# Studies on β-methylated end-capped bithiophenes

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**The reactivity of a variety of differently β-methylated oxidized α,α′-blocked (end-capped) bithiophenes has been studied. Electroanalytical methods such as cyclic voltammetry and studies with a rotating-ring disc electrode (RRDE) are employed, revealing two oxidation peaks. While the first electron transfer yields radical cations of increased stability as the number of β-methyl groups is increased, the second electron transfer is irreversible. For the first time, a dependence of the stability of radical cations (first oxidation step) on the degree of β-methylation is reported. Compounds with methylated 3-β-positions form more stable radical cations than 4-β-methylated ones. The stability of the oxidized end-capped bithiophene 6 can be explained by a reversible dimerization. The presence of β-substitution also exerts an influence on the reaction products of the chemical oxidation with $FeCl_3 \cdot 6H_2O$, which have been isolated and purified by chromatography. In the case of bithiophene derivatives with methylated 3,3′-positions the main products are bithiophene-5-carbaldehydes; bithiophene derivatives with free 3-positions form bis(bithiophene)-methanes. The reactive centers are α-methyl groups, not, as one might expect, free β-ring positions. In neither case has a β,β′-linkage between two thiophene rings been observed.**

## Introduction

It is well known that by blocking the reactive α-positions of oligothiophenes the stability of their radical cations increases[1] because α,α′-polymerization is not possible. Compounds blocked in such a way have been used in studies relating their electronic and physical properties to their chain length.[2] Radical cations of non β-methylated end-capped terthiophene derivatives are stable intermediates,[3] which means that end-capped bithiophenes, normally known as less stable, are useful for studying the dependence of stability on β-methylation after oxidation. We expect a differentiation in reactivity of the substituted and non-substituted β-positions of the bithiophene structure. Our results may help us understand the possibilities for branching which occur during the oxidation of polymerizable thiophene monomers, which are, up to now, unclear. It is evident that these side reactions influence the structure and therefore also the electrical conductivity of the resulting polymers.

## Results and discussion

To study the reactivity of oxidized end-capped bithiophenes we investigated the oxidation behaviour of different β-methylated compounds **1**–**10**. The synthesis of the compounds **1**, **4** and **10** are described in the literature.[4–6] Compounds **2** and **3** and **5**–**9** were prepared starting with methylbromothiophenes using the cross-coupling method according to Kumada[7] (Scheme 1).

### Electrochemical oxidation

By voltammetric investigations at the stationary and rotating disc electrode (RDE) respectively two oxidation steps were detected. Regardless of β-methylation the peak potentials of the first electron transfer $E^1_{pa}$ were in the range of 1.0 to 1.15 V *vs.* SCE (Table 1). The peak current ratios determined from cyclic voltammetry showed that the stability of the radical cations increases with increasing β-methylation. No information about the relationship between an increase in stability and the blocking of the different β-positions was obtained. Table 1 also contains all other values of our voltammetric investigations.

