Design and synthesis of -conjugated molecules
Pouwer, Kornelis Lammert

IMPORTANT NOTE: You are advised to consult the publisher’s version (publisher’s PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
1995

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

Copyright
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

Take-down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.
Chapter three

Synthesis of well-defined oligomers and polymers containing thiophene, phenylene and pyrrole moieties using the Stetter reaction.

3.1 Introduction

Oligomers can be used to assess conformational and optical features of \( \pi \)-conjugated polymers. Additionally, they can serve as monomers. To be useful models, oligomers must be structurally well-defined and consequently, unambiguous reactions are required for their synthesis. For the synthesis of a-thiophene oligomers a number of methods have been developed\(^1\). These methods can be divided into two groups namely, the direct coupling of thiophene rings and the ring closure reactions of appropriate precursor compounds. Many different reaction conditions are used for the first approach of direct coupling including the \text{Ullmann} coupling of iodothiophenes with copper\(^2\), the cross-coupling reaction of a dihalocompound with organometallics like magnesium, zinc or tin with a palladium or nickel catalyst\(^3\), the \text{copper(II)}chloride oxidation of lithium derivatives\(^4\) and the iodine oxidation of di-(2-thienyl) boranes\(^5\). In the second approach thiophenes have been synthesized by the ring closure reaction of diacetylenes with hydrogen sulfide\(^6\) and diketosulfides with Lawesson's reagent\(^7\), in which case small amounts of the \( \beta \)-isomer are obtained as

scheme 3.1 Thiophene synthesis by the ring-closure reaction of 1,4-diketones

\(^{1}\) For a review see: Nakayama, J.; Konishi, T.; Hoshino, M. \textit{Heterocycles} 1988, 27, 1731
\(^7\) Nakayama, I.; Nakamura, Y.; Murabayashi, S.; Hoshino, M. \textit{Heterocycles} 1987, 26, 939
well. Furthermore, thiophenes have been synthesized by the cyclization reaction of 1,4-diketones with hydrogen sulfide, \( P_2S_5 \), or Lawesson’s reagent. The 1,4-diketones in turn have been prepared by the Friedel-Crafts reaction of thiophene with succinoyl chloride, oxidative dimerization of acetyl aryl compounds either as the lithium anions with copper(II) chloride or as the silyl-enol ethers with silver oxide and through the Michael addition of cyanohydrin anions to unsaturated carbonyl compounds. The latter approach is known as the Stetter reaction (scheme 3.2). The Stetter reaction was actually observed by Smith as early as 1890.

\[ \text{scheme 3.2 The Stetter reaction} \]

The successful synthesis in our laboratories of \( \alpha \)-terthienyl and, more recently, of substituted oligomers of thiophene, prompted us to investigate in detail the scope and limitations of the procedure, in which the Stetter reaction is used in combination with the subsequent ring closure reactions of the 1,4-diketones with Lawesson’s reagent.

### 3.1.1 The mechanism of the Stetter reaction

The Stetter reaction is based on the Michael addition of a cyanohydrin to an \( \alpha,\beta \)-unsaturated carbonyl compound, to give a 1,4-diketone (scheme 3.2). The catalyst is either a cyanide ion or an ylide. The latter is made in situ by the deprotonation of a thiazolium salt, which shows catalytic features similar to the cyanide ion (figure 3.1). The mechanism of the Stetter reaction is outlined in scheme 3.3. Addition of the catalyst to the aldehyde yields the cyanohydrin anion (the donor, 3.2),

\[ \text{figure 3.1} \]

---

10 Scheeren, J. W.; Oomes, P. H. J.; Nivard, R. J. F. *Synthesis* 1973, 149  
13 Merz, A.; Ellinger, F. *Synthesis* 1991, 462  
which in turn can add to the \( \alpha,\beta\)-unsaturated carbonyl moiety (the acceptor, 3.4), affording the 1,4-diketone 3.5 (eq. b). However, the donor can also add to a second aldehyde molecule to form the \( \alpha \)-hydroxy ketone 3.3 (benzoin), in what is known as the benzoin condensation (eq. a). Since the benzoin condensation is reversible and the Michael addition of the cyanohydrin to the \( \alpha,\beta\)-unsaturated carbonyl moiety is irreversible under the reaction conditions employed, the reaction is driven to completion via the 1,4-addition path (eq b).

\[
\begin{align*}
\text{ArCHO} & \overset{\text{CN}}{\rightleftharpoons} \text{ArCN} & \text{CN} & \overset{\text{OH}}{\rightleftharpoons} \text{ArCN} \\
3.2 & & & \\
\text{ArOH} & \overset{\text{CN}}{\rightleftharpoons} \text{ArCN} & \overset{\text{OH}}{\rightleftharpoons} \text{ArCN} \\
3.3 & & & \\
\text{Ar} & \overset{\text{3.2}}{\rightleftharpoons} \text{ArCN} & \overset{\text{CN}}{\rightleftharpoons} \text{ArCN} & \overset{\text{OH}}{\rightleftharpoons} \text{ArCN} \\
3.4 & & & \\
\text{ArCN} & \overset{\text{CN}}{\rightleftharpoons} \text{ArCN} & \overset{\text{OH}}{\rightleftharpoons} \text{ArCN} \\
3.5 & & & \\
\end{align*}
\]

**Scheme 3.3 The mechanism of the Stetter reaction**

The reaction is fairly general, but some limitations have been established with respect to the substitution pattern of the different aromatic rings when \( \text{NaCN} \) is employed as the catalyst\(^{18} \). Aryl aldehydes may bear neutral or electron withdrawing groups, but electron donating substituents hamper the Stetter reaction. The reactivity of the Michael acceptor seems not to be influenced by the nature of the substituents. Substituents that may be employed as solubilizing side-chains in the target oligomers, therefore, can be introduced in the aromatic moiety of the donor, unless the side-chain is electron donating, or at the aromatic moiety of the acceptor. Alternatively, solubilizing functionalities can be attached to the aliphatic moiety of the acceptor. In this case the side-chain has an influence on the reactivity of the acceptor. The \( \alpha,\beta\)-unsaturated ketones used in the Stetter reaction

can be prepared independently or in-situ during the reaction. A variety of precursors and modified \( \alpha,\beta \)-unsaturated ketones have been used\(^{16} \). The different types of Michael acceptors and their syntheses are outlined in schemes 3.4 to 3.8 below.

The Mannich base is readily synthesized from the aryl methyl ketones \((R=H)\) by reaction with formaldehyde and an amine, usually dimethylamine. Conversion into the diketone proceeds via the elimination of the amine and subsequent addition of the cyano-hydrin to the generated \( \alpha,\beta \)-unsaturated ketone (scheme 3.4). When propionyl aryl compounds are used, substituted diketones are obtained \((R=CH_3)\).

- Unsaturated esters can be prepared by the esterification of the corresponding acids. Since these compounds contain two electron withdrawing groups there are, theoreti-
cally, two different 1,4-additions possible, but the aromatic ketone moiety is the more activating one, and consequently only 1,4-addition relative to the ketone occurs. This affords the carboxylate ester substituted diketones (scheme 3.7). α,β-Unsaturated esters are very reactive and this may cause problems with respect to storage and side reactions. These difficulties can be circumvented by the use of β-bromo esters as precursor compounds.

![Scheme 3.7](image)

**scheme 3.7**

- Chalcones are readily synthesized by the condensation of aryl methyl ketones with aryl aldehydes. Chalcones are activated enones and give the aryl substituted diketones in good yields (scheme 3.8). Substituents can be introduced on the aryl groups.

![Scheme 3.8](image)

**scheme 3.8**

Cyclization of 1,4-diketones affords furans, pyrroles and thiophenes. Furans are made by the acid catalyzed ring closure\(^9\), and thiophenes are obtained upon ring closure with \(\text{P}_2\text{S}_5\) or Lawesson’s reagent\(^{12}\). Unsubstituted as well as N-substituted pyrroles are

![Scheme 3.9](image)

**scheme 3.9**
formed upon the reaction of a 1,4-diketone with ammonia, ammonium carbonate, or ammonium acetate and primary amines, respectively (scheme 3.9).

In this chapter we will describe the use of the Stetter reaction in the synthesis of a number of well-defined oligomers containing different aromatic rings. The scope and limitations for the synthesis of polymers using the Stetter reaction are discussed.

3.2 Oligomers

The Stetter reaction is a powerful method for the synthesis of a large variety of 1,4-diketones, both substituted and unsubstituted. Ring closure of the 1,4-diketones affords, for example, thiophenes. The combination of these two methods provides an attractive method for the synthesis of a diversity of well-defined aromatic oligomers. This approach allows the selective introduction of different kinds of substituents and a large variety of aromatic rings. In this section we will give examples of the synthesis of well-defined oligomers, containing different substituents and aromatic rings and we will determine the scope and limitations of the various Michael acceptors and donors. Solubilizing side chains are introduced either in the aldehyde functionality or in the double bond moiety of the Michael acceptor, or its precursor.

3.2.1 Synthesis

A first example of a well-defined oligomer synthesis is outlined in scheme 3.10. The synthesis of 3’-dodecyl-5,5’’’-diphenyl-[2,2';5',2';5',2''';5''',2''''''']quinquethiophene (3.14) is based on a combination of the Stetter reaction and subsequent cyclization with Lawesson’s reagent (LR) to afford the thiophene ring. Introduction of the dodecyl side chain was accomplished by alkylation of the diketone 3.8, which after ring closure with Lawesson's reagent afforded the dodecyl substituted terthienyl 3.11. The introduction of the side chain via the alkylation is effective when applied to symmetrical diketones but is not very feasible when tetraketones are used since the alkylation does not discriminate between the two methylene groups of the 1,4-diketone moiety. Alkylation of tetraketones, therefore, will afford a mixture of regioisomers. Consequently, the synthesis of tetraketones requires substituents attached to the dialdehyde. Thus, 1,4-di-thiophen-2-yl-butan-1,4-dione (3.8) was synthesized in 77% yield by the reaction of thiophene-2-carbaldehyde (3.6) and 3-dimethylamino-1-thiophen-2-yl-propan-1-one (3.7) with

NaCN as catalyst at room temperature. Alkylation with n-dodecylbromide, subsequent hydrolysis of enol ether and ring closure of diketone with Lawesson's reagent afforded 3'-dodecyl-[2,2';5',2'']-terthiienyl in 20% overall yield. Formylation of under Vilsmeier-Haack conditions afforded dialdehyde in 51% yield. 3'-Dodecyl-[2,2';5',2'']-terthiienyl-5,5'-dicarbaldehyde was allowed to react with 3-dimethylamino-1-phenyl-propan-1-one and NaCN as catalyst and the resulting tetraketone was ring closed with Lawesson's reagent (LR). This afforded 3''-dodecyl-5,5''''-diphenyl-[2,2';5',2''';5'',2''';5'''';2''''']-quinquethiophene as a soluble red solid in 51% yield. The absorption maximum, recorded in CHCl₃, was found at 429 nm.

