (KBr) ν/cm^{-1}: 2975 (m); 2937 (m); 2913 (st); 2855 (m); 1540 (schw); 1442 (st); 1392 (m); 1373 (m); 986 (m). ^{1}H-NMR ($CDCl_3$, TMS, 250 MHz) δ/ppm: 2.28 (s, 6H) [CH_3-5,5‴]; 2 (m, 24 H) [CH_3-3,3′,3″,3‴,4,4′,4″,4‴]. ^{13}C-NMR ($CDCl_3$, TMS, 250 MHz) δ/ppm: 136.41; 136.225; 136.077; 133.341; 132.607; 130.048; 129.191; 124.822; 14.135; 14.101; 14; 13.186; 12.572. MS *m/e* (I_{rel}/%): 470 (100.0) [M$^+$]; 469 (3.4) [(M − H)$^+$]; 456 (8.4) [(M − CH_2)$^+$]; 235 (12.5) [M^{2+}]; 220 (3.1) [(M − 2CH_3)$^{2+}$]. Anal. Calcd for $C_{26}H_{30}S_4$ (470.8): C, 66.33; H, 6.42; S, 27.25. Found: C, 66.15; H, 6.37; S, 27.56.

3,3′,3″,3‴,3⁗,3⁗′,4,4′,4″,4‴,4⁗,4⁗′,5,5⁗′-Tetradecamethyl-2,2′;5′,2″;5″,2‴;5‴,2⁗;5⁗,2⁗′-sexithiophene (4). From 0.5 g (1.4 mmol) of **3** and 1.95 g (7.2 mmol) of $FeCl_3$·6H_2O in 27 mL of CH_2Cl_2/acetonitrile (1:3). Yellowish crystals, mp 213 °C (CH_3OH/$CHCl_3$). Yield: 300 mg (65%).

IR (KBr) ν/cm^{-1}: 2915 (st); 2851 (st); 1443/1430 (st); 1388 (m); 1370 (m); 985 (st); 916 (st). ^{1}H-NMR ($CDCl_3$, TMS, 250 MHz) δ/ppm: 2.368 (s, 6H) [CH_3-5,5⁗′]; 2.27 (s, 12H); 2.255 (s, 6H); 2.17 (s, 6H); 2.14 (s, 6H); 2.12 (s, 6H) [CH_3-3,3′,3″,3‴,3⁗,3⁗′,4,4′,4″,4‴,4⁗,4⁗′]. ^{13}C-NMR ($CDCl_3$, TMS, 250 MHz) δ/ppm: 136.498; 136.449; 136.392; 136.179; 133.444; 132.72; 130.231; 129.686; 129.496; 129.125; 124.846; 14.263; 14.118; 13.286; 12.685. MS *m/e* (I_{rel}/%): 690 (100.0) [M]$^{\bullet+}$; 345 (44.2) [M]$^{2+}$. Anal. Calcd for $C_{38}H_{42}S_6$ (691.1): C, 66.04; H, 6.13; S, 27.83. Found: C, 66.28; H, 6.05; S, 27.99.

3′,3″,4,4′,4″,4‴,5,5‴-Octamethyl-2,2′;5′,2″;5″,2‴-quaterthiophene (6). (a) From 0.5 g (2.2 mmol) of **5** and 3.05 g of $FeCl_3$·6H_2O in 42 mL of acetonitrile. Yellow/gold colored leaflets, mp 158 °C. Yield: 150 mg (40.7%).

(b) Analogously to the preparation of **2**, the reaction was carried out of 3.46 g (18.1 mmol) of 2-bromo-4,5-dimethylthiophene (**14**) in 20 mL of dry ether and 0.66 g (27.1 mmol) of Mg turnings in 5 mL of dry ether, with a small amount of iodine, followed by reaction with a solution of 3.44 g (9.1 mmol) of 5,5′-dibromo-3,3′,4,4′-tetramethyl-2,2′-bithiophene (**20**) and 196 mg (0.362 mmol) of $NiCl_2$dppp in 100 mL of dry ether. Yellow/gold colored leaflets, mp 158 °C ($CHCl_3$). Yield: 1.76 g (44%).