Fig. 1 shows the cyclic voltammogram and rotating disc

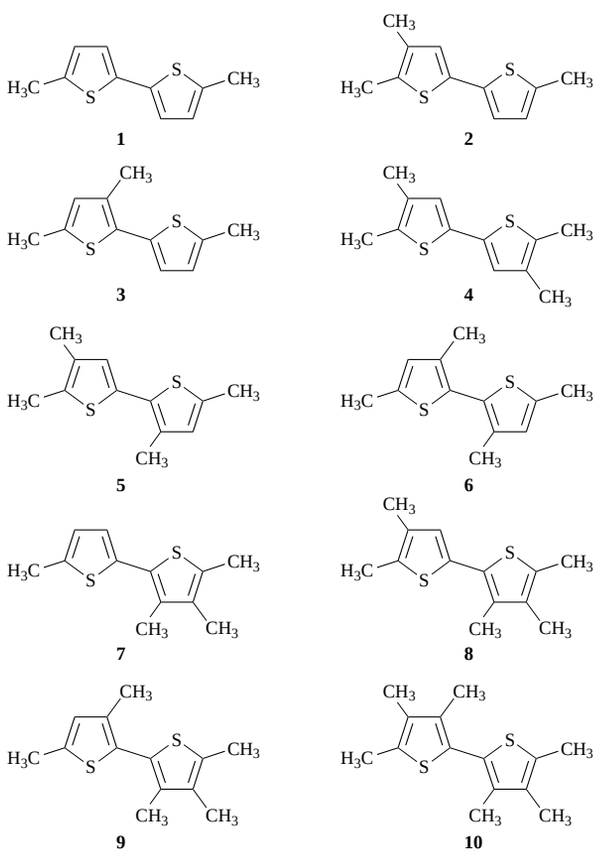


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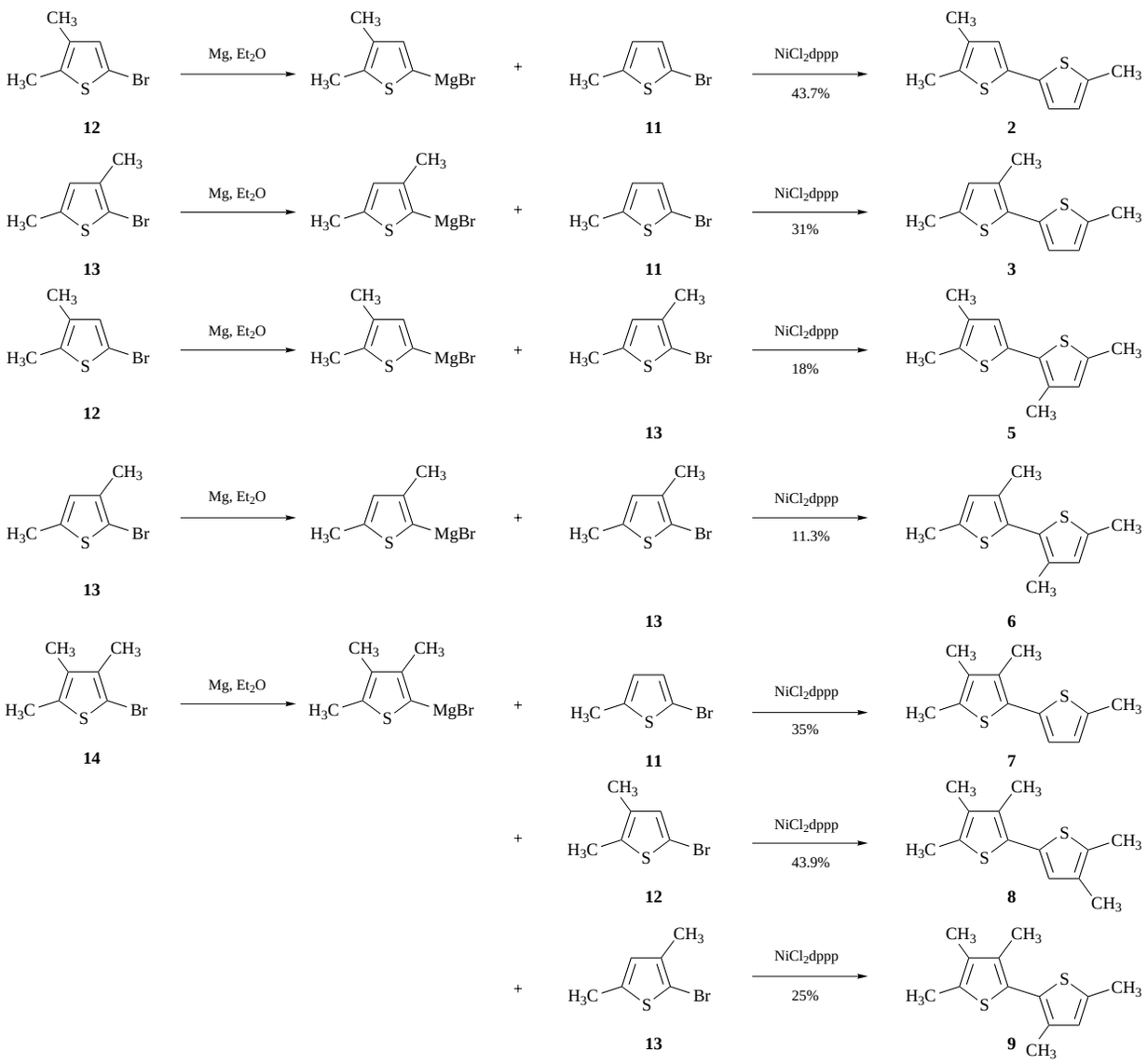
**Table 1** Electrochemical data of the 'end-capped' 2,2′-bithiophene derivatives **1** to **10**, potentials in V *vs*. SCE; $c = 5 \times 10^{-4}$ mol l$^{-1}$, 0.1 M $TEABF_4$–ACN, Pt-disc ($d = 6$ mm), $v = 200$ mV s$^{-1}$ (cyclic voltammetry, $E^1_{pa}$, $E^1_{pc}$, $E^2_{pa}$, $\Delta E^1_p$, $\Delta E_{pa}$, $i^1_{pc}/i^1_{pa}$), $v = 10$ mV s$^{-1}$ (voltammetry at the rotating disc electrode, $\omega = 3000$ min$^{-1}$, $E^1_{1/2}$, $E^2_{1/2}$)

| Comp. | $E^1_{1/2}$ [a] | $E^1_{pa}$ [b] | $E^1_R$ [c] | $E^1_{pc}$ [d] | $E^2_{1/2}$ [e] | $E^2_{pa}$ [f] | $\Delta E^1_p$ [g] | $i^1_{pc}/i^1_{pa}$ [h] | $\Delta E_{pa}$ [i] |
|---|---|---|---|---|---|---|---|---|---|
| **1** | 1.12 | 1.15 | 1.30 | — | 1.66 | 1.59 | — | — | 0.44 |
| **2** | 1.05 | 1.08 | 1.23 | 0.99 | 1.51 | 1.48 | 0.09 | 0.59 | 0.40 |
| **3** | 1.06 | 1.09 | 1.24 | 1.00 | 1.61 | — | 0.09 | 0.46 | — |
| **4** | 0.99 | 1.03 | 1.18 | 0.93 | 1.51 | 1.45 | 0.10 | 0.69 | 0.41 |
| **6** | 1.06 | 1.09 | 1.24 | 1.00 | 1.52 | 1.54 | 0.09 | 0.71 | 0.45 |
| **5** | 1.01 | 1.03 | 1.18 | 0.94 | 1.55 | 1.52 | 0.08 | 0.62 | 0.49 |
| **7** | 1.03 | 1.05 | 1.20 | 0.97 | 1.44 | 1.52 | 0.08 | 0.62 | 0.47 |
| **8** | 0.99 | 1.00 | 1.15 | 0.91 | 1.44 | 1.35 | 0.09 | 0.73 | 0.35 |
| **9** | 1.03 | 1.07 | 1.22 | 0.99 | 1.44 | 1.45 | 0.08 | 0.79 | 0.38 |
| **10** | 1.01 | 1.09 | 1.24 | 0.99 | 1.42 | 1.40 | 0.10 | 0.71 | 0.30 |

[a] Half-wave potential of the first oxidation. [b] Anodic peak potential of the first oxidation. [c] Reverse potential. [d] Cathodic peak potential of the first oxidation. [e] Half-wave potential of the second oxidation. [f] Anodic peak potential of the second oxidation. [g] Peak separation for the first oxidation. [h] Peak current ratio of the first oxidation. [i] Peak potential gap for the first and second oxidation.




**Scheme 1**

voltammogram of compound **10**. As can be seen, the first electron transfer is reversible and the second one is irreversible; the peak potentials $E^2_{pa}$ for all bithiophenes investigated are in the range 1.40 to 1.59 V (SCE). Under special conditions, such as low temperature and $SO_2$ as solvent, compound **10** showed a reversible second electron transfer.[8]

A better differentiation in the stability of the radical cations than by cyclic voltammetric investigations is possible by employing a rotating-ring disc electrode (RRDE).[9] The characteristic parameter is the collection coefficient $N$ defined as quotient between ring and disc current $N = i_R/i_D$. For unstable intermediates, $N$ is a function of the rotation rate $\omega$. In the case of stable intermediates a maximal value for $N$ is measured ($N_0$). $N_0$ depends only on the geometric parameters of the RRDE. There must be a guarantee that the ring current exclusively characterises the reduction of the monomeric radical cations.

**Table 2** Collection coefficient $N$ in dependence of the rotation $\omega$/min$^{-1}$ of the RRDE, measured for the β-methylated 'end-capped' bithiophene derivatives **1** to **10**. $c = 5 \times 10^{-4}$ mol$^{-1}$, 0.1 M $TEABF_4$–ACN, SCE, $v = 10$ mV s$^{-1}$, Pt-RRDE, ring potential = 0.7 V (SCE), 25 °C