Clearly, the Stetter reaction has proceeded well, using Mannich bases as precursors for the Michael acceptors. Dialdehyde , however, has not provided much

---

1. NaCN, DMF, toluene.
2. LR, toluene.
3. DMF.
4. POC₃, DMF.
5. HCl, H₂O.
6. Acetone.
7. NaCN, DMF.
information about the influence of substituents on the reactivity of aldehydes in the Stetter reaction, because the three substituents (two formyl groups and a n-dodecyl group) are located on different rings. To get a better insight in the influence of the substituents both the side chain and the aldehyde functionalities must be connected to the same ring. A dialdehyde of this type (3.16) has been used for the synthesis of 3'''-dodecyl-[2,2',5',2''',5''',2''',5''',2''''']-quinquethienyl (3.19). The complete reaction sequence is outlined in scheme 3.11. 3-Dodecylthiophene (3.15) was transformed to the 2,5-dialdehyde 3.16 in 86% yield by quenching the bis-anion with DMF in analogy to the literature procedure for the unsubstituted thiophene. Reaction with 4-oxo-4-thiophen-2-yl-but-2-enoic acid (3.17) and catalyst 3.1 afforded tetraketone 3.18 in 44% yield. 5-(2-Hydroxyethyl)-3,4-dimethyl-1,3-thiazoliumiodide (3.1) was used as catalyst since cyanide ions cannot be used when unsaturated acids are employed as Michael acceptor. Ring-closure of the tetraketone with Lawesson's reagent afforded 3'''-dodecyl-[2,2',5',2''',5''',2''',5''',2''''']-quinquethienyl (3.19) as an orange solid with a $\lambda_{\text{max}}$ of 407.5 nm, recorded in CHCl$_3$, in a yield of 62%. Although the dodecyl functionality is slightly electron donating, the reactiv-

![Scheme 3.11](image)

ety of dialdehyde 3.16 is not much lower than that of dialdehyde 3.12. The lower overall yield of 3.19 compared to that of 3.14 (51% and 27% respectively) is mainly due to isolation and purification of tetraketone 3.18. To investigate the influence of strongly electron donating substituents, 2,5-bis-hexyloxy-terephthaldehyde (3.23) was synthesized and subjected to the Stetter reaction. Since the Stetter reaction of aldehydes with electron donating substituents fails when cyanide ions are used, thiazolium salt 3.1 is the obvious choice of catalyst. Thus, 1,4-bis-hexyloxy-benzene (3.21) was synthesized by alkylation.

---

hydroquinone (3.20) with hexyl bromide and the dibromide 3.22 was obtained in 76% yield by the action of bromine in acetic acid\textsuperscript{26}. Lithiation by bromine-lithium exchange with n-butyl lithium and quenching of the anion with DMF gave 2,5-bis-hexyloxyterephthaldehyde (3.23) in 63% yield (scheme 3.12). Dialdehyde 3.23 was subjected to the Stetter reaction with $\alpha,\beta$-unsaturated acid 3.17 and catalyst 3.1 and afforded 1,4-bis-(4-oxo-4-thiophen-2-yl-butyryl)-2,5-bis-hexyloxy-benzene (3.24) in a yield of 61%. Apparently, electron donating substituents do not hamper the Stetter reaction when catalyst 3.1 is used. Tetraketone 3.24 was converted to 1,4-bis-(5-(2,2'-bithiophen-5-yl)-2,5-bis-hexyloxy-benzene (3.25) in 86% yield by ring closure with Lawesson's reagent (scheme 3.13). Ring-closure with ammonium acetate afforded 1,4-bis-(5-thiophen-2-yl-[1H]-pyrrol-2-yl)-2,5-bis-hexyloxy-benzene (3.26) in a yield of 75% (scheme 3.13). Both

\begin{equation}
3.17 + 3.23 \xrightarrow{\text{cat 3.1}} 3.24
\end{equation}

\begin{equation}
3.25 \xrightarrow{\text{LR, toluene}} 3.26
\end{equation}

\textit{scheme 3.13}

compounds had an orange color with absorption maxima (recorded in CHCl₃) at 404.4 and 405.1 nm, respectively. The introduction of the pyrrole moiety increases the sensitivity of the compound toward oxidation as seen by the appearance of a second absorption signal in the UV spectrum at 550 nm upon exposure to air.

A variety of substituted aldehydes have been used in the Stetter reaction, resulting in soluble oligomers, after cyclization of the resulting diketones. A different approach to obtain soluble oligomers is the use of substituted Michael acceptors in the Stetter reaction. Substituents can be attached either to the aromatic ring or to the double bond, or its precursor, of the Michael acceptor. We will describe the use of the latter option. For this approach, it is not possible to use all Michael acceptors described in schemes 3.4 to 3.8, since the selective introduction of a substituent in the unsaturated acid moiety is far from trivial. Unsaturated keto-esters (see scheme 3.7) affords oligomers with the ester group as solubilizing functionality. To overcome problems with respect to storage of the unsaturated keto-esters, we used D-bromo esters as precursor compounds. These are easily converted to the unsaturated esters by the elimination of hydrogen bromide under the basic reaction conditions employed in the Stetter reaction with the thiazolium salt 3.1 as catalyst. Thiophene was acylated with 3-chlorocarbonyl-propionic acid dodecyl ester (3.28), synthesized in two steps from succinic anhydride (3.27) in 74% yield and the resulting keto ester 3.29 was treated with bromine²⁷ to give 3-Bromo-4-0x0-4-thiophen-2-yl-butyric acid dodecyl ester (3.30) in 83% yield (scheme 3.14). Bromide 3.30 was brought into reaction

![scheme 3.14](image)

with 2-thiophene aldehyde (3.6), catalyst 3.1 (10 mol %) and triethylamine (3 equivalents). The resulting diketone was ring-closed with Lawesson's reagent affording [2,2',5',2'']-terthiophene-4'-carboxylic acid dodecyl ester (3.31) in 43% yield (based on 3.30) as an oil that rapidly became colored (scheme 3.15). The reaction of [2,2']-bithienyl-5,5'-

---

dicarbaldehyde (3.32, synthesized according to a literature procedure\textsuperscript{29}) with ester 3.30 under the same reaction conditions as described in scheme 3.15 afforded tetraketone 3.33 in 88%. 'H-NMR revealed that the all-keto isomer 3.33 was the only isomer present. Upon ring closure with Lawesson's reagent, [2,2';5',2'';5''',2'''',2''',5''''',2'''''',5'''',2'''''']-sexithio-

\begin{align*}
\text{scheme 3.15}
\end{align*}

\begin{align*}
\text{dicarbaldehyde} (3.32, \text{synthesized according to a literature procedure}^{29}) \text{ with ester 3.30 under the same reaction conditions as described in scheme 3.15 afforded tetraketone 3.33 in 88\%. 'H-NMR revealed that the all-keto isomer 3.33 was the only isomer present. Upon ring closure with Lawesson's reagent, [2,2';5',2'';5''',2'''',5'''',2'''''',5'''',2'''''']-sexithio-}
\end{align*}

\begin{align*}
\text{scheme 3.16}
\end{align*}

\begin{align*}
\text{unsaturated keto ester arising from the retro-Michael reaction}^{31}. \text{Compound 3.34 showed an increase in solubility relative to unsubstituted thiophene oligomers in common organic solvents (for a comparison; $\alpha$-sexithieryl is insoluble in ether$^{4a}$, while $\alpha$-quinquethieryl is insoluble in hexane$^{2b}$. Compound 3.34 on the other hand is soluble in ether and can be recrystallized from hexane) In CHCl}_3, \text{the red microcrystalline compound 3.34 had an absorption maximum of 434.4 nm.}
\end{align*}

Since the ester substituent attached to the double bond of the Michael acceptor has proven to be very effective for the Stetter reaction, other Michael acceptors with

\text{References}
\text{\textsuperscript{29} Curtis, R. F.; Phillips, G. T. \textit{Tetrahedron} 1967, 23, 4419}
\text{\textsuperscript{30} March, J. \textit{"Advanced Organic Chemistry"}, 3\textsuperscript{rd} ed., John Wiley and Sons, Inc., 1985, p 918}
substituents attached to the double bond, or its precursor, were examined as well. Chalcones have frequently been used in the Stetter reaction$^3$. However, when unsubstituted chalcones are used (see scheme 3.8, Ar$'=$ phenyl), the only side group incorporated in the resulting oligomer, after cyclization of the diketone, is the phenyl ring, and the solubilizing effect of the phenyl ring is limited. Therefore, we have introduced an alkoxy functionality in the chalcone. The synthesis of the substituted chalcone 3.38 is outlined in scheme 3.17. p-Hydroxybenzaldehyde (3.35) was alkylated with n-hexyl bromide to give 3.36 in 72 % yield. Condensation of 3.36 with 1,4-diacyltbenzene (3.37) afforded chalcone 3.38 in 45% yield. Notwithstanding the presence of the substituents the solubility of 1,4-bis-[3-(4-hexyloxy-phenyl)-acryloyl]-benzene (3.38) was limited (<10 mg/ml in DMF at 25°C). This low solubility probably arises from the fact that the alkoxy functionalities are end groups of the $\pi$-system and not side chains. It is known$^{32}$ for oligothiophenes that end groups are almost ineffective as solubilizing functionalities. Due to this limited solubility it was not possible to add a solution of the chalcone to a mixture of an aldehyde and NaCN. Slow addition was anticipated to prevent the addition of the cyanide ion to the chalcone$^{33}$. We employed catalyst 3.1. Thus, benzaldehyde (3.39) and chalcone 3.38 were allowed to react at 80°C for four days affording tetraketone 3.40 in 8%. Ring-closure with ammonium acetate afforded 2,5-Bis-[4-(4-hexyloxy-phenyl)-5-phenyl-1H-pyrrol-2-y]-benzene (3.41) in 50% (scheme 3.18). Although oligomer 3.41 is far more soluble (>50 mg/ml in CHCl$_3$ at 25°C) than compound 3.38, the low yield of tetraketone 3.40 strongly limits the applicability of chalcon 3.38 in the Stetter reaction. For the introduction of a methyl substituent in the Michael acceptor, the substituted Mannich base was used, synthesized as depicted in scheme 3.19. 1,4-Bis-propionyl benzene (3.43) was synthesized by the reaction of terephthaldehyde (3.42) with ethyl magnesiumiodide and subsequent oxidation of the alcohol in 38% yield. Condensation with

\[ \text{scheme 3.17} \]

\[ \text{3.35} \rightarrow \text{3.36} \rightarrow \text{3.38} \]
dimethylamine and formaldehyde afforded the bis-Mannich base 3.44 in 28% yield. However, the corresponding tetraketone could not be isolated from the reaction of 3.44 with benzaldehyde, the only isolated compound was the elimination product 3.45. The electron donating methyl group reduces the reactivity of the Michael acceptor considerably.