IR (KBr) ν/cm^{-1}: 3066 (schw); 2973 (schw); 2943 (m); 2912 (st); 2852 (m); 1544 (m); 1444 (st); 1381 (m); 1199 (m); 1003 (m); 980 (m); 888 (m); 853 (m); 829 (st). ^{1}H-NMR ($CDCl_3$, TMS, 250 MHz) δ/ppm: 6.88 (s, 2H) [H3,3‴]; 2.42 (s, 6H) [CH_3-5,5‴]; 2.36 (s, 6H); 2.22 (s, 6H); 2.16 (s, 6H) [CH_3-3′,3″,4,4′,4″,4‴]. ^{13}C-NMR ($CDCl_3$, TMS, 250 MHz) δ/ppm: 137.361; 133.474; 132.988; 131.475; 131.446; 128.627; 127.401; 14.285; 14.216; 13.519; 12.954. MS *m/e* (I_{rel}/%): 442 (100.0) [M$^+$]; 441 (3.7) [(M − H)$^+$]; 221 (16.5) [M^{2+}]. Anal. Calcd for $C_{24}H_{26}S_4$ (442.7): C, 65.11; H, 5.92; S, 28.97. Found: C, 65.01; H, 5.73; S, 29.60.

3′,3″,3⁗,4,4′,4″,4‴4⁗,4⁗′,5,5‴,5⁗′-Dodecamethyl-2,2′;5′,2″;5″,2‴;3‴,2⁗;5⁗,2⁗′-sexithiophene (7). Isolated as a second fraction from the column chromatography of **6**. Brownish solid material, mp 62−64 °C. Yield: 23 mg (6.2%).

IR (KBr) ν/cm^{-1}: 2917 (st); 2853 (st); 1441 (st); 812 (st). ^{1}H-NMR ($CDCl_3$, TMS, 250 MHz) δ/ppm: 6.82 (s, 1H); 6.78 (s, 1H); 2.36 (s, 9H) [CH_3-5,5‴,5⁗′]; 2.3 (s, 3H); 2.16−2 (m, 24H) [CH_3-3′,3″,3⁗,4,4′,4″,4‴,4⁗,4⁗′]. ^{13}C-NMR ($CDCl_3$, TMS, 250 MHz) δ/ppm: 128.756; 14.226; 13.563; 12.999. MS *m/e* (I_{rel}/%): 662 (100.0) [M]$^{\bullet+}$; 648 (26.3) [M − CH_2]$^+$; 632 (8.0) [M − 2CH_3]$^+$; 331 (35.2) [M]$^{2+}$. Anal. Calcd for $C_{36}H_{38}S_6$ (663.1): C, 65.21; H, 5.77; S, 29.01. Found: C, 65.05; H, 5.99; S, 30.30.

3′,3″,4′,4″,5,5‴-Hexamethyl-2,2′;5′,2″;5″,2‴-quaterthiophene (9). Analogously to the preparation of **2**, the reaction was carried out of 3.42 g (19.3 mmol) of 2-bromo-5-methylthiophene (**12**)[12] in 20 mL of dry ether, 0.7 g (29 mmol) of Mg turnings, and a small quantity iodine in 5 mL of dry ether, followed by reaction of this Grignard solution with 3.67 g (9.7 mmol) of 5,5′-dibromo-3,3′,4,4′-tetramethyl-2,2′-bithiophene (**20**) and 209 mg (0.386 mmol) of $NiCl_2$dppp in 100 mL of dry ether, and purification by column chromatography on silica gel with hexane. Yellow powder, mp 142 °C. Yield: 0.90 g (22.5%).

IR (KBr) ν/cm^{-1}: 3069 (schw); 2954 (schw); 2910 (m); 2854 (m); 1532 (m); 1440 (st); 1219 (m); 1164 (schw); 1052 (m); 1015 (m); 978 (m); 880 (st); 790 (st). ^{1}H-NMR ($CDCl_3$, TMS, 250 MHz) δ/ppm: 6.92 (d, 2H, J = 5 Hz) [H3,3‴]; 6.7 (d, 2 Hz, J = 5 Hz) [H4,4‴]; 2.48 (s, 6H) [CH_3-5,5‴]; 2.28 (s, 6H); 2.08 (s, 6H) [CH_3-3′,3″,4′,4″]. ^{13}C-NMR ($CDCl_3$, TMS, 250 MHz) δ/ppm: 139.829; 137.392; 134.027; 133.713; 131.386; 127.517; 125.677; 125.549; 15.228; 14.266; 14.198. MS *m/e* (I_{rel}/%): 414 (100.0) [M$^+$]; 413 (4.3) [(M − H)$^+$]; 399 (2.4) [(M − CH_3)$^+$]; 207 (12.9) [M^{2+}]. Anal. Calcd for $C_{22}H_{22}S_4$ (414.7): C, 63.72; H, 5.35; S, 30.93. Found: C, 63.55; H, 5.20; S, 31.00.