| | $N$ at $\omega$/min$^{-1}$ | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Comp. | 500 | 1000 | 1500 | 2000 | 2500 | 3000 | 3500 | 4000 | 4500 | 5000 |
| **1** | 0.046 | 0.068 | 0.082 | 0.095 | 0.104 | 0.112 | 0.117 | 0.122 | 0.125 | 0.128 |
| **2** | 0.072 | 0.095 | 0.110 | 0.122 | 0.132 | 0.139 | 0.146 | 0.152 | 0.156 | 0.159 |
| **3** | 0.144 | 0.161 | 0.188 | 0.197 | 0.204 | 0.208 | 0.211 | 0.212 | 0.216 | 0.218 |
| **4** | 0.095 | 0.131 | 0.149 | 0.160 | 0.166 | 0.170 | 0.175 | 0.178 | 0.179 | 0.182 |
| **6** | 0.187 | 0.203 | 0.212 | 0.215 | 0.216 | 0.219 | 0.220 | 0.221 | 0.219 | 0.218 |
| **5** | 0.124 | 0.152 | 0.167 | 0.177 | 0.185 | 0.191 | 0.196 | 0.199 | 0.200 | 0.194 |
| **7** | 0.128 | 0.152 | 0.162 | 0.171 | 0.174 | 0.179 | 0.182 | 0.184 | 0.184 | 0.184 |
| **8** | 0.146 | 0.180 | 0.195 | 0.205 | 0.212 | 0.215 | 0.218 | 0.219 | 0.220 | 0.220 |
| **9** | 0.212 | 0.221 | 0.226 | 0.227 | 0.227 | 0.229 | 0.228 | 0.226 | 0.226 | 0.225 |
| **10** | 0.158 | 0.179 | 0.185 | 0.185 | 0.188 | 0.188 | 0.189 | 0.189 | 0.188 | 0.185 |

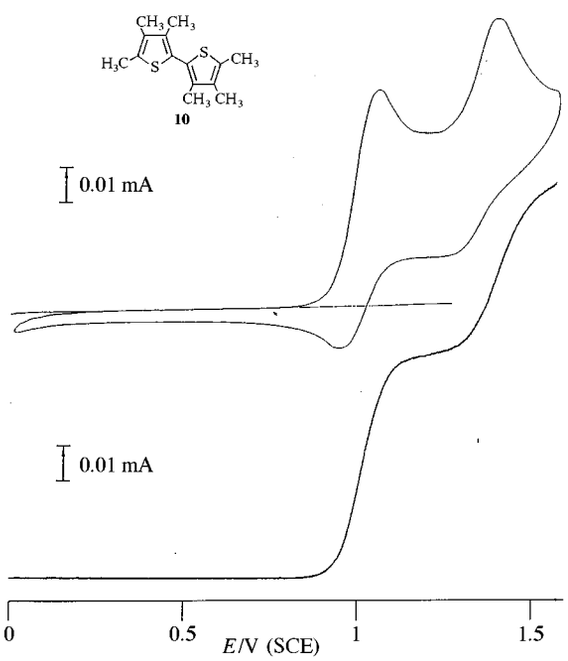



**Fig. 1** Cyclic voltammogram and voltammogram of compound **10**, $c = 5 \times 10^{-4}$ mol l$^{-1}$, 0.1 M $TEABF_4$–ACN (SCE), stationary and rotating disc electrode ($d = 6$ mm), $v = 200$ mV s$^{-1}$ (cyclic voltammetry) and $v = 10$ mV s$^{-1}$, $\omega = 3000$ min$^{-1}$ (voltammetry), 25 °C

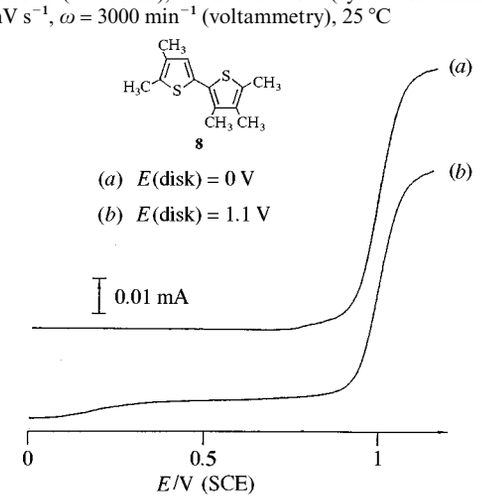



**Fig. 2** Voltammogram (*a*) and ring current voltammogram (*b*) of compound **8**, $c = 5 \times 10^{-4}$ mol l$^{-1}$, 0.1 M $TEABF_4$–ACN (SCE), Pt-RRDE, $\omega = 3000$ min$^{-1}$, $v = 10$ mV s$^{-1}$, 25 °C

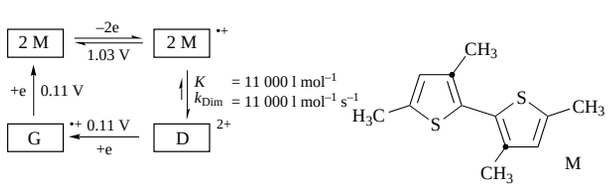
This can be controlled by a ring current voltammogram, while the species investigated is oxidized at the disc. Fig. 2 shows voltammograms for compound **8** at disc potentials of 0 V and 1.1 V respectively.

Voltammogram (*b*) (see Fig. 2) demonstrates that in addition to the monomeric radical cation the reduction of product occurs in the range 0.0 to 0.4 V *vs.* SCE. Applying a ring potential of +0.7 V (SCE), no products of chemical follow-up reactions were detectable.

For an exact differentiation between the individual collection coefficients of the compounds **1**–**10**, an RRDE with a broad gap between ring and disc was necessary.[17]

In Table 2 the collection coefficients of the RRDE in dependence of the rotation rate are listed. As the radical cation of compound **1** is extremely unstable, the collection coefficients are low and are strongly dependent of the rotation rate $\omega$.

This behaviour is in contrast, for instance, to that of compound **6**. Down to $\omega = 2000$ min$^{-1}$ the radical cations of **6** are stable within the timescale of the experiment; the collection coefficient $N$ is in the range of $N_0$ meaning that **6** forms stable radical cations. Comparing the $N$ values of **1** and **10** we decided that $N$(1000 min$^{-1}$) is suitable for a differentiation in reactivity. Fig. 3 relates structure to reactivity on the basis of the $N$ values given for the bithiophene derivatives **1**–**10**. For compounds with methylation at the marked 3,3′-β-positions (see Fig. 3) higher stabilization (higher $N$-values) is observed, in contrast to the compounds with methylated 4,4′-β-positions (not marked), in particular for compounds **1**, **2** and **3**. To gain a better understanding of this, compound **4** (with methylated 4,4′-β-positions) and compound **6** (with methylated 3,3′-β-positions) were investigated in detail by cyclic voltammetry. It has been found by Tschuncky *et al.*[10] that the radical cations of **6** give a reversible dimerization according to Scheme 2. More detailed information is given in ref. 10.




**Scheme 2**

We can conclude that the radical cations of monomer **4** react (in contrast to compound **6**) according to a pseudo first-order reaction, as the cyclic voltammograms show no change with different monomer concentrations (Fig. 4). Kinetic analysis of the follow-up-reaction of **4** is possible by employing a working curve developed by Olmstead.[11] Here, rate constant $k = 140$ s$^{-1}$ was found. The results of the cyclic voltammetric investigations are in accordance with the results of the investigations with the RRDE. It was found that the radical cations of **6** with blocked 3,3′-positions are stable. The lower collection coefficients of compounds with nonmethylated 3,3′-β-positions can be explained by a dimerization reaction that is pseudo first-order.