\[ \text{scheme 3.18} \]

\[ \text{CHO} \quad \text{1) } \text{EtMgI} \quad \text{2) } \text{Na}_2\text{Cr}_2\text{O}_7 \quad \text{H}_2\text{SO}_4 \quad \text{Me}_2\text{N} \quad \text{H}_2\text{O} \]

\[ \text{3.42} \quad \text{3.43} \quad \text{3.44} \quad \text{3.45} \]

\[ \text{scheme 3.19} \]
3.2.2 Absorption spectroscopy

To obtain information about the influence of the substituents on the effective conjugation length of the oligomers, we have determined the $\lambda_{\text{max}}$ values and compared these data to the $\lambda_{\text{max}}$ of unsubstituted oligothiophenes consisting of an equal number of rings. The data are summarized in table 3.1. Oligomer 3.14, consisting of five thiophene rings and two phenyl end-groups displays a $\Delta\lambda$ of 429 nm, whereas for unsubstituted septithienyl the $\lambda_{\text{max}}$ is found at 440 nm. The oligomers with five rings; 3.19, 3.25 and 3.26 have $\lambda_{\text{max}}$ of 407.5 nm, 404.4 nm and 405.1 nm, respectively. Unsubstituted quinquethienyl has a $\lambda_{\text{max}}$ of 416 nm. Alkyl substituents have a considerable influence, although there is only one substituent present in oligomer 3.14 and 3.25, the hypsochromic shift is 11 and 8.5 nm, respectively. The positioning of the alkyl group, dividing the compounds into two parts probably accounts for the significant decrease. Oligomer 3.14 displays an extra blue shift as a result of the phenyl groups. Electron donating substituents cause a red shift, and the hexyloxy-substituted benzene ring in compound 3.25 has an influence similar to that of a thiophene ring; the $\lambda_{\text{max}}$ of the five-ring oligomers are almost the same. However, the ester substituents in oligomer 3.34 have no negative influence on the conjugation length. A comparison with the unsubstituted and the didodecyl substituted sexthiienyl derivatives shows this clearly. Oligomer 3.34 has a $\lambda_{\text{max}}$ of 434.4 nm, whereas

<table>
<thead>
<tr>
<th>compound</th>
<th>number of rings (n)</th>
<th>(\lambda) (CHCl(_3)) (nm)</th>
<th>(n)</th>
<th>(\lambda) (CHCl(_3)) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.14</td>
<td>7</td>
<td>429</td>
<td>7</td>
<td>440(^a) (in benzene)</td>
</tr>
<tr>
<td>3.19</td>
<td>5</td>
<td>407.5</td>
<td>5</td>
<td>416(^a)</td>
</tr>
<tr>
<td>3.25</td>
<td>5</td>
<td>404.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.26</td>
<td>5</td>
<td>405.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.34</td>
<td>6</td>
<td>434.4</td>
<td>6</td>
<td>432(^b)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>416(^c)</td>
</tr>
</tbody>
</table>

\(^a\) see ref 1, \(^b\) Bäuerle, P.; Segelbacher, U.; Gaudl, K.-U.; Huttenlocher, D.; Mehring, M. Angew. Chem., Int. Ed. Engl. 1993, 32, 76. \(^c\) \(\lambda_{\text{max}}\) of 3\(^{\text{iv}}\),4\(^{\text{iv}}\)-didodecyl-\(\alpha\)-sexithienyl.

a-sexithienyl has a $\lambda_{\text{max}}$ of 432 nm. Didodecyl-a-sexithienyl on the other hand displays a

maximum absorption value of 416 nm.

3.2.3 Discussion

Ester groups form a new class of solubilizing moieties, when attached directly to the aromatic backbone of thiophene oligomers as in compound 3.34, and can be readily introduced using unsaturated keto-ester precursor 3.30 in the Stetter reaction. High yields of ketone 3.33 are obtained, with complete regioregularity of the ester groups. Synthesis of the unsaturated keto-esters can be accomplished by the esterification of the acids, but the bromide precursor has a higher stability, and therefore is easier to handle and purify. Elimination of hydrogen bromide from bromide 3.30 is carried out in situ by triethylamine, already present in the reaction mixture for the generation of the catalyst from thiazoliurn salt 3.1. Ring closure of tetraketone 3.33 with Lawesson's reagent affords thiophene oligomer 3.34, but only in a yield of 34%. This moderate yield arises from the fact that probably due to the elevated temperature of the cyclization reaction, retro Michael reactions occur\textsuperscript{30}. The ester functionality of 3.34 has an excellent solubilizing effect but does not reduce the conjugation length as is seen for the alkyl substituted thiophene oligomers. Two examples of substituted oligothiophenes with an $\lambda_{max}$ surpassing that of the unsubstituted parent compounds have been described\textsuperscript{32,35}, but in these instances the alkyl substituents are attached at the a-positions of the exterior thiophene rings, therefore are end groups, and do not increase the solubility. For the surprisingly high $\lambda_{max}$ of compound 3.34, the explanation must be found in the geometry of the ester functionalities. The ester functionality is planar and therefore can have a perpendicular orientation with respect to the thiophene ring, with minimal interaction. Consequently, the thiophene rings in 3.34 can maintain a co-planar orientation with maximal conjugation. For an alkyl substituent in for example compound 3.19, there remains considerable interaction between two protons and the thiophene rings in the perpendicular orientation, because of the $sp^3$-configuration of the methylene group, resulting in the observed decrease of the $\lambda_{max}$ relative to the unsubstituted analog. Alternatively, the high $\lambda_{max}$ of compound 3.34 can be explained in terms of an active interaction between the ester functionality and the thiophene ring, particularly between the lone-pairs of the carbonyl group and the empty d-orbitals of sulfur at the adjacent thiophene ring. This interaction, a kind of back-donation, forces the two adjacent thiophene rings into co-planarity. This geometry, however, the

ester group is in conjugation with the thiophene backbone. Since ester groups are electron withdrawing, this would result in a blue shift of the $\lambda_{\text{max}}$ of compound 3.34. The observed $\lambda_{\text{max}}$, however, does not display a blue shift, and therefore the gain in conjugation by the forced coplanarity compensates for the blue shift induced by the electron withdrawing ability of the ester functionality. The first explanation, with the ester group perpendicular relative to the thiophene rings, the ester group is not in conjugation with the thiophene backbone, and the only effect is the gain in coplanarity of the thiophene rings, making this the most plausible explication for the high $\lambda_{\text{max}}$ of compound 3.34.

The introduction of substituents in chalcone 3.38 is accomplished using substituted benzaldehyde 3.36. The solubility of 3.38, however, is limited because the solubilizing functionalities are end groups. This low solubility prevents the use of NaCN as catalyst, since the cyanide can add 1,4 to chalcone 3.38. The low yield of tetraketone 3.40 obtained by the thiazolium ylide catalyzed reaction of 3.38 with benzaldehyde arises from the fact that the thiazolium derived 'cyanohydrin' is less reactive than its cyanide counterpart. This difference in reactivity stems from the fact that the thiazolium derived 'cyanohydrins' are ylides and therefore are intramolecularly stabilized, whereas the cyanide cyanohydrin species are salts. Furthermore, chalcone 3.38 has an alkoxy substituent at the para position of the phenyl group. The alkoxy group is electron donating and therefore reduces the electron withdrawing ability of the phenyl group attached to the double bond. Consequently, 3.38 is less reactive in the Michael reaction. A similar decrease in reactivity is observed for substituted Mannich base 3.34 where the electron donating methyl group is attached adjacent to the amine functionality. However, in this instance the reduction of reactivity of 3.34 as Michael acceptor is so drastic that the cyanide catalyzed addition of benzaldehyde is not found at all.

For the synthesis of 1,4-diketones, using the Stetter reaction, both the unsubstituted Mannich bases 3.7 and 3.13 and unsaturated acid 3.17 have proven to be good Michael acceptors that afford the diketones in high yields. An advantage is the one step synthesis of acid 3.17 compared with the three steps required for the preparation of the free Mannich bases. A combination of two factors is responsible for the successful use of dialdehydes 3.16 and 3.23, containing electron donating substituents. The first reason is that the aldehydes contains two formyl groups, so the electron donating effect of the electron donating substituents is, at least partly, neutralized by the second aldehyde functionality. On the other hand, the cyanide catalyzed reaction of the hexyloxy substituted aldehyde 3.23 with Mannich base 3.13 fails, so this is not the only reason. Secondly, the unsaturated acid 3.17 is a better Michael acceptor than the Mannich bases 3.7 and 3.13.
Ring-closure with Lawesson's reagent gives high yields of the corresponding thiophenes, except for the ester substituted diketones. Pyrroles have been obtained in good yields upon ring closure with ammonium acetate. These compounds are, as could be expected, more sensitive toward oxidation than their thiophene counterparts. From UV analysis it is clear that alkyl substituents have a negative effect on the effective conjugation length. This blue shift arises from the steric hindrance between the substituent and the adjacent thiophene ring. With the introduction of phenyl rings, the $\lambda_{\text{max}}$ is shifted further to the blue region, but alkoxy substituents compensate for this effect. This relative red shift arises from the electron donating capacity of the alkoxy groups, but also because alkoxygroups are sterically smaller compared to alkyl functionalities. All these compounds on the other hand are far more soluble than their unsubstituted counterparts. These results show that substitution of aromatic compounds by alkyl groups is not favorable for the highest possible conjugation length, but the increase in solubility compensates for the decrease in conjugation.

3.3 Polymers

The combination of the Stetter reaction and subsequent cyclization of the 1,4-diketones as for example in scheme 3.11 has proven very effective for the synthesis of well-defined oligomers, containing a variety of substituents and aromatic rings. We therefore decided to investigate the use of this method for the preparation of $\pi$-conjugated polymers. For the synthesis of 1,4-diketone polymers, using the Stetter reaction, there are two different approaches. The first is the use of two monomers, one containing two donor moieties and the other two acceptor moieties; an AA-BB-polymerization. Secondly, monomers containing both an acceptor and a donor functionality, can be polymerized in an A-B-polymerization. Both approaches have been investigated and the results are given below.

3.3.1 AA-BB-Polymerization

For the synthesis of poly-1,4-diketones using the Stetter reaction in an AA-BB-polymerization, both dialdehydes as well as bis-Michael acceptors are required. The synthesis of several dialdehydes has been described in the previous section. Thiophene-2,5-dicarbaldehyde (3.46) was synthesized in 71% yield according to a literature procedure (scheme 3.20). Although several Michael acceptors have proven useful for the synthesis of

---

oligomers, not all of them are suitable as monomers since for synthesis of a polymer high conversions of the reactions are required. Obvious reasons are the low reactivity of chalcones and substituted Mannich bases, but also the expected insolubility of bis-unsaturated acids. Although the corresponding 1,4-diketones have been obtained in high yields, carboxylic esters are not suitable because in the cyclization reaction moderate yields have been obtained. Therefore, we have decided to use the Mannich base as precursor for the Michael acceptor. The synthesis of several bis-Mannich bases is outlined in schemes 3.21 to 3.23 below. The bis-Mannich base 3.48 of 1,4-diacetylbenzene (3.37) can be synthesized using the standard method with paraformaldehyde, dimethylamine hydrochloride and hydrochloric acid in ethanol. Higher yields, up to 84%, were obtained when dimethyl(methylene)ammonium chloride (3.47) was used (scheme 3.21). Although 2,5-

\[
\text{scheme 3.20}
\]

\[
\text{scheme 3.21}
\]

\[
\text{scheme 3.22}
\]