3′,3‴,3⁗,3⁗′,4′,4‴4⁗′,4⁗′′,5,5″,5‴′,5⁗′′′-Dodecamethyl-2,2′;5′,3″;2″,2⁗′;5⁗′,2⁗′′;5⁗′′,2⁗′′′;3⁗′′′,2⁗′′′′;5⁗′′′′,2⁗′′′′′-octithiophene (10). From 0.5 g (2.4 mmol) of **8** and 3.25 g (12 mmol) of $FeCl_3$·6H_2O in 45 mL of acetonitrile; purification of the reaction product by column chromatography on silica gel (with CH_2Cl_2) and preparative HPLC (reverse phase, CH_3OH/THF, 3:1). Yellow crystals, mp 157−159 °C. Yield: 198 mg (46.5%).

IR (KBr) ν/cm^{-1}: 3060 (schw); 2972 (schw); 2937 (m); 2913 (st); 2854 (m); 1534 (schw); 1440 (st); 1373 (m); 1002 (m); 831 (m); 195 (st). ^{1}H-NMR ($CDCl_3$, TMS, 500 MHz) δ/ppm: 6.857

(d, 2H, $J = 3.75$ Hz); 6.782 (q, 2H, $J = 1.25$ Hz); 6.682 (q v. d, 2H, $J = 3.75$ Hz, $J = 1.25$ Hz); 2.495 (d, 6H, $J = 1.25$ Hz); 2.477 (d, 6H, $J = 1.25$ Hz); 2.202 (s, 6H); 1.972 (s, 6H); 1.91 (s, 6H); 1.846 (s, 6H). ^{13}C-NMR ($CDCl_3$, TMS, 500 MHz) δ/ppm: 139.456; 136.589; 136.232; 135.826; 134.549; 133.341; 132.724; 130.532; 130.451; 130.122; 129.732; 129.574; 128.784; 125.447; 125.331; 15.321; 15.243; 14.14; 14.03; 13.914. MS (FAB$^+$, xenon, DMSO/*m*-NO_2-C_6H_4-CH_2OH): 827 (0.1) [M + H]$^+$; 826 (0.1) [M]$^+$. Anal. Calcd for $C_{44}H_{42}S_8$ (827.3): C, 63.88; H, 5.12; S, 31.00. Found: C, 64.13; H, 5.01; S, 31.27.

3′,3‴,3⁗,3⁗′,4′,4‴,4⁗,4⁗′,5,5″,5‴,5⁗,5⁗′-Dodecamethyl-2,2′;5′,3″;2″,2‴;5‴,2⁗;5⁗,2⁗′;4⁗′,2⁗′′;5⁗′′,2⁗′′′-octithiophene (11). Isolated as a second fraction from the column chromatography of **10**. Yellow crystals, mp 95−115 °C. Yield: 40.5 mg (9.5%).

IR (KBr) ν/cm^{-1}: 3062 (schw); 2973 (m); 2937 (m); 2914 (st); 2854 (m); 1533 (st); 1440 (st); 1374 (m); 1002 (m); 833 (m); 795 (st). ^{1}H-NMR ($CDCl_3$, TMS, 500 MHz) δ/ppm: 6.96 (s, 1H); 6.918 (d, 1H, $J = 3.75$ Hz); 6.868 (d, 1H, $J = 3.75$ Hz); 6.791 (q, 1H, $J = 1.25$ Hz); 6.721 (q v. d, 1H, $J = 3.75$ Hz, $J = 1.25$ Hz); 6.691 (q v. d, 1H, $J = 3.75$ Hz, $J = 1.25$ Hz); 2.506 (s, 6H); 2.482 (d, 3H, $J = 1.25$ Hz); 2.416 (s, 3H); 2.298 (s, 6H); 2.214 (s, 3H); 2.07 (s, 3H); 2.048 (s, 3H); 2.035 (s, 3H); 1.945 (s, 3H); 1.86 (s, 3H). MS (FAB$^+$, xenon, DMSO/*m*-NO_2-C_6H_4-CH_2OH): 826 (100.0) [M]$^+$; 812 (6.9) [M − CH_2]$^+$. Anal. Calcd for $C_{44}H_{42}S_8$ (827.3): C, 63.88; H, 5.12; S, 31.00. Found: C, 64.28; H, 5.05; S, 31.35.