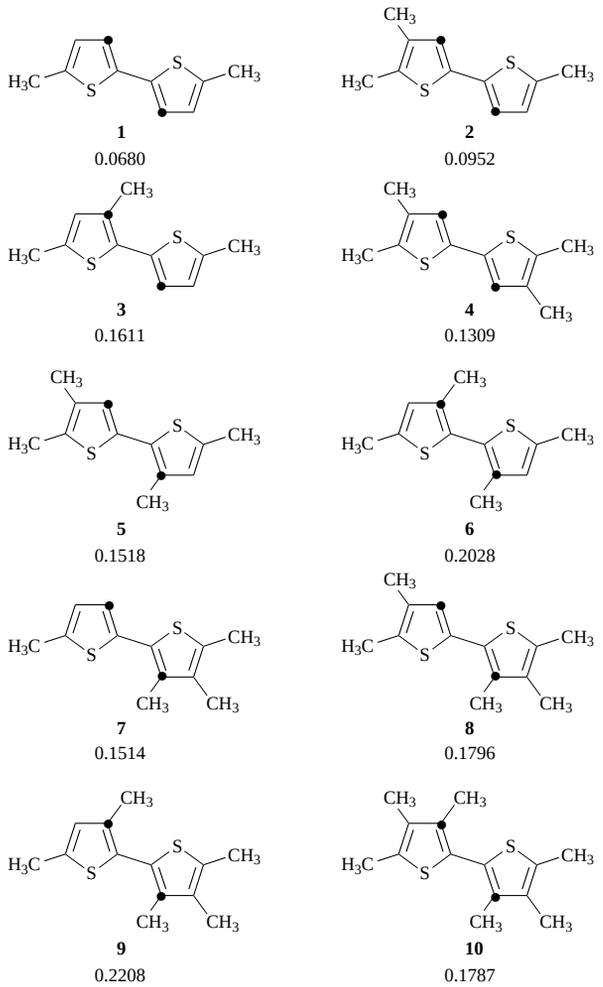



**Fig. 3** Structure–reactivity relationship on the basis of collection coefficient (*N*) values. 3,3′-β-positions are marked.

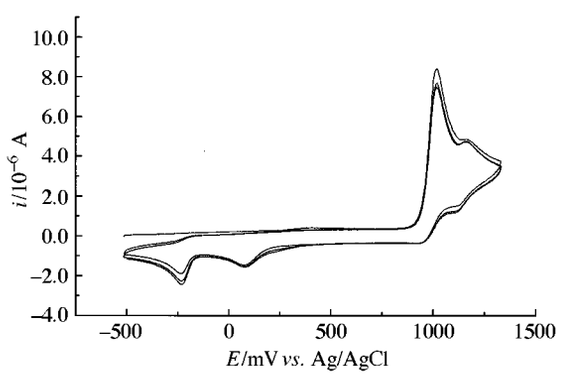
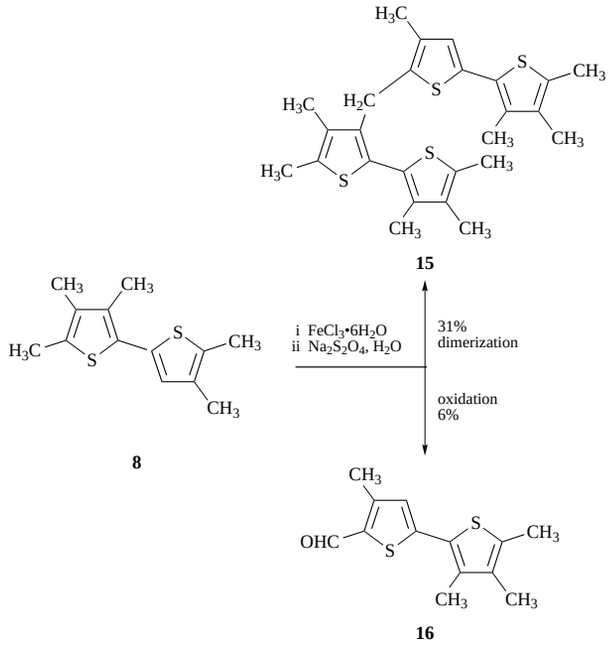



**Fig. 4** Cyclic voltammogram of 4,4′,5,5′-tetramethyl-2,2′-bithiophene (**4**), $c = 10^{-3}$ mol $l^{-1}$, 0.1 M $TBAPF_6$–ACN (Ag/AgCl), Pt-disc ($d$ = 2 mm), $v$ = 380 mV $s^{-1}$, 25 °C

## Chemical oxidation

In order to determine possible oxidation products the monomers **4**, **6**, **8**, **9** and **10** were oxidized with $FeCl_3 \cdot 6H_2O$. In contrast to water-free $FeCl_3$ and other reagents, this reagent reacts very gently. The oxidation products formed were isolated and purified by chromatography. It was found that the structures of the oxidation products depend on the type of β-methylation. The oxidation of compounds with two methylated 3,3′-β-positions (**6**, **9** and **10**) yields bithiophene-5-carbaldehydes as the main products. If neither, or only one, 3-β-position is methylated (**4**, **8**), mainly bithienylmethanes are formed. Both of these reactions (carbaldehyde-formation and dimerization) were found in the case of **8**, which has one methylated and one unsubstituted 3,3′-β-position (Scheme 3). In this case (3′,4,4′,5′-tetramethyl-2,2′-bithiophen-5-yl)(3′,4,4′,5,5′-pentamethyl-2,2′-bithiophen-3-yl)methane (**15**) and 3,4,4′,5-tetramethyl-2,2′-bithiophene-5′-carbaldehyde (**16**) were formed.