---

38 Tramontini, M. Synthesis 1973, 703
diacetyltiophene (3.52) was readily synthesized in two steps from chloroacetone (3.49), sodium sulfide and glyoxal (3.50) in 20% overall yield as outlined in scheme 3.2240, the synthesis of the bis-Mannich base 3.53 was troublesome. From the reaction with dimethylamine and formaldehyde or dimethyl(dimethylene)ammonium chloride the product was isolated with a purity of approximately 85 to 90%. We were not able to increase the purity by crystallization, due to the amorphous nature of 3.53. Therefore, the bithienyl derivative was synthesized as depicted in scheme 3.23. [2,2’]-Bithienyl (3.54) was synthesized by the CuCl₂ oxidation of the anion derived from thiophene and n-BuLi according to a modified literature procedure4 and acylated in analogy with a literature procedure41 with acetic anhydride and phosphoric acid affording 5,5'-diacetyl-[2,2’]-bithienyl (3.55) in 28% yield. The bis-Mannich base 3.56 was obtained upon the acid catalyzed condensation of 3.55 with dimethylamine and para-formaldehyde in DMF as solvent. In this case the product could be isolated with high purity.

\[
\begin{align*}
\text{HNMe}_2\cdot\text{HCl} & \quad \text{H}_2\text{CO}, \text{HCl, DMF} \\
\text{Me}_2\text{N} & \quad \text{DMF}
\end{align*}
\]

scheme 3.23

Since alkyl groups attached to the aliphatic moiety of the Mannich base, as in compound 3.44 drastically reduces the reactivity in the Stetter reaction, solubilizing side chains have to be attached to the aromatic rings. Synthesis of the dodecyl substituted thiophene bis-Mannich base is outlined in scheme 3.24. The diacetyl compound was synthesized by the acylation of the cuprate42 since the introduction of two acyl groups via Friedel-Craft acylation is ineffective43. 3-Dodecylthiophene (3.15) was brominated afford-
ing the dibromide 3.57 in 91%. The dibromide 3.57 was converted to the cuprate and quenched with acetyl chloride affording 2,5-diacetyl-3-dodecylthiophene (3.58) in 63% yield (scheme 3.24). Subsequent condensation with dimethylamine and paraformaldehyde afforded the bis-Mannich base 3.59 as the hydrochloride salt. However, the stability of the product was very low; within a few hours, the yellow solid completely lost its initial solubility in water. Therefore, other substituted thiophene derivatives were used. The bis-Mannich bases of 3'-dodecyl-[2,2']-bithienyl (3.60) and 3''-dodecyl-[2,2',5',2'']-terthienyl (3.11) were synthesized as outlined in scheme 3.25 and 3.26, respectively. The diacetyl derivatives 3.61 and 3.63 were prepared by the acylation with acetic anhydride in 54% and 35% yield, respectively, and were transformed into the bis-Mannich bases 3.62 and 3.64 with dimethylamine and paraformaldehyde and were obtained as the hydrochloride salts in yields of 40% and 70%, respectively. Of the last two compounds, bithienyl derivative 3.62 suffered from identical problems as the thiophene analog, although the stability was
higher. Consequently, only the terthienyl derivative 3.64, obtained in a yield of 70%, could be used in the polymerization reaction.

\[
\text{HNMe}_2 \cdot \text{HCl} \quad \overset{\text{H}_2 \text{CO}, \text{HCl}, \text{DMF}}{\longrightarrow} \quad \text{Me}_2\text{N} \cdot (2 \cdot \text{HCl})
\]

scheme 3.26

Polymerization (scheme 3.27 and table 3.2) was carried out by dissolving equimolar amounts of both an aldehyde (3.42, 3.46, 3.12, or 3.16) and a free Mannich base (obtained from the hydrochloric acid salt (3.48, 3.56 or 3.64) upon treatment with ammonia and extraction of the amine with CH\(_2\)Cl\(_2\)) in DMF in a nitrogen atmosphere. Upon addition of ten to twenty mol percent sodium cyanide, the solution turned dark as a result of cyanohydrin formation. The reaction mixture was stirred at room temperature for a few days. During the reaction, the mixtures became viscous and all the products of table 3.2, except poly-1,4-diketone 3.75, precipitated. The reaction was terminated by pouring the mixture into water and the resulting solid was collected, washed with water, ethanol and dried. All compounds were insoluble in organic solvents except the last entry; poly-1,4-diketone 3.75 prepared from 3-dodecylthiophene-2,5-dicarbaldehyde (3.16). The insolubility of poly-14-diketone 3.72 can be explained in terms of the ratio alkyl side chain versus aromatic rings. With respect to solubility, the 1,4-diketone moiety is comparable with the thiophene ring, and polyketone 3.72 can be regarded as having one alkyl substituent on every four units. Polystiophene derivatives with one alkyl substituent on every three thiophene rings already display a diminished solubility\(^{44}\). Therefore, it is not surprising that a decrease in side chain content is accompanied with a further decrease in solubility. Poly-1,4-diketones were transformed to the thiophenes by ring-closure with Lawesson’s reagent. Due to the insolubility of the polymers, the solvent greatly affected the degree of conversion of the diketone. Going from benzene via toluene, xylene, chlorobenzene to dichlorobenzene, the IR spectra of the product displayed a significant decrease in carbonyl

---

vibration intensity. Pyrroles were obtained upon the reaction with ammonia in an autoclave at 250°C (polymer 3.66) or with ammonium acetate in dichlorobenzene (polymer 3.73). The different polymers are outlined in table 3.2.

\[
\text{OHC}^-\text{Ar-CHO} + \text{Me}_2\text{N}^-\text{Ar}^-\text{CO}^-\text{NMe}_2 \xrightarrow{\text{NaCN \ DMF}} \begin{array}{c}
\text{Polyketone} \\
\text{ring closure} \\
\text{Polyarene}
\end{array}
\]

\[\begin{array}{c}
\text{Het}^-\text{Ar}^-\text{Het}^-\text{Ar}^- \xrightarrow{\text{n}} \text{Het}^-\text{Ar}^-\text{Het}^-\text{Ar}^-
\end{array}\]

**Scheme 3.27** AA-BB-Polymerization reaction. (\(\text{Ar}, \text{Ar}'\) and Het are defined in table 3.2)

**Table 3.2** Polymers obtained by the AA-BB-polymerization

<table>
<thead>
<tr>
<th>Polyketone</th>
<th>Ar</th>
<th>Ar'</th>
<th>Polyarene</th>
<th>Het</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.65</td>
<td></td>
<td></td>
<td></td>
<td>3.66</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H</td>
</tr>
<tr>
<td>3.67</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.68</td>
<td></td>
<td></td>
<td></td>
<td>3.69</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.70</td>
<td></td>
<td></td>
<td></td>
<td>3.71</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.72</td>
<td></td>
<td></td>
<td></td>
<td>3.73</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H</td>
</tr>
<tr>
<td>3.74</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.3.2 Characterization

Due to the insolubility of the compounds of table 3.2 (except polymer 3.75), the most useful tool for the structural analysis is IR spectroscopy. Important absorptions are the carbonyl and the aromatic vibrations that are found in the region between 1600 cm\(^{-1}\) and 1700 cm\(^{-1}\) and between 700 cm\(^{-1}\) and 800 cm\(^{-1}\), respectively. The intensive carbonyl vibrations are dependent on the type of aromatic ring attached to the carbonyl group. For the all-phenylene diketone 3.65 the absorption is found at 1680 cm\(^{-1}\), whereas for the thiophene diketones 3.66 and 3.72 the signals are found at 1649 cm\(^{-1}\) and 1651 cm\(^{-1}\), respectively. Mixed diketone 3.70 has two carbonyl signals at 1678 cm\(^{-1}\) and 1663 cm\(^{-1}\).

Proof of the polydiketone structures is obtained from the solid state NMR spectrum of poly-1,4-diketone 3.65 (figure 3.2). The \(^{13}\)C-NMR spectrum clearly shows the expected structure with four distinct carbon atoms, no end group resonances and a high degree of regularity. Of the polymers, only polyketone 3.75 is soluble. \(^{1}\)H-NMR spectroscopy reveals the expected 1,4-diketone structure. In the aromatic region, signals are found at 7.2 and 7.7 ppm, arising from the ring protons without and with neighboring carbonyl groups, respectively. The diketone resonances are found at 3.3 to 3.4 ppm, comparable to oligomer diketones. For the alkyl side chains the benzylic signals are located at 2.8 ppm. However, the spectrum displays additional resonances at 3.0 ppm. These signals are thought to arise from non-1,4-diketone units (see figure 3.3), due to side reactions of the enone moieties similar to the polymerization of acrylates. The intensity of the signal is approximately 10
to 15 percent. Consequently, the polydiketone 3.75 has not been used in the cyclization reaction. Upon ring closure of the other poly-1,4-diketones, the carbonyl absorptions vanish and the aromatic absorptions become more intensive. This is especially noticed for the all-thiophene polymers 3.69 and 3.74, which have a strong absorption at 789 cm$^{-1}$ and 787 cm$^{-1}$, respectively. Copolymer 3.71 displays a similar effect with an absorption at 785 cm$^{-1}$. The polyaromatics are highly colored, ranging from dark brown to purple-black. Additionally, the dodecyl substituted polymers 3.73 and 3.74 have a green metallic luster.

Conductivities of the polyarenes were determined using four-point measurements. The measurements were preformed on pressed pellets after doping with iodine. Higher temperatures were required to ensure complete oxidation and the measurements were performed at the same temperatures to prevent de-doping due to evaporation of the dopant during the cooling process. The results are summarized in table 3.3. The highest conductivities, 0.5 and 0.7 Scm$^{-1}$, are found for the dodecyl substituted polymers 3.73 and 3.74, respectively. Although both polymers are insoluble, the solubilizing effect of the side chain results in a higher molecular weight of poly-1,4-diketone 3.72, and the corresponding cyclization products have a greater conjugation length. Additionally, the side chain may induce some ordering in the materials. Consequently, the dodecyl substituted polymers display the highest conductivity. Polythiophene (3.69) displays a conductivity value of 0.02 Scm$^{-1}$, whereas copolymers 3.66 and 3.67, although made up of only 50% heterocyclic rings, have higher values of 0.14 and 0.025 Scm$^{-1}$, respectively. These higher values are believed to arise from the higher temperature at which the measurements have been performed. A value of 0.008 Scm$^{-1}$ for polymer 3.71 is in agreement with a low content of heterocyclic rings in the material, and a corresponding low amount of charge carriers.