2-Bromo-4,5-dimethylthiophene (14). Following R. M. Kellog et al.,[12] 73.0 g (0.41 mol) of *N*-bromosuccinimide (NBS) was added in portions to a solution of 44.0 g (0.39 mol) of 2,3-dimethylthiophene (**13**)[13] in 465 mL of $CHCl_3$/CH_3COOH (1:1) in an exothermic reaction; the reaction mixture was allowed to cool down to room temperature; then, the same volume of water was added, and the organic phase was separated, washed with 100 mL of 3 N NaOH and three times, each with 100 mL of water, and then dried with $CaCl_2$. The solvent was then distilled off and the product purified by distillation in vacuo. Colorless liquid, bp 46 °C (0.005 mbar), n_D^{20}: 1.5651. Yield: 54.5 g (73%).

IR (KBr) ν/cm^{-1}: 3074 (m); 2974 (m); 2918 (st); 2858 (st); 1561 (m); 1442 (st); 1384 (m); 1191 (st); 1003 (m); 956 (m); 863 (m); 826 (st); 701 (st). ^{1}H-NMR ($CDCl_3$, TMS, 250 MHz) δ/ppm: 6.63 (s, 1H) [H3]; 2.23 (s, 3H) [CH_3-5]; 2.06 (s, 3H) [CH_3-4]. MS *m*/*e* (I_{rel}/%): 192, 190 (99.5, 100.0) [M$^+$]; 191, 189 (40.5, 33.5) [(M − H)$^+$]; 178, 176 (9.2, 9.2) [(M − CH_2)$^+$]; 177, 175 (36.0, 34.3) [(M − CH_3)$^+$]; 111 (58.1) [(M − Br)$^+$]. Anal. Calcd for C_6H_7BrS (191.1): C, 37.71; H, 3.69; Br, 41.81; S, 16.78. Found: C, 37.52; H, 3.58; Br, 42.11; S, 16.53.

2-Bromo-3,4,5-trimethylthiophene (16). Following R. M. Kellog et al.[12] and the synthesis of **14**, 6.0 g (48 mmol) of 2,3,4-trimethylthiophene (**15**)[13] and 8.5 g (48 mmol) of NBS in 50 mL of $CH_3COOH/CHCl_3$ (1:1) were reacted. Yellowish liquid, bp 48 °C (0.12 mbar), n_D^{20}: 1.5628. Yield: 7.0 g (72%).

IR (KBr) ν/cm^{-1}: 2979 (m); 2916 (st); 2856 (st); 1440 (st); 1389 (st); 1200 (m); 1016 (m); 965 (st). ^{1}H-NMR ($CDCl_3$, TMS, 250 MHz) δ/ppm: 2.39 (s, 3H) [CH_3-5]; 2.18 (s, 3H) [CH_3]; 2.14 (s, 3H) [CH_3]. MS *m*/*e* (I_{rel}/%): 206/204 (84.9/84.2) [(M)$^+$]; 191/189 (30.7/29.5) [(M − CH_3)$^+$]; 125 (100.0) [(M − Br − H)$^+$]; 110 (12.8) [(M − H − Br − CH_3)$^+$]; 91 (28.6) [$C_7H_7^+$]. Anal. Calcd for C_7H_9BrS (205.1): C, 40.99; H, 4.42; Br, 38.96; S, 15.63. Found: C, 41.15; H, 4.25; Br, 38.75; S, 15.79.

2-Bromo-3,4-dimethylthiophene (18). Following R. M. Kellog et al.[12] and the synthesis of **14**, 85.7 g (0.76 mol) of 3,4-dimethylthiophene (**17**)[13] was reacted with 136.2 g (0.76 mol) of NBS in 900 mL of $CH_3COOH/CHCl_3$ (1:1). Colorless liquid, bp 42 °C (0.07 mbar), n_D^{20}: 1.5682. Yield: 130.0 g (89%).

IR (KBr) ν/cm^{-1}: 3091 (schw); 2974 (m); 2942 (m); 2917 (st); 2858 (m); 1464 (m); 1442 (st); 1385 (m); 1356 (m); 1184 (m); 1023 (m); 964 (st); 854 (m); 729 (st). ^{1}H-NMR ($CDCl_3$, TMS, 250 MHz) δ/ppm: 6.78 (s, 1H) [H5]; 2.14 (s, 3H) [CH_3-3]; 2.06 (s, 3H) [CH_3-4]. MS *m*/*e* (I_{rel}/%): 192, 190 (58.0, 58.5) [M$^+$]; 111 (100.0) [(M − Br)$^+$]. Anal. Calcd for C_6H_7BrS (191.1): C, 37.71; H, 3.69; Br, 41.81; S, 16.78. Found: C, 37.98; H, 3.42; Br, 41.65; S, 16.89.