**Scheme 3**

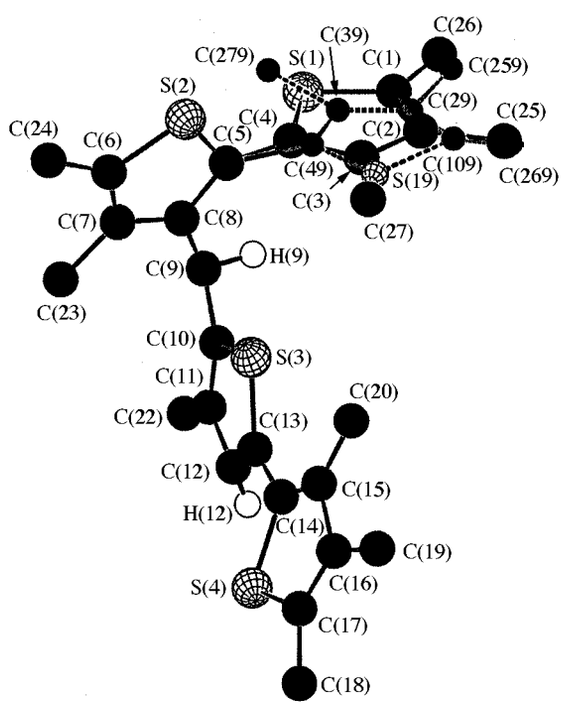



**Fig. 5** Structure of (3′,4,4′,5′-tetramethyl-2,2′-bithiophen-5-yl)-(3′,4,4′,5,5′-pentamethyl-2,2′-bithiophen-3-yl)methane (**15**) as determined by X-ray analysis

The structure of the bithienylmethane **15** which is the main oxidation product of **8**, was determined by X-ray analysis (Fig. 5).[12] The crystal used for the measurement was obtained by recrystallization from methanol. The clear, colourless crystal was mounted on a glass fibre needle. The measurement was performed on a large four-circle Eulerian cradle (Huber, type 512). After structure solution a conventional refinement (Xtal 3.4) revealed a statistical disorder. The X-ray analysis (Fig. 5) confirms that an α-methyl group of one bithiophene molecule was connected with a 3-β-position of another bithiophene molecule. The reactive α-position of the bithiophene system

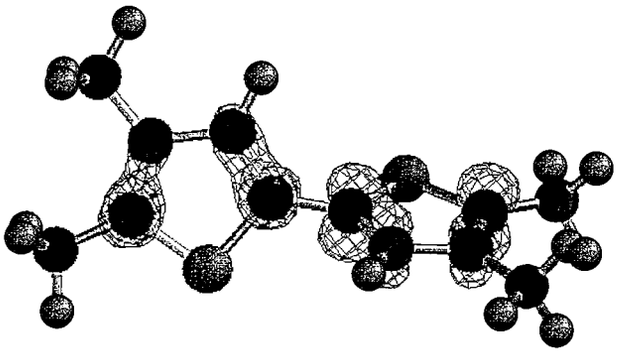
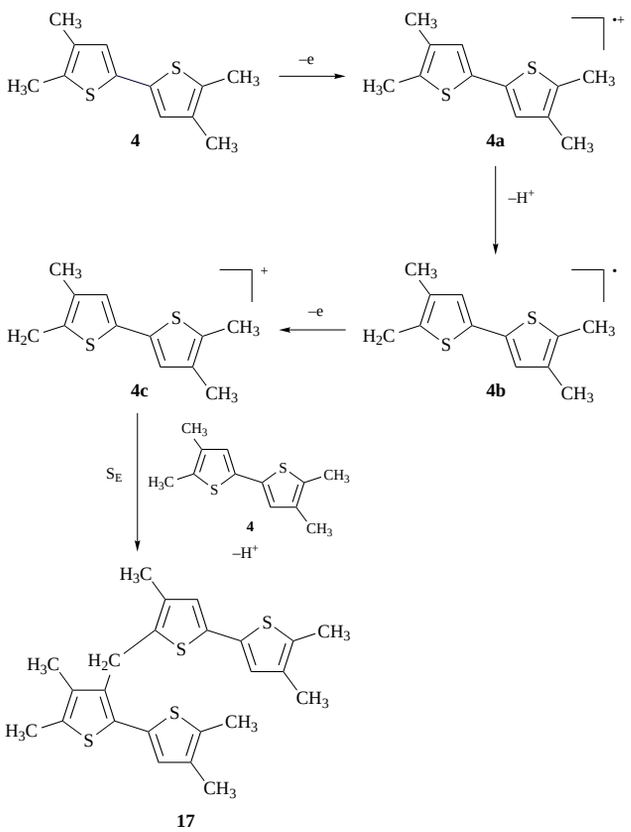


**Fig. 6** HOMO of 4,4′,5,5′-tetramethyl-2,2′-bithiophene (**4**), calculated by PM3/SPARTAN



**Scheme 4**

activates the α-methyl group for this 'benzyl type radical' reaction. The preferred attack of an α-methyl group at a 3-β-position in compound **4** according to a reaction of a pseudo-first order was explained by quantum mechanical calculations (PM3/SPARTAN). In the 3-position in both thiophene systems a somewhat higher electron density occurs in contrast to the 4-β-positions. Fig. 6 shows the electron density distribution for the HOMO of compound **4**.

On the basis of these results the following mechanism for the formation of **17** by oxidative condensation of **4** was proposed (Scheme 4).

After the oxidation of **4** to the radical cation **4a**, a deprotonation at an α-methyl group occurred. The resulting radical **4b** is oxidized to the corresponding cation **4c**. This positively charged intermediate is capable of reacting with a 3-β-position of high electron density according to a pseudo-first order reaction. This coupling step can also be explained as an $S_E$-reaction. After a further deprotonation the main product, the bithienylmethane derivative **17**, is formed. Aldehydes arise by a side reaction of radical cations or the cations of the bithiophene derivatives with water.[13] A ligand water molecule from the $FeCl_3 \cdot 6H_2O$ acts as a nucleophile to attack an α-methyl group of the educt, the most reactive centre in **8** (Scheme 3). The end-capped methylated bithiophenes **6**, **9** and **10** which also have methyl groups in the 3-β-positions form α-carbaldehydes as main products during the oxidation reaction with $FeCl_3 \cdot 6H_2O$.[14]

## Conclusion

Increasing the number of β-methyl groups is observed to increase the stability of the radical cations of end-capped bithiophenes **1**–**10**. Compounds with methyl groups only at 3-β-positions form radical cations with a higher stability than corresponding 4-β-methylated ones also with unsubstituted 3-β-positions. The chemical follow-up reactions of radical cations are not, as one might expect, β,β-ring couplings. Instead, bithienylmethanes are formed by coupling of activated α-methyl groups with 3-β-ring positions of high electron density of another bithiophene molecule. Nyberg[15] found analogous reactions for methylated benzene derivatives. α-Methyl groups were activated by α-ring positions.[16] If the 3-β-ring positions are methylated then side reactions of the radical cations with nucleophiles are observed, such as reaction with water to form methylated bithiophene-5-carbaldehydes.

## Experimental

### Bithiophene preparation

**4,5,5′-Trimethyl-2,2′-bithiophene (2).** 0.95 g (39.3 mmol) Mg cuttings in 10 ml dry diethyl ether (hereafter referred to as ether) and several iodine crystals were placed in a 100 ml three-necked flask fitted with a reflux condenser, drying tube, dropping funnel and gas inlet. Under an inert gas atmosphere, 5.00 g (26.2 mmol) 2-bromo-4,5-dimethylthiophene (**12**) in 20 ml dry ether were added slowly (dropwise). After addition was completed, the reaction mixture was refluxed for 2 h with stirring and then transferred into a dropping funnel under the inert gas to separate it from the unreacted Mg.