<table>
<thead>
<tr>
<th>Polyarene</th>
<th>Conductivity (S.cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.66</td>
<td>0.14 (100 °C)</td>
</tr>
<tr>
<td>3.67</td>
<td>0.025 (100 °C)</td>
</tr>
<tr>
<td>3.69</td>
<td>0.02 (70 °C)</td>
</tr>
<tr>
<td>3.71</td>
<td>0.008 (70 °C)</td>
</tr>
<tr>
<td>3.73</td>
<td>0.5 (70 °C)</td>
</tr>
<tr>
<td>3.74</td>
<td>0.7 (70 °C)</td>
</tr>
</tbody>
</table>
3.3.3 AB-Polymerization

Alternatively, polydiketones can be synthesized using monomers containing both a donor and an acceptor moiety. These kinds of monomers have the advantage of an inherent equimolar distribution of the two reactants in the polymerization reaction. Thus, 2-acetyltiophene (3.76) was protected as the glycol ketal 3.77, deprotonated and the anion quenched with DMF affording after hydrolysis 5-acetyl-thiophene-2-carbaldehyde (3.78)\(^ {44} \) (scheme 3.28). 3-Dodecylthiophene (3.15) was acylated affording a mixture of both 2- and

\[
3.76 
\xrightarrow{\text{HO OH}} \text{p-TsOH, benzene} \rightarrow 3.77 
\]

\[
\text{3.77} \xrightarrow{\text{1) LDA, 2) DMF, 3) HCl, acetone}} \rightarrow 3.78
\]

5-acetyl-3-dodecylthiophene (3.79). Protection with ethylene glycol and crystallization afforded the 2,3-isomer 3.80 in 35% yield (from 3.15), which was converted to 5-acetyl-4-dodecyl-thiophene-2-carbaldehyde (3.81) by formylation and hydrolysis in 42% as outlined in scheme 3.29. The Mannich base of this compound should give, after polymerization and ring closure, a substituted polythiophene with complete regioregularity. It turned out, however, that both compound 3.78 and 3.81 could not be transformed into the corresponding Mannich bases. We therefore decided to use unsaturated acid precursor 3.89.

\[
3.15 \xrightarrow{\text{H}_3\text{PO}_4, \text{Ac}_2\text{O}} \rightarrow 3.79 \xrightarrow{\text{1) HO OH, p-TsOH, benzene, 2) crystallization}} \rightarrow 3.80
\]

\[
\text{3.79} \xrightarrow{\text{1) LDA, 2) DMF, 3) HCl, acetone}} \rightarrow 3.81
\]

\( ^{44} \) Carpenter, A. J.; Chadwick, D. J. *Tetrahedron* 1985, 41, 3803
instead of the Mannich base. The synthesis is outlined in scheme 3.30. Thus, 2-bromo-3-dodecylthiophene (3.82) was deprotonated and the anion was quenched with DMF affording the aldehyde 3.83 in 91%. Aldehyde 3.83 was protected as the acetal 3.84 with ethylene glycol in a yield of 93%. Bromo lithium exchange with butyllithium afforded the anion, which was quenched with succinic anhydride (3.27), to afford acetal 3.85 in 42%. Besides 3.85 substantial amounts (up to 50%) of the debrominated compound 3.86 were obtained, which upon hydrolysis gave 4-dodecylthiophene-2-carbaldehyde (3.87). Acetal 3.85 was hydrolysed to 4-(3-dodecyl-5-formyl-thiophen-2-yl)-4-oxo-butyric acid (3.88). Bromination of 3.88 with bromine in chloroform afforded the precursor monomer 3.89 in 60% yield. The polymerization of 3.89 (scheme 3.31) was carried out with thiazolium salt 3.1 as catalyst and triethylamine as base. Triethylamine was used to deprotonate the thiazolium salt and the acid group, but also the induce the elimination of hydrogen bromide affording the double bond. Workup afforded a soluble product. $^1$H-NMR displayed one signal in the aromatic region at 7.6 ppm, and the 1,4-diketone-CH$_2$ resonances at 3.4 ppm. However, the largest signal in the region between 2.4 and 3.6 ppm, was found at 3.0 ppm. Based on these NMR data, poly-1,4-diketone 3.90 appears to be contaminated with over 50% of moieties such as 3.91, arising from reactions of acrylate functionalities. We
were not able to isolate the desired polyketone \textbf{3.90} from this mixture, and therefore, the reaction mixture was not used in the subsequent cyclization reaction.

\begin{center}
\begin{tikzpicture}
  \node at (0,0) {\includegraphics[width=0.5\textwidth]{scheme3.31.png}};
\end{tikzpicture}
\end{center}

\textit{scheme 3.31}

\subsection*{3.3.4 Discussion}

The polymerization of \textit{bis-Mannich} bases and dialdehydes using the Stetter reaction is a powerful method for the synthesis of \textit{poly-1,4-diketones}. Both the dialdehydes and diacetyl compounds are readily available. The \textit{bis-Mannich} bases have been prepared by using dimethyl(methylene)ammonium chloride (3.47) or by the standard method with DMF as solvent to afford the products in good yields and in high purity (except for 3.53). Introduction of a dodecyl side chain greatly influences the stability of the \textit{bis-Mannich} compounds 3.59 and 3.62. This decreased stability must be due to the dodecyl substituent because the \textit{unsubstituted} Mannich compounds 3.53 and 3.56 are stable, with respect to storage and preparation. However, electronic effects cannot account for the decreased stability of the dodecyl substituted Mannich bases. Since alkyl groups are only slightly electron donating, the effect of the alkyl substituent will be compensated for by a second electron withdrawing carbonyl group in thiophene derivative 3.59. It is more likely that the dodecyl substituents cause micelle formation of the Mannich bases. The resulting proximity of the \textit{amine} functionalities causes the elimination of the \textit{amines} and subsequent polymerization of the double bonds. The obtained polydiketones exhibit the expected structure as shown by IR and solid state \textit{^{13}C}-NMR spectroscopy. The fact that \textit{poly-1,4-diketone} 3.75 is contaminated with \textit{non-1,4-diketone} moieties, suggests that some structural defects may be present (particularly for the terthienyl derived polymers 3.72, 3.73 and 3.74). If
this is the case, however, the corresponding polythiophene would display the existence of these ketone moieties as well. Although these ketone functionalities are transformed into the thioketones during the cyclization reaction, the work-up procedure with NaOH will hydrolyse the thioketone groups, which normally are instable, back into the ketone functionalities. No ketone signals are found in IR, however, implying that the amount of non-1,4-diketone moieties is small. Upon ring closure with ammonia and Lawesson’s reagent the 1,4-diketones units are converted to pyrrole rings and thiophene rings, respectively. Since the diketones are insoluble, this is a heterogeneous reaction, which requires high temperatures to accomplish complete ring closure. A possible side reaction could be furan formation, but upon heating the terthienyl diketone polymer in dichlorobenzene for 16 h, the diketone was recovered virtually unchanged. The conductivities of the polymers, although the values are lower than reported for substituted polythiophenes, confirm the structure of the materials. To put the values in perspective it is important to realize that the measurements were performed on pressed pellets. High conductivities are only obtained of thin films in the order of one to ten μm, whereas pressed pellets have thicknesses of a few hundred μm.

The synthesis of a polythiophene via the Stetter reaction using the A-B polymerization reaction failed, since the mono Mannich bases could not be prepared from the formyl acetyl thiophenes. A first explanation might be that the aldehyde moiety interferes with the Mannich reaction, but protection of the aldehyde as its ethylene glycol acetal did not afford the Mannich base, not when the reaction was carried out with dimethyl(methylene)ammonium chloride (3.45) nor when the anion of the acetyl functionality was quenched with 3.45. In the first case the acetal was recovered unchanged, while in the second case a mixture of unidentified products was obtained. Furthermore, the preparation of the Mannich base 3.7 proceeds even when an equivalent of thiophene-2-carbaldehyde (3.6) is added. From the fact, however, that quenching of the lithium derivative with 3.45 results in a complex reaction mixture, the conclusion can be drawn that the Mannich base is formed, but since it is derived as the free amine, it is not stable under these conditions. Attempts to protect the aldehyde of 3.78 by the formation of the dimeric benzoin, which can be used in the Stetter reaction directly, were unsuccessful. It turned out that the actual reaction that took place with NaCN was the Cannizzaro reaction, and the isolated product the corresponding ester. A good explanation for both effects is hard to give, since diacetyl compounds undergo the Mannich reaction and the dialdehydes can be used in the Stetter reaction, which requires the formation of a cyanohydrin species. Fur-

thermore, aromatic dialdehydes have been polymerized via the benzoin condensation\textsuperscript{46}. The synthesis of a monomer with the bromo acid precursor \textbf{3.89} as acceptor functionality, turned out to be more feasible, although the introduction of the keto acid moiety proceeded in low yields. This low yield stems from the low reactivity of succinic anhydride and is not due to the addition of a second equivalent of the lithium anion to the obtained keto acid as has been reported for the addition of lithium anions to phthalic anhydride\textsuperscript{47}. Polymerization, however, did not afford the 1,4-diketone polymer with a satisfactory purity, because of the high reactivity of the unsaturated acid. The acrylate polymerization could not be suppressed using another base instead of triethylamine.

\section*{3.4 Concluding remarks}

In this chapter we have described the synthesis of oligomers and polymers using the Stetter reaction. The reaction has proved to be very effective for the synthesis of oligomers with a large diversity of aromatic rings, introduced both in the diketone synthesis and the ring closure reactions. Side chains can be introduced readily, achieving solubility, but diminishing the conjugation length. Carboxylic esters, however, do not reduce the effective conjugation length.

Synthesis of polymers turned out to be more demanding, although the conversions in the diketone synthesis are high. The insolubility of the diketones prevents, to some extent, characterization and purification. With the introduction of side chains in the Mannich base, the resulting increase in reactivity is accompanied by side reactions. Ring closure reactions proceed in high yields, and although this heterogeneous reaction requires high temperatures, furan formation is negligible.

\section*{3.5 Experimental section}

For general remarks, see section 2.4

The synthesis of compounds \textbf{3.15} and \textbf{3.60} has been described in chapter two. Compounds \textbf{3.12}, \textbf{3.13} and \textbf{3.32} were synthesized according to the literature procedures. UV spectra were recorded on a Perkin-Elmer Lambda 5 UV/VIS spectrophotometer. Conductivities were measured using a four probe method on pressed bars (20 x 5 x -0.5 to 1 mm\textsuperscript{3}). Iodine doped samples were obtained by adding solid iodine to the bar and the measurements carried out at the temperature described in the text during the doping process, until a constant

\begin{footnotesize}
\begin{enumerate}[\textbf{46}]
\item Parham, W. E.; Piccirilli, R. M. \textit{J. Org. Chem.} 1976, 41, 1269
\end{enumerate}
\end{footnotesize}
value was reached. The measurements were carried out at Philips Research Laboratories, Eindhoven under supervision of Dr. E. E. Havinga

3'-Dodecyl-[2,2';5',2'']-terthienyl (3.11)\textsuperscript{35}

A mixture of 1,4-di-thiophen-2-yl-butan-1,4-dione (3.8) (20 g, 80 mmol), KOH (powdered, 22.5 g), n-dodecylbromide (40 g, 160 mmol) in DMSO (85 ml) was stirred for 2 days. The mixture was poured into water and extracted with toluene (3×200 ml). The organic layers were washed with water, brine and dried (Na\textsubscript{2}SO\textsubscript{4}). The solvent was removed and the residue dissolved in acetone (250 ml). 3N HCl (100 ml) was added and the mixture refluxed for 3 h. Most of the acetone was evaporated and the aqueous phase extracted with toluene (3×150 ml). The combined organic layers were washed with water, a NaHCO\textsubscript{3} solution, brine and dried (Na\textsubscript{2}SO\textsubscript{4}). The solvent was removed and the residue distilled (kugelrohr 130°C 0.1 mbar) taking of the excess dodecylbromide and the arisen dodecanol. The residue was dissolved in toluene (150 ml), Lawesson's reagent (25 g, 62 mmol) was added and the mixture refluxed for 2.5 h. The colored mixture was poured into 2N NaOH, the layers were separated and the aqueous phase extracted with toluene. The organic layers were washed with water, brine and dried (Na\textsubscript{2}SO\textsubscript{4}). Most of the solvent was removed, the residue dissolved in hexane, filtered over Al\textsubscript{2}O\textsubscript{3}, and distilled (kugelrohr). Crystallization from n-BuOH afforded 16.5 g (49%) of 3.11. mp: 38.2-39.5°C \textsuperscript{(lit\textsuperscript{35} 39-40°C). }\textsuperscript{1}H-NMR (CDCl\textsubscript{3}) \textsuperscript{6}: 0.91 (t, 3H), 1.28 (m, 18H), 1.67 (m, 2H), 2.74 (t, 2H), 7.03 (s, 1H), 7.05 (m, 2H), 7.16 (m, 2H), 7.21 (dd, 1H), 7.31 (dd, 1H) ppm. \textsuperscript{13}C-NMR (CDCl\textsubscript{3}) \textsuperscript{6}: 14.0 (q), 22.6 (t), 29.2 (t), 29.3 (t), 29.6 (t), 30.4 (t), 31.8 (t), 123.4 (d), 124.2 (d), 125.2 (d), 125.7 (d), 126.4 (d), 127.3 (d), 127.7 (d), 135.0 (s), 140.1 (d) ppm.