5,5′-Dibromo-3,3′,4,4′-tetramethyl-2,2′-bithiophene (20). To a solution of 13.83 g (36.4 mmol) of 3,3′,4,4′-tetramethyl-2,2′-bithiophene (**19**)[14] in 70 mL of $CH_3COOH/CHCl_3$ (1:1) 23.3 g (130.9 mmol) of NBS was added in portions while being stirred for 2 h under reflux; the precipitate was separated by filtration, the solution was neutralized, washed with water, and dried with Na_2SO_4, and the solvent was distilled off. Colorless crystals, mp 157 °C ($CH_3OH/CHCl_3$). Yield: 18.93 g (80%).

IR (KBr) ν/cm^{-1}: 2940 (m); 2912 (m); 2846 (schw); 1549 (m); 1440 (st); 1385 (st); 1353 (m); 1143 (m); 997 (m); 968 (st); 875 (m). ^{1}H-NMR ($CDCl_3$, TMS, 250 MHz) δ/ppm: 2.12 (s, 6H); 2.04 (s, 6H) [CH_3-3,3′,4,4′]. ^{13}C-NMR ($CDCl_3$, TMS, 250 MHz) δ/ppm: 137.421; 136.859; 128.386; 109.597; 14.489; 14.25. MS *m*/*e* (I_{rel}/%): 382, 380, 378 (58.4, 100.0, 50.9) [M$^+$]; 301, 299 (15.0, 15.4) [(M − HBr)$^+$]; 286, 284 (6.0, 5.9) [(M − HBr − CH_3)$^+$]; 257, 255 (6.5, 7.0) [(M − CSH − Br)$^+$]; 220 (10.9) [(M − 2Br)$^+$]; 190 (7.4) [M^{2+}]; 176 (9.4) [(M^{2+}) − CH_2]; 110 (6.6) [(C_6H_6S)$^+$]. Anal. Calcd for $C_{12}H_{12}Br_2S_2$ (380.2): C, 37.91; H, 3.18; Br, 42.03; S, 16.87. Found: C, 37.63; H, 3.05; Br, 42.07; S, 17.25.

5-Bromo-3,3′,4,4′,5′-pentamethyl-2,2′-bithiophene (21). Following R. M. Kellog et al.[12] and the synthesis of **14**, the reaction was carried out of 14.35 g (60.8 mmol) of 3,3′,4,4′,5-pentamethyl-2,2′-bithiophene (**1**) in 60 mL of $CH_3COOH/CHCl_3$ (1:1) and 11.36 g (63.8 mmol) of NBS. The solution became blue during the reaction. Colorless crystals, mp 143 °C ($CH_3OH/CHCl_3$). Yield: 10.91 g (57%).

IR (KBr) ν/cm^{-1}: 2974, 2939 (m); 2911 (st); 2850 (m); 1441 (st); 1385, 1356 (m); 1248, 1178 (m); 987 (st); 913 (st); 561 (st). ^{1}H-NMR ($CDCl_3$, TMS, 250 MHz) δ/ppm: 2.36 (s, 3H) [CH_3-5′]; 2.16 (s, 3H); 2.06 (s, 6H); 2.02 (s, 3H) [CH_3-3,3′,4,4′]. ^{13}C-NMR ($CDCl_3$, TMS, 250 MHz) δ/ppm: 137.203; 137.084; 135.903; 133.439; 133.206; 129.946; 123.972; 108.623; 14.49; 14.254; 13.998; 13.276; 12.636. MS *m*/*e* (I_{rel}/%): 316, 314 (100.0, 93.7) [M$^+$]; 301, 299 (8.2, 8.0) [(M − CH_3)$^+$]; 235 (27.3) [(M − Br)$^+$]; 220 (15.4) [(M − Br − CH_3)$^+$]; 202 (9.1) [(M − Br − SH)$^+$]; 191 (12.8) [(M − Br − CS)$^+$]. Anal. Calcd for $C_{13}H_{15}BrS_2$ (315.3): C, 49.52; H, 4.80; Br, 25.34; S, 20.34. Found: C, 49.77; H, 4.63; Br, 24.82; S, 20.78.

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References and Notes

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