This Grignard solution was then added to a 100 ml three-necked flask (fitted with a reflux condenser, drying tube and gas inlet) which contained 4.63 g (26.2 mmol) 2-bromo-5-methylthiophene (**11**) in 50 ml dry ether and 460 mg (0.85 mmol) $NiCl_2$dppp [1,3-bis(diphenylphosphano)propane-nickel(II) chloride] in such a way that a controlled reflux took place. After 2 h refluxing with stirring, the mixture was poured into 100 ml 3 M HCl at 0 °C. This was followed by extraction with ether (3 × 100 ml); the combined organic phases were then washed three times with 100 ml water and dried with $CaCl_2$, the solvent was removed *in vacuo* and the crude product purified by chromatography on silica gel (40–63 μm) with hexane; yield 2.38 g **2**, 44%; colourless crystals, mp 56 °C (MeOH); $\nu$(KBr)/cm$^{-1}$ 3047 (w), 2941 (w), 2909 (m), 2849 (m), 1543 (m), 1444 (st), 1223 (w), 1183 (m), 1046 (m), 886 (m), 845 (m), 825 (m) and 794 (st); $\delta_H$($CDCl_3$, TMS, 250 MHz, *J*/Hz) 6.84 (d, 1H, *J* = 3.75, H3′), 6.76 (s, 1H, H3), 6.6 (d, 1H, *J* = 3.75, H4′), 2.44 (s, 3H, $CH_3$-5′), 2.32 (s, 3H, $CH_3$-5) and 2.12 (s, 3H, $CH_3$-4); $\delta_C$($CDCl_3$, TMS, 62.89 MHz) 138.19, 135.57, 133.59, 132.78, 131.44, 125.89, 125.70, 122.60, 15.25, 13.50 and 12.96; *m*/*z* 208 ($M^+$, 100%), 207 [$(M - H)^+$, 44], 193 [$(M - CH_3)^+$, 17], 175 [$(M - SH)^+$, 14] and 104 ($M^{2+}$, 5) (Found: C, 63.27; H, 5.62; S, 31.75. $C_{11}H_{12}S_2$ requires C, 63.41; H, 5.81; S, 30.78%).

**3,5,5′-Trimethyl-2,2′-bithiophene (3).** Analogously to the preparation of **2**, compound **3** was prepared by reaction of 5.00 g (26.2 mmol) 2-bromo-3,5-dimethylthiophene (**13**) in 20 ml dry ether, 0.94 g (39.3 mmol) Mg cuttings in 10 ml dry ether and some iodine crystals; coupling of the resulting Grignard reagent with 4.63 g (26.2 mmol) 2-bromo-5-methylthiophene (**11**) in 50 ml dry ether, 82 mg (0.15 mmol) $NiCl_2$dppp; and purification by column chromatography on silica gel with hex-

ane, HPLC (reversed-phase, MeOH); yield 1.7 g **3**, 31%; colourless liquid, bp >270 °C; $n_D^{20}$ = 1.6288; $\nu$(KBr)/cm$^{-1}$ 3062 (m), 2968 (m), 2944 (m), 2917 (st), 2858 (m), 1540 (m), 1440 (st), 1379 (m), 1244 (m), 1133 (m), 1050 (m), 912 (m), 874 (m), 827 (st) and 799 (st); $\delta_H$($CDCl_3$, TMS, 250 MHz, *J*/Hz) 6.82 (d, 1H, *J* = 3.75, H3′), 6.64 (d, 1H, *J* = 3.75, H4′), 6.5 (s, 1H, H4), 2.48 (s, 3H), 2.4 (s, 3H, $CH_3$-5,5′) and 2.28 (s, 3H, $CH_3$-3); $\delta_C$($CDCl_3$, TMS, 62.89 MHz) 139.04, 137.05, 134.61, 133.11, 129.58, 128.94, 125.41, 124.76, 15.17 and 15.06; *m*/*z* 208 ($M^+$, 100%), 207 [$(M - H)^+$, 34], 193 [$(M - CH_3)^+$, 17], 175 [$(M - SH)^+$, 10] and 104 ($M^{2+}$, 5) (Found: C, 63.34; H, 5.72; S, 30.86. $C_{11}H_{12}S_2$ requires C, 63.41; H, 5.81; S, 30.78%).

**3,4′,5,5′-Tetramethyl-2,2′-bithiophene (5).** Analogously to the preparation of **2**, compound **5** was prepared by reaction of 5.00 g (26.2 mmol) 2-bromo-4,5-dimethylthiophene (**12**) in 20 ml dry ether, 0.94 g (39.3 mmol) Mg cuttings in 10 ml dry ether and some iodine crystals; coupling of the resulting Grignard reagent with 5.00 g (26.2 mmol) 2-bromo-3,5-dimethylthiophene (**13**) in 50 ml dry ether, 82 mg (0.15 mmol) $NiCl_2$dppp; and purification by column chromatography on silica gel with hexane, HPLC (reversed-phase, MeOH–water); yield 1.05 g **5**, 18%; colourless liquid, bp >270 °C; $\nu$(KBr)/cm$^{-1}$ 3053 (w), 2968 (m), 2942 (m), 2917 (st), 2858 (m), 1556 (m), 1443 (st), 1378 (m), 1207, 1197, 1133 (m), 883 (m), 854 (m) and 827 (st); $\delta_H$($CDCl_3$, TMS, 250 MHz, *J*/Hz) 6.74 (s, 1H, H3′), 6.5 (s, 1H, H4), 2.4 (s, 3H), 2.3 (s, 3H, $CH_3$-5,5′), 2.26 (s, 3H) and 2.1 (s, 3H, $CH_3$-3,4′); $\delta_C$($CDCl_3$, TMS, 62.89 MHz) 136.76, 133.21, 132.82, 132.10, 131.95, 129.56, 128.98, 127.70, 15.61, 15.15, 13.44 and 12.82; *m*/*z* 222 ($M^+$, 100%), 221 [$(M - H)^+$, 30], 207 [$(M - CH_3)^+$, 17], 189 [$(M - SH)^+$, 8] and 111 ($M^{2+}$, 7) (Found: C, 64.57; H, 6.33; S, 29.48. $C_{12}H_{14}S_2$ requires C, 64.82; H, 6.35; S, 28.83%).