To DMF (40 ml), POCl\textsubscript{3} (11.3 ml) was added keeping the temperature below 30°C. To this mixture was added 3'-dodecyl-[2,2';5',2'']-terthienyl-5,5''-dicarbaldehyde (3.12)\textsuperscript{21} and the temperature was brought to 100°C and remained at this temperature for 2 h, followed by 4 h at RT. The solid cake was poured into NaOH (35 g) in ice-water (250 ml) and left overnight. The mixture was extracted with toluene (5×100 ml). The organic layers were washed with water, brine and dried (Na\textsubscript{2}SO\textsubscript{4}). The volume was reduced, hexane added and the solution filtered over celite. Chromatography (Al\textsubscript{2}O\textsubscript{3}, toluene-hexane 1:1) and crystallization from MeOH afforded 6.1 g (52%) of 3.12 as yellow crystals. mp: 78.9-81.8°C. \textsuperscript{1}H-NMR (CDCl\textsubscript{3}) \textsuperscript{6}: 0.88 (t, 3H), 1.26 (m, 18H), 1.67 (m, 2H), 2.72 (s, 1H), 7.27 (m, 2H), 7.69 (d, 1H), 7.73 (d, 1H), 9.88 (s, 1H), 9.90 (s, 1H) ppm. \textsuperscript{13}C-NMR (CDCl\textsubscript{3}) \textsuperscript{6}: 14.0 (q), 22.6 (t), 29.2 (t), 29.3 (t), 29.4 (t), 29.5 (t), 29.6 (t), 30.1 (t), 31.8 (t), 124.6 (d), 126.4 (d), 129.1 (d), 131.0 (s), 135.4 (s), 136.6 (d), 137.1 (d), 142.0 (s), 142.7 (s), 143.1 (s), 144.9 (s), 145.8 (s), 182.3 (d), 182.4 (d) ppm. HRMS calcd. for C\textsubscript{26}H\textsubscript{32}O\textsubscript{2}S\textsubscript{3}: 472.156, found: 472.156.

5,5''''-Diphenyl-3''-dodecyl-[2,2';5',2''';5''',2''''']-quinquethienyl (3.14)

A mixture of 3-dimethylamino-1-phenylpropan-1-one (3.13) (0.38 g, 2.15 mmol), 3''-dodecyl-[2,2';5',2'']-terthienyl-5,5''-dicarbaldehyde (3.12) (0.5 g, 1.06 mmol) and NaCN (10 mg) in DMF (15 ml) was stirred at RT for 2 days. The mixture was poured into water, acidified with HCl and extracted with CH\textsubscript{2}Cl\textsubscript{2} (3×70 ml). The organic layers were washed with water, brine and dried (Na\textsubscript{2}SO\textsubscript{4}). The volume was reduced and the
solution filtered over Al₂O₃. The crude diketone obtained was dissolved in toluene (20 ml) after which Lawesson's reagent (1 g, 2.5 mmol) was added and the mixture refluxed for 2 h. After cooling and reduction of the volume the residue was filtered over Al₂O₃ and recrystallized from toluene. This gave 400 mg (51%) of 3.14 as an orange-red solid. mp: 172.5-175°C. 'H-NMR (CDCl₃) δ: 0.87 (t, 3H), 1.26 (m, 18H), 1.69 (m, 2H), 2.78 (t, 2H), 7.10 (m, 7H), 7.27 (m, 2H), 7.38 (m, 6H), 7.61 (d, 4H) ppm. UV(CHCl₃) λₘₐₓ=429 nm. HRMS calcd. for C₄₄H₄₄S₅: 732.205, found 732.205.

3-Dodecylthiophene-2,5-dicarbaldehyde (3.16)

To a solution of 3-dodecylthiophene (3.15) (13 g, 51.6 mmol) and TMEDA (15.6 ml, 104 mmol) in hexane (75 ml) was added n-BuLi (2.5 M, 45 ml). The mixture was stirred for 1 h at RT and refluxed for 45 min. After cooling to -60°C, THF (100 ml) was added to dissolve most of the white suspension and the solution was cooled to -80°C. DMF (25 ml) was then added and the mixture was allowed to reach RT. It was hydrolyzed with saturated NH₄Cl solution (100 ml) and extracted with ether (3x 100 ml). The combined organic layers were washed with water, brine and dried (Na₂SO₄). After evaporation of the solvents the residue was filtered over silica using hexane to remove the impurities and ether to give the product. Subsequent distillation (kugelrohr) afforded 13.7 g (86%) of 3.16 as an off-white semi solid. (bp: 200°C 0.05 mbar) ¹H-NMR (CDCl₃) δ: 0.84 (t, 3H), 1.23 (m, 18H), 1.68 (m, 2H), 2.98 (t, 2H), 7.65 (s, 1H), 9.95 (s, 1H) ppm. ¹³C-NMR (CDCl₃) δ: 13.9 (q), 22.5 (t), 28.3 - 29.4 (t), 31.1 (t), 31.7 (t), 137.0 (d), 143.0 (s), 151.8 (s), 182.7 (d), 183.1 (d) ppm. Anal. calcd. for C₁₈H₂₈O₂S: C 70.08, H 9.15, S 10.39, found: C 70.08, H 9.19, S 10.39.

3-Dodecyl-2,5-bis-(4-oxo-4-thiophen-2-yl-butyryl)-thiophene (3.18)

Na₂CO₃ (460 mg) was added to a solution of 4-oxo-4-thiophen-2-yl-butyric acid (3.17) (790 mg, 4.3 mmol, prepared according to the literature with CH₂Cl₂ as solvent) in DMF (20 ml) and stirred for 5 min. To this solution were added 3-dodecylthiophene-2,5-dicarbaldehyde (3.16) (650 mg, 2.1 mmol), catalyst 3.1 (40 mg) and NEt₃ (0.5 ml). The mixture was stirred for 15 min at 80°C and then poured into cold diluted HCl and extracted with CH₂Cl₂ (2x100 ml). The combined organic layers were washed with water, brine and dried (Na₂SO₄). Evaporation of the solvents, chromatography (silica hexane-ether 1:1) and crystallization from 2-propanol afforded 540 mg (44%) of 3.18. mp: 57.9-58.9 ¹H-NMR (CDCl₃) δ: 0.87 (t, 3H), 1.25 (m, 18H), 2.97 (t, 2H), 3.38 (m, 8H), 7.15 (m, 2H), 7.65 (m, 3H), 7.81 (m, 2H) ppm. HRMS calcd. for C₃₂H₄₀O₄S₃: 584.209, found: 584.208.

3''''-Dodecyl-[2,2';5',2''''-quinque tetrayl] (3.19)

A mixture of tetraketone 3.18 (210 mg, 0.36 mmol) and Lawesson's reagent (600 mg, 2.4 mmol) in toluene (20 ml) was refluxed overnight. The highly colored solution was evaporated and chromatographed (silica, hexane) to give 130 mg (62%) of 3.19 as an orange solid. mp: 81.2-82.7°C ¹H-NMR (CDCl₃) δ: 0.90 (t, 3H), 1.28 (m, 18H), 1.69 (m, 2H), 2.76 (t, 2H), 7.01-7.25 (m, 11H) ppm. UV(CHCl₃) λₘₐₓ=407.5 nm. HRMS calcd. for C₃₂H₃₉S₃: 580.142, found: 580.142.
1,4-Bis-(hexyloxy)-benzene (3.21)

A mixture of hydroquinone (3.20) (15.0 g, 136 mmol), hexylbromide (47 g, 286 mmol), NaI (42 g), KOH (19 g) and EtOH (250 ml) was refluxed for 2 days. After cooling to 0°C, the dark colored product was collected on a glass filter and washed with plenty of water. The now slightly brown colored solid was recrystallized twice from EtOH to give 26.7 g (80%) of 3.21 as a white solid mp: 46.3-47.4°C. (lit 4?39-40°C).

'H-NMR (CDCl3) δ: 0.95 (t, 6H), 1.35 (m, 8H), 1.45 (m, 4H), 1.8 (quintet, 4H), 3.9 (t, 4H), 6.8 (s, 4H) ppm.

13C-NMR (CDCl3) δ: 13.95 (q), 22.54 (t), 25.66 (t), 29.3 (t), 31.54 (t), 68.51 (t), 115.24 (d), 153.05 (s) ppm.

1,4-Dibromo-2,5-bis-(hexyloxy)-benzene (3.22)

To a solution of 1,4-bis-(hexyloxy)-benzene (3.21) (20.0 g, 74 mmol) in acetic acid (100 ml) and ether (10 ml) was added a solution of bromine (8 ml, 15 mmol) in acetic acid (20 ml). The mixture was stirred for 24 h and the solvents were evaporated. The resulting white solid was collected and recrystallized from ethanol to give 24 g (76%) 3.22. mp: 63.0-64.1°C. 1H-NMR (CDCl3) δ: 0.95 (t, 3H), 1.35 (m, 8H), 1.45 (m, 4H), 1.8 (quintet, 4H), 3.95 (t, 4H), 7.1 (s, 2H) ppm. 13C-NMR (CDCl3) δ:13.95 (q), 22.49 (t), 25.53 (t), 29.01 (t), 31.41 (t), 70.2 (t), 111.02 (s), 118.34 (d), 149.94 (s) ppm. Anal. calced. for C18H28Br2O2: C 49.56, H 6.47, Br 36.63, found: C 49.77, H 6.54, Br 36.66, HRMS calcd. for C18H28Br2O2: 434.046, found: 434.047.

2,5-Bis-(hexyloxy)-terephthaldehyde (3.23)

1,4-Dibromo-2,5-bis-(hexyloxy)-benzene (3.22) (14.8 g, 34 mmol) in THF (80 ml) was added to a solution of n-BuLi (1.5 M, 50 ml) in 200 ml THF, keeping the temperature below -60°C. The temperature was allowed to raise to -40°C, resulting in a solid cake, hard to stir. The mixture was kept between -30 and -50°C for 1 h. It was then cooled to -80°C and dry DMF (10 ml, 130 mmol) was added. The cooling bath was removed, resulting in a clear, almost colorless solution at 10°C. Addition of NH4Cl (100 ml 25%) gave a yellow organic layer that was separated. THF was removed and the residue dissolved in ether (100 ml). The aqueous layer was extracted with ether (2x50 ml) and the combined organic layers were washed with water, brine and dried (MgSO4). After evaporation of the solvent, the product was recrystallized from 2-propanol giving 7.2 g (63%) of 3.23 as yellow crystals mp: 74.1-75.0°C. 1H-NMR (CDCl3) δ: 0.95 (t, 6H), 1.35 (m, 8H), 1.45 (m, 4H), 1.8 (quintet, 4H), 4.0 (t, 4H), 7.4 (s, 2H) ppm. 13C-NMR (CDCl3) δ:13.58 (q), 22.40 (t), 25.54 (t), 28.87 (t), 31.31 (t), 69.04 (t), 111.40 (d), 129.04 (s), 154.98 (s), 189.11 (d) ppm. Anal. calced. for C20H30O4: C 71.82, H 9.04, found: C 71.54, H 9.02, HRMS calcd. for C20H30O4: 334.214, found: 334.215.

1,4-Bis-(4-oxo-4-thiophen-2-yl-butyryl)-2,5-bis-(hexyloxy)-benzene (3.24)

A mixture of 4-oxo-4-thiophen-2-yl-but-2-enoic acid (3.17) (1.85 g, 10 mmol) and Na2CO3 (1.06 g, 10 mmol) in DMF (15 ml) were stirred for 15 min. After addition of 1,4-bis-(hexyloxy)-terephthaldehde (3.23) (1.1 g, 3.3 mmol), catalyst 3.1 (400 mg) and NEt3 (1 ml) the mixture was heated to 80°C and kept at that

---


92
temperature overnight. The mixture was poured into cold diluted HCl and extracted with CH$_2$C$_2$ (2x100 ml). The organic phase was washed with water, a NaHC$_3$ solution, brine and dried (Na$_2$SO$_4$). The solvent was evaporated and the residue chromatographed (silica, hexane-ether 1:1) to afford 1.2 g (61%) of 3.24 as a slightly yellow solid. mp: 94.4-96.5°C. $^1$H NMR (CDCl$_3$) $\delta$: 0.86 (t, 6H), 1.31 (m, 8H), 1.45 (m, 4H), 1.82 (quintet, 4H), 3.34 (t, 4H), 3.48 (t, 4H), 4.05 (t, 4H), 7.14 (dd, 2H), 7.35 (s, 2H), 7.63 (dd, 2H) ppm. $^{13}$C NMR (CDCl$_3$) $\delta$: 13.8 (q), 22.4 (t), 25.6 (t), 29.0 (t), 31.3 (t), 33.5 (t), 38.1 (t), 69.1 (t), 114.1 (d), 127.9 (d), 130.8 (s), 131.7 (d), 133.2 (d), 143.8 (s), 151.9 (s), 199.9 (s) ppm. HRMS calcd. for C$_{34}$H$_{42}$O$_6$S$_2$: 610.242, found: 610.242.

1,4-Bis-(2,2′-bithiophen-5-yl)-2,5-bis-(hexyloxy)-benzene (3.25)

Tetraketone 3.24 (100 mg, 0.16 mmol) was dissolved in toluene (15 ml) and an excess of Lawesson's reagent (0.5 g) was added. The mixture was refluxed overnight giving a highly colored solution. The solvent was removed and the residue chromatographed (silica, hexane) and crystallized from 2-propanol. This afforded 85 mg (86%) of 3.25 as orange crystals mp: 150.2-152.4°C. $^1$H NMR (CDCl$_3$) $\delta$: 0.94 (t, 6H), 1.41 (m, 8H), 1.59 (m, 4H), 1.94 (quintet, 4H), 4.11 (t, 4H), 7.05 (dd, 2H), 7.18 (d, 2H), 7.23 (m, 6H), 7.47 (d, 2H) ppm. $^{13}$C NMR (CDCl$_3$) $\delta$: 14.0 (q), 22.5 (t), 25.9 (t), 29.3 (t), 31.6 (t), 69.6 (t), 111.7 (d), 122.5 (s), 123.1 (d), 123.4 (d), 124.0 (d), 125.6 (d), 127.7 (d), 137.1 (s), 137.7 (s), 138.0 (s), 149.1 (s) ppm. UV(CHCl$_3$) $\lambda_{max}$=404.4 nm. HRMS calcd. for C$_{34}$H$_{38}$O$_2$S$_4$: 606.175, found: 606.175.

1,4-Bis-(5-thiophen-2-yl-1H-pyrrol-2-yl)-2,5-bis-(hexyloxy)-benzene (3.26)

A solution of tetraketone 3.24 (200 mg, 0.33 mmol) and NH$_4$OAc (1 g) in HOAc (25 ml) was refluxed for 16 h. The dark colored mixture was cooled and poured into 200 ml water and extracted with CH$_2$C$_2$ (3x100 ml). The combined organic layers were washed with water, a NaHC$_3$ solution, brine and dried (Na$_2$SO$_4$). The solvent was evaporated and the residue chromatographed (silica, ether). This afforded 140 mg (75%) of 3.26 as a rapidly colorizing solid. $^1$H NMR (CDCl$_3$) $\delta$: 0.91 (t, 6H), 1.38 (m, 8H), 1.58 (m, 4H), 1.98 (m, 4H), 6.49 (b, 2H), 6.60 (b, 2H), 7.17 (m, 8H), 10.24 (s, 2H) ppm. UV(CHCl$_3$) $\lambda_{max}$=405.1 nm. oxidized 550 nm. HRMS calcd. for C$_{34}$H$_{40}$N$_2$O$_2$S$_2$: 572.253, found: 572.253.

3-Chlorocarbonyl-propionic acid dodecy ester (3.28)

A mixture of n-dodecanol (8.6 g, 43 mmol) and succinic anhydride (3.27) (4.6 g, 43 mmol) in xylene (15 ml) was refluxed overnight. The xylene was evaporated and the residue crystallized from hexane giving 6.1 g (50%) of succinic acid monododecyl ester as a white solid. mp: 47.4-49.4°C (lit$^{49}$: 47.0-7.2°C). This was converted to the acid chloride by refluxing it for 3 h in SOCl$_2$ (25 ml). The solvent was evaporated and the residue distilled (kugelrohr, 180°C, 1 mm Hg). The acid chloride 3.28, 5.8 g (90%) was obtained as a solidifying oil. $^1$H NMR (CDCl$_3$) $\delta$: 0.83 (t, 3H), 1.23 (m, 18H), 1.58 (m, 2H), 2.62 (t, 2H), 3.16 (t, 2H), 4.05 (t, 2H) ppm.

---

To a solution of 3.28 (6.2 g, 20 mmol) and thiophene (1.9 g, 23 mmol) in CH₂Cl₂ (50 ml) was added SnCl₄ (2.5 ml, 21 mmol). The dark mixture was stirred at RT for 3.5 h, poured into diluted HCl and the layers separated. The organic layer was washed with water and dried. After the solvent was removed the residue was crystallized from hexane to give 5.2 g (74%) of 3.29 as an off white solid. mp: 34.3-35.6°C. ¹H-NMR (CDCl₃) δ: 0.87 (t, 3H), 1.25 (m, 18H), 1.60 (m, 2H), 2.75 (t, 2H), 3.24 (t, 2H), 4.07 (t, 2H), 7.12 (dd, J=5.1 Hz, J=3.8 Hz, 1H), 7.63 (dd, J=5.1 Hz, J=1.3 Hz, 1H), 7.75 (dd, J=3.8 Hz, J=0.9 Hz, 1H) ppm. ¹³C-NMR (CDCl₃) δ: 14.0 (q), 22.5 (t), 25.7 (t), 28.1 (t), 28.4 (t), 29.1 (t), 29.2 (t), 29.4 (t), 29.4 (t), 29.5 (t), 31.8 (t), 33.8 (t), 64.8 (t), 127.9 (d), 131.8 (d), 133.4 (d), 143.5 (s), 172.6 (s) ppm.

3-Bromo-4-oxo-4-thiophen-2-yl-butyric acid dodecyl ester (3.30)

To a solution of 4-oxo-4-thiophen-2-yl-butyric acid dodecyl ester (3.29) (4 g, 11.4 mmol) in CHCl₃ (50 ml) was added 0.5 ml of a solution of bromine (1.83 g, 11.5 mmol) in CHCl₃ (5 ml). The reaction mixture was refluxed to start the reaction and after the bromine color had disappeared the rest of the bromine solution was slowly added. The mixture was stirred for another hour at RT and poured into water. The layers were separated and the aqueous layer extracted with 50 ml CHCl₃. The combined organic layers were washed with water (3x100 ml), brine and dried (Na₂SO₄). Evaporation of the solvent and crystallization from hexane gave 4.1 g (83%) of 3.30. mp: 32.3-32.5°C. ¹H-NMR (CDCl₃) δ: 0.87 (t, 3H), 1.24 (m, 18H), 1.57 (m, 2H), 3.67 (d, 2H), 4.08 (t, 2H), 4.92 (t, 1H), 7.12 (m, 2H), 7.21 (m, 1H), 7.27 (m, 1H), 7.40 (m, 2H), 7.52 (s, 1H) ppm. ¹³C-NMR (CDCl₃) δ: 13.9 (q), 22.5 (t), 25.7 (t), 28.3 (t), 29.0 (t), 29.2 (t), 29.3 (t), 29.4 (t), 29.5 (t), 31.8 (t), 38.5 (t), 40.1 (d), 65.3 (t), 128.2 (d), 133.2 (d), 135.0 (d), 140.5 (s), 169.9 (s), 185.4 (s) ppm.