**3,3′,5,5′-Tetramethyl-2,2′-bithiophene (6).** Analogously to the preparation of **2**, compound **6** was prepared by reaction of 5.00 g (26.2 mmol) 2-bromo-3,5-dimethylthiophene (**13**) in 20 ml dry ether, 0.94 g (39.3 mmol) Mg cuttings in 10 ml dry ether and some iodine crystals; coupling of the resulting Grignard reagent with 5.00 g (26.2 mmol) 2-bromo-3,5-dimethylthiophene (**13**) in 50 ml dry ether, 160 mg (0.3 mmol) $NiCl_2$dppp; and purification by column chromatography on silica gel (40–63 μm) with hexane, HPLC (reversed-phase, MeOH–water); yield 0.66 g **6**, 11%; colourless crystals, mp 61 °C; $\nu$(KBr)/cm$^{-1}$ 3066 (w), 2940 (m), 2914 (m), 2850 (m), 1547 (w), 1499 (w), 1431 (m), 1379 (m), 1352 (m), 1209 (st), 1134 (st), 877 (st) and 832 (st); $\delta_H$($CDCl_3$, TMS, 250 MHz) 6.6 (s, 2H, H4,4′), 2.48 (s, 6H, $CH_3$-5,5′) and 2.12 (s, 6H, $CH_3$-3,3′); $\delta_C$($CDCl_3$, TMS, 62.89 MHz) 138.88, 135.98, 128.35, 127.28, 15.20 and 14.65; *m*/*z* 222 ($M^+$, 100%), 221 [$(M - H)^+$, 25], 208 [$(M - CH_2)^+$, 38], 207 [$(M - CH_3)^+$, 34], 193 [$(M - CH_3 - CH_2)^+$, 10], 147 [$(M - 2CH_3 - CSH)^+$, 6] and 111 ($M^{2+}$, 8) (Found: C, 64.59; H, 6.24; S, 29.17. $C_{12}H_{14}S_2$ requires C, 64.82; H, 6.35; S, 28.83%).

**3,4,5,5′-Tetramethyl-2,2′-bithiophene (7).** Analogously to the preparation of **2**, compound **7** was prepared by reaction of 5.50 g (27 mmol) 2-bromo-3,4,5-trimethylthiophene (**14**) in 20 ml dry ether, 0.98 g (40.5 mmol) Mg cuttings in 10 ml dry ether and some iodine crystals; coupling of the resulting Grignard reagent with 4.80 g (27 mmol) 2-bromo-5-methylthiophene (**11**) in 50 ml dry ether, 160 mg (0.3 mmol) $NiCl_2$dppp; and purification by column chromatography on silica gel (40–63 μm) with hexane; yield 2.1 g **7**, 35%; colourless liquid, bp >270 °C; $n_D^{20}$ = 1.6248; $\nu$(KBr)/cm$^{-1}$ 3064 (w), 2972, 2937 (m), 2916 (st), 2857 (st), 1544 (m), 1444 (st), 1391, 1372 (m), 1254, 1210, 1209, 1157, 1101, 1048, 1001 (m), 880 (m) and 794 (st); $\delta_H$($CDCl_3$, TMS, 250 MHz, *J*/Hz) 6.82 (d, 1H, *J* = 3.75, H3′), 6.66 (d, 1H, *J* = 3.75, H4′), 2.48 (s, 3H), 2.32 (s, 3H, $CH_3$-5,5′), 2.22 (s, 3H) and 2.02 (s, 3H, $CH_3$-3,4); $\delta_C$($CDCl_3$, TMS, 62.89 MHz) 139.11, 134.74, 134.04, 133.69, 130.88, 126.84, 125.39, 125.15, 15.17, 14.12, 13.17 and 12.68; *m*/*z* 222 ($M^+$, 100%), 221 [$(M - H)^+$, 24], 207 [$(M - CH_3)^+$, 24], 189 [$(M - SH)^+$, 9] and 111 ($M^{2+}$, 3) (Found: C, 64.71; H, 6.27; S, 28.95. $C_{12}H_{14}S_2$ requires C, 64.82; H, 6.35; S, 28.83%).

**3,4,4′,5,5′-Pentamethyl-2,2′-bithiophene (8).** Analogously to the preparation of **2**, compound **8** was prepared by reaction of 8.70 g (42.4 mmol) 2-bromo-3,4,5-trimethylthiophene (**14**) in 20 ml dry ether, 1.54 g (63.6 mmol) Mg cuttings in 10 ml dry ether and some iodine crystals; coupling of the resulting Grignard reagent with 8.10 g (42.4 mmol) 2-bromo-4,5-dimethylthiophene (**12**) in 50 ml dry ether, 160 mg (0.3 mmol) $NiCl_2$dppp; and purification by column chromatography on silica gel (40–63 μm) with hexane; yield 4.40 g **8**, 44%; colourless crystals, mp 71 °C (MeOH–$CHCl_3$); $\nu$(KBr)/cm$^{-1}$ 2944 (m), 2911 (st), 2851 (m), 1557 (m), 1438 (m) and 829 (st); $\delta_H$($CDCl_3$, TMS, 250 MHz) 6.76 (s, 1H, H3′), 2.36 (s, 6H, $CH_3$-5,5′), 2.24 (s, 3H), 2.15 (s, 3H) and 2.06 (s, 3H, $CH_3$-3,4,4′); $\delta_C$($CDCl_3$, TMS, 62.89 MHz) 134.10, 133.52, 133.27, 132.28, 132.08, 130.71, 128.18, 126.88, 14.16, 13.53, 13.21, 12.91 and 12.72; *m*/*z* 236 ($M^+$, 100%), 221 [$(M - H)^+$, 18], 203 [$(M - SH)^+$, 7], 118 ($M^{2+}$, 9) and 103 [$(M^{2+}) - CH_3$, 6] (Found: C, 65.89; H, 6.68; S, 27.25. $C_{13}H_{16}S_2$ requires C, 66.05; H, 6.82; S, 27.13%).

**3,3′,4,5,5′-Pentamethyl-2,2′-bithiophene (9).** Analogously to the preparation of **2**, compound **9** was prepared by reaction of 11.60 g (56.5 mmol) 2-bromo-3,4,5-trimethylthiophene (**14**) in 20 ml dry ether, 2.00 g (85 mmol) Mg cuttings in 10 ml dry ether and some iodine crystals; coupling of the resulting Grignard reagent 10.80 g (56.5 mmol) 2-bromo-3,5-dimethylthiophene (**13**) in 50 ml dry ether, 160 mg (0.3 mmol) $NiCl_2$dppp; and purification by column chromatography on silica gel (40–63 μm) with hexane, HPLC (reversed-phase, MeOH–water); yield 3.30 g **9**, 25%; colourless crystals, mp 55 °C; $\nu$(KBr)/cm$^{-1}$ 3062 (w), 2970 (w), 2947 (m), 2912 (st), 2851 (m), 1560 (w), 1507 (w), 1445 (st), 1429 (st), 1376 (m), 1253 (w), 1210 (m), 1176 (m), 1131 (m), 1101 (w), 908 (st) and 821 (st); $\delta_H$($CDCl_3$, TMS, 250 MHz) 6.62 (s, 1H, H4′), 2.5 (s, 3H), 2.4 (s, 3H, $CH_3$-5,5′), 2.14 (s, 3H), 2.1 (s, 3H) and 2.06 (s, 3H, $CH_3$-3,3′,4); $\delta_C$($CDCl_3$, TMS, 62.89 MHz) 138.84, 136.29, 135.86, 133.24, 132.33, 128.32, 127.62, 125.09, 15.20, 14.62, 13.99, 13.21 and 12.63; *m*/*z* 236 ($M^+$, 100), 235 [$(M - H)^+$, 18], 221 [$(M - CH_3)^+$, 22], 206 [$(M - 2CH_3)^+$, 5], 203 [$(M - SH)^+$, 5] and 118 ($M^{2+}$, 6) (Found: C, 65.91; H, 6.77; S, 27.32. $C_{13}H_{16}S_2$ requires C, 66.05; H, 6.82; S, 27.13%).

### Chemical oxidation of 8 with $FeCl_3 \cdot 6H_2O$ in acetonitrile

Compound **8** (0.50 g, 2.1 mmol) was dissolved in approximately 40 ml acetonitrile. After bubbling Ar through the solution for 10 min, 2.86 g (10.6 mmol) of powdered $FeCl_3 \cdot 6H_2O$ were added at room temperature, the mixture stirred for 30 min, then 200 ml $CH_2Cl_2$ were added and shaken together with a saturated aqueous solution of $Na_2S_2O_4$; a yellow colour indicated the completion of the reduction. This was then followed by extraction with water (3 × 100 ml), 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 (at first 1:20, later 1:10) was used as an eluent for the product. The given yields are calculated from the true amount of oxidized educt. The remaining material from the educt was converted to undetectable products by unknown side reactions during the oxidation and reduction process. This behaviour was found for all oxidation reactions.

**Product 1: (3′,4,4′,5′-tetramethyl-2,2′-bithiophen-5-yl)-(3′,4,4′,5,5′-pentamethyl-2,2′-bithiophen-3-yl)methane (15).** Yield 130 mg, 31.5%; colourless crystals, mp 165–167 °C (MeOH–$CHCl_3$); $\nu$(KBr)/cm$^{-1}$ 2917 (st), 2853 (st), 1553 (m), 1441 (st), 1372 (m), 1198 (m), 1149 (m), 1002 (m) and 812 (m); $\delta_H$($CDCl_3$, TMS, 250 MHz) 6.72 (s, 1H), 3.92 (s, 2H), 2.38 (s,

3H), 2.36 (s, 3H), 2.34 (s, 3H), 2.2 (s, 3H), 2.12 (s, 3H), 2.08 (s, 9H) and 2 (s, 3H); $\delta_C$($CDCl_3$, TMS, 62.89 MHz) 138.80, 137.38, 137.09, 135.79, 133.98, 133.25, 133.14, 132.84, 132.64, 132.34, 130.49, 127.96, 127.68, 127.20, 127.02, 124.28, 26.79, 14.02, 13.60, 13.29, 13.21, 13.15, 12.80, 12.66, 12.59 and 12.53; *m*/*z* 470 ($M^{\bullet+}$, 100%), 455 [$(M - CH_3)^+$, 12], 248 [$(M - 222)^+$, 61] and 235 ($M^{2+}$, 35) (Found: C, 66.58; H, 6.34; S, 27.51. $C_{26}H_{30}S_4$ requires C, 66.33; H, 6.42; S, 27.25%).

**Product 2: 3,4,4′,5-tetramethyl-2,2′-bithiophene-5′-carbaldehyde (16).** Yield 25 mg, 5.7%; yellow crystals, mp 98–100 °C; *ν*(KBr)/$cm^{-1}$ 2933 (st), 2854 (m), 1631 (st), 1476 (m), 1431 (m), 1351 (m) and 1224 (st); $\delta_H$($CDCl_3$, TMS, 250 MHz) 10 (s, 1H, CHO), 6.94 (s, 1H, H3′), 2.56 (s, 3H, $CH_3$-5), 2.38 (s, 3H), 2.32 (s, 3H) and 2.08 (s, 3H, $CH_3$-3,4,4′); *m*/*z* 250 ($M^{\bullet+}$, 100%), 235 [$(M - CH_3)^+$, 15], 221 [$(M - CHO)^+$, 6], 177 [$(M - CS - CHO)^+$, 4] and 94 ($C_6H_5OH^+$, 11) (Found: C, 62.11; H, 5.39; O, 6.61; S, 25.89. $C_{13}H_{14}OS_2$ requires C, 62.36; H, 5.64; O, 6.39; S, 25.61%).

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## References

1 P. Bäuerle, *Adv. Mater.*, 1992, **4**, 102.
2 D. D. Cunningham, L. Laguren, H. B. Mark, Jr., Ch. van Pham and H. Zimmer, *J. Chem. Soc.*, *Chem. Commun.*, 1987, 1021.
3 M. G. Hill, K. R. Mann and L. L. Miller, *J. Am. Chem. Soc.*, 1992, **114**, 2728.
4 R. E. Atkinson, R. F. Curtis and G. T. Phillips, *J. Chem. Soc.* (*C*), 1967, 2011.
5 A. Wiersema and S. Gronowitz, *Acta Chem. Scand.*, 1970, **24**, 2593.
6 W. A. Herrmann and D. Andrejewski, *Chem. Ber.*, 1986, **119**, 878.
7 M. Kumada, K. Tamao and K. Sumitani, *Org. Synth.*, **58**, 127.
8 J. Heinze, M. Störzbach and J. Mortensen, *Ber. Bunsenges. Phys. Chem.*, 1987, **91**, 960.
9 L. Müller, *Z. Chem.*, 1972, **12**, 209.
10 P. Tschuncky, J. Heinze, G. Engelmann and G. Koßmehl, in preparation.
11 M. L. Olmstead, R. G. Hamilton and R. S. Nicholson, *Anal. Chem.*, 1969, **41**, 260.
12 D. Zobel, unpublished work. X-Ray structure; data deposited at the Karlsruhe Information Centre, 28th August 1997; E-Mail: crysdata@fiz; csd-number: 407565.
13 W. H. Hartford and M. Darvin, *Chem. Rev.*, 1958, **58**, 1.
14 G. Engelmann, PhD thesis, Humboldt-Universität zu Berlin, 1995.
15 K. Nyberg, *Acta Chem. Scand.*, 1971, **25**, 2499.
16 A. Alberti, L. Favaretto and G. Seconi, *J. Chem. Soc.*, *Perkin Trans. 2*, 1990, 931.
17 K. B. Prater and A. J. Bard, *J. Electrochem. Soc.*, 1970, **117**, 335.

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