[2,2';5',2'']-Terthiophene-4'-carboxylic acid dodecyl ester (3.31)

A mixture of the bromide 3.30 (1.6 g, 3.7 mmol), thiophene-2-carbaldehyde (3.6) (420 mg, 3.8 mmol), catalyst 3.1 (100 mg, 0.4 mmol) in DMF (30 ml) was heated to 90°C, NEt₃ (1.5 ml) was added, and the reaction was kept at 90°C overnight. It was poured into cold diluted HCl and extracted with ether (3x100 ml). The organic phase was washed with water, brine (2x100 ml) and dried (Na₂SO₄). Evaporation of the solvent and crystallization from hexane gave 1 g (59%) of the diketone as a colored oil of 90% purity (based on ¹H-NMR). ¹H-NMR (CDCl₃) δ: 0.85 (t, 3H), 1.29 (m, 18H), 1.52 (m, 2H), 3.67 (d, 2H), 4.08 (t, 2H), 4.92 (t, 1H), 7.12 (m, 2H), 7.62 (d, 1H), 7.68 (d, 1H), 7.79 (d, 1H), 7.94 (d, 1H) ppm. The crude diketone (1 g), Lawesson’s reagent (700 mg, 1.78 mmol) and toluene (50 ml) were heated at 80°C for 1 h and refluxed for another 2.5. The toluene was removed and the residue chromatographed (silica, hexane-ether 3:1) giving 740 mg (74%) of 3.31 as a rapidly colorizing oil. ¹H-NMR (CDCl₃) δ: 0.85 (t, 3H), 1.25 (m, 18H), 1.72 (m, 2H), 4.27 (t, 2H), 7.07 (m, 2H), 7.21 (m, 1H), 7.27 (m, 1H), 7.52 (s, 1H) ppm. ¹³C-NMR (CDCl₃) δ: 13.1 (q), 21.6 (t), 24.9 (t), 27.5 (t), 28.2 (t), 28.3 (t), 28.4 (t), 28.6 (t), 30.8 (t), 64.0 (t), 124.3 (d), 124.2 (d), 125.1 (d), 126.0 (d), 126.7 (d), 126.9 (d), 127.3 (s), 128.2 (d), 132.5 (s), 134.2 (s), 134.7 (s), 140.2 (s), 161.8 (s) ppm. HRMS calcd. for C₂₅H₃₂O₂S₃: 460.156, found: 460.156.
5,5'-Bis-(2-dodecylhexoxycarbonyl-4-oxo-4-thiophen-2-yl-butryl)-[2,2']-bithienyl (3.33)

A mixture of [2,2']-bithienyl-5,5'-dicarbaldehyde (3.32) (160 mg, 0.72 mmol), bromide 3.30 (640 mg, 1.5 mmol), catalyst 3.1 (20 mg) in DMF (10 ml) was heated to 80°C. NEt3 (0.5 ml) was added and the mixture kept at 80°C for 4 days. It was poured into cold diluted HCl and extracted with ether (3x100 ml). The organic layers were washed with water, brine and dried (Na2SO4). The solvents were removed and the crude material chromatographed (silica, hexane-ether 1:1). Crystallization from 2-propanol afforded 585 mg (88%) of 3.33 as a slightly colored solid. mp: 136-138°C. 1H-NMR (CDCl3) δ: 0.87 (t, 6H), 1.21 (m, 36H), 1.56 (m, 4H), 3.72 (d, 4H), 4.11 (t, 4H), 4.91 (t, 2H), 7.15 (dd, 2H), 7.36 (d, 2H), 7.66 (dd, 2H), 7.83 (dd, 2H), 7.90 (d, 2H) ppm. 13C-NMR (CDCl3) δ: 13.1 (q), 21.7 (t), 24.7 (t), 28.3 (t), 28.1 (t), 28.3 (t), 28.5 (t), 28.6 (t), 30.9 (t), 37.2 (t), 48.7 (d), 65.2 (t), 125.3 (d), 127.2 (d), 131.6 (d), 133.2 (d), 133.5 (d), 141.0 (s), 141.1 (s), 143.7 (s), 167.4 (s), 185.5 (s) ppm.

[2,2':5,2'':5',2'':5'''2',2'''5'''2'''']-Sexthiophene-4',3'''-dicarboxylic acid didodecyl ester (3.34)

A mixture of tetraketone 3.33 (180 mg, 0.2 mmol) and Lawesson's reagent (200 mg, 0.5 mmol) in toluene (20 ml) was refluxed for 3 h. The mixture was cooled, poured into a NaHCO3 solution and extracted with ether (3x50 ml). The combined organic layers were washed with water, brine and dried (Na2SO4). The solvents were evaporated, the residue chromatographed (silica, pentane-ether 20:1) and crystallized from hexane. This gave 60 mg (34%) of 3.34 as a dark-red micro-crystals. mp: 105.4-106.6°C. 1H-NMR (CDCl3) δ: 0.86 (t, 6H), 1.24 (m, 32H), 1.72 (m, 4H), 4.28 (t, 4H), 7.04 (m, 2H), 7.18 (d, 2H), 7.25 (m, 4H), 7.43 (d, 2H), 7.53 (s, 2H) ppm. UV (CHCl3) λmax 434.4 nm. Anal. calcd. for C50H62O4S6: C 65.32, H 6.80, S 20.93, found: C 65.49, H 6.83, S 21.20.

p-Hexyloxy-benzaldehyde (3.36)

A mixture of p-hydroxy benzaldehyde (3.35) (15 g, 123 mmol), n-hexylbromide (20.3 g, 124 mmol), KOH pellets (85%, 8.1 g) and NaI (18 g) in 96% EtOH (150 ml) was refluxed for 18 h. The solvent was evaporated and water was added. The aqeous phase was extracted with ether (3x100 ml). The organic layers were combined, washed with water, brine and dried (MgSO4). Evaporation of the solvent and distillation gave 18.4 g (72%) of 3.36 as a colorless oil bp 127-130°C 0.7 mm Hg (lit5', 154-155°C 6 mm Hg).

1,4-Bis-[3-(4-hexyloxy-phenyl)-acycloxy]-benzene (3.38)

p-Hexyloxy-benzaldehyde (3.36) (7.35 g, 36 mmol) and 1,4-diacyetyl benzene (3.37) (2.9 g, 18 mmol) were dissolved in boiling EtOH (100 ml). To the still hot solution 40% NaOH (1 ml) was added. In a few min, stirring became impossible and after 15 min. the mixture was poured into diluted HCl (100 ml). The obtained dark yellow solid was isolated and recrystallized from CHCl3 giving 4.2 g (45%) of 3.38 as yellow.
crystals. mp 198.9-199.4°C. 1H-NMR (CDCl₃) δ: 0.90 (t, 6H), 1.45 (m, 12H), 1.79 (quintet, 4H), 4.00 (t, 4H), 6.91 (d, J=8.5 Hz, 4H), 7.35 (d, J=15.6 Hz, 2H), 7.57 (d, J=8.5 Hz, 4H), 7.77 (d, J=15.6 Hz, 2H), 8.06 (s, 4H) ppm. 13C-NMR (CDCl₃) δ: 13.8 (q), 22.4 (t), 25.6 (t), 29.1 (t), 31.3 (t), 68.3 (t), 115.1 (d), 119.8 (d), 127.4 (s), 128.4 (d), 141.6 (s), 145.5 (d), 161.6 (s), 216.0 (s) ppm. Anal. calcd. for C₃₆H₄₂O₄: C 80.26, H 7.86, found: C 79.61, H 7.76.

1,4-Bis-[3-(4-hexyloxy-phenyl)-4-oxo-4-phenyl-butyryl]-benzene (3.40)

A mixture of chalcone 3.38 (1 g, 1.9 mmol), freshly distilled benzaldehyde (3.39) (500 mg), catalyst 3.1 (400 mg) and NEt₃ (0.5 ml) in DMF (40 ml) was stirred for 5 days at 80°C. The reaction mixture was poured into diluted HCl (100 ml) and extracted with CHCl₃ (3x100 ml). The combined organic layers were washed with water, a saturated NaHCO₃ solution, brine and dried. Evaporation of the solvents gave a dark oil which was filtered over deactivated Al₂O₃ with CHCl₃ and chromatographed (silica, ether) giving 100 mg (8%) of 3.40. 1H-NMR (CDCl₃) δ: 0.86 (t, 6H), 1.17 (m, 8H), 1.29 (m, 4H), 1.71 (quintet, 4H), 3.24 (dd, 2H), 3.69 (t, 4H), 4.15 (dd, 2H), 5.23 (dd, 2H), 6.80 (d, 4H), 7.22 (d, 4H), 7.38 (m, 6H), 8.0 (m, 8H). 13C-NMR (CDCl₃) δ: 13.8 (q), 22.5 (t), 25.6 (t), 29.1 (t), 31.4 (t), 44.0 (t) 47.8 (d) 67.8 (t), 115.0 (d), 128.1 (d), 128.3 (d), 129.0 (d), 129.9 (s), 132.7 (d), 136.2 (s), 139.5 (s), 158.3 (s), 197.6 (s), 198.7 (s).

1,4-Bis-[3-(4-hexyloxy-phenyl)-5-phenyl-1H-pyrrol-2-yl]-benzene (3.41)

A mixture of tetraketone 3.40 (90 mg, 0.1 mmol) and NH₄OAc (1 g) in HOAc (10 ml) was refluxed overnight. The resulting dark solution was cooled and poured into water and extracted with ether (3x50 ml). The organic layers were washed with water, a saturated NaHCO₃ solution, brine and dried (Na₂SO₄). Evaporation of the solvent, chromatography (silica, ether/pentane) and recrystallization from ether/pentane afforded 40 mg (56%) of 3.41 as a solid. mp: 162.9-165.8°C. 1H-NMR (CDCl₃) δ: 0.95 (t, 6H), 1.38 (m, 8H), 1.50 (m, 4H), 1.81 (quintet, 4H), 3.98 (t, 4H), 6.69 (s, 2H), 6.88 (d, 4H), 7.35 (m, 14), 5.58 (s, 4H), 8.43 (s, 2H). 13C-NMR (CDCl₃) δ: 6.14.0 (q), 22.6 (t), 25.7 (t), 29.2 (t), 31.6 (t), 67.9 (t), 108.5 (d), 114.3 (d), 123.7 (s), 124.0 (d), 126.7 (d), 127.2 (d), 128.5 (s), 128.6 (d), 129.3 (d), 129.7 (d), 130.0 (s), 131.7 (s), 133.0 (s), 157.5 (s).

1,4-Bispropionylbenzene (3.43)

Ethylbromide (30 g, 270 mmol) in ether (100 ml) was added to Mg (6.3 g, activated with iodine) at such a rate to maintain a gentle reflux. To the Grignard reagent terephthaldehyde (3.41) (11.6 g, 87 mmol) in THF (150 ml) was added with cooling. The resulting slightly green emulsion was stirred for another 30 min and poured into ice-water (600 ml) and H₂SO₄ (16 ml). The aqueous phase was extracted with ether (3x100 ml). The combined organic layers were washed with water, a saturated NaHCO₃ solution, brine and dried. The solvent was evaporated and the resulting oil dissolved in acetone (200 ml). The solution was cooled and Jones reagent (81 ml) was added in 20 min. The acetone was evaporated and water and NaHSO₃ were added. The aqueous phase was extracted with CH₂Cl₂ (3x100 ml), the combined organic layers were washed...
with water, brine and dried (MgSO₄). Evaporation of the solvent and recrystallization from EtOH gave 6.2 g (38%) of 3.43 as white crystals mp: 100.2-103.5°C. (lit² 100-102°C.) ¹H-NMR (CDCl₃) δ:1.25 (t, 6H), 3.05 (q, 4H), 8.05 (s, 4H) ppm. ¹³C-NMR (CDCl₃) δ:8.0 (q), 32.0 (t), 128.1 (d), 139.7 (s), 199.8 (s) ppm.

**1,4-Bis-(3-dimethylamino-2-methyl-propionyl) benzene (3.44)**

A mixture of 3.43 (5.4 g, 28.4 mmol), dimethylamine.HCl (5.1 g), 35% formaldehyde (5.5 ml) and HCl (conc, 1 ml) in EtOH (65 ml) was refluxed for 4 days. The resulting clear solution was poured into water (100 ml) and extracted with CH₂Cl₂ (2x100 ml). The aqueous phase was made alkaline with 0.1 M NaOH and extracted with CH₂Cl₂ (3x75 ml). The organic layers were washed with brine and dried (Na₂SO₄). Evaporation of the solvent afforded 2.5 g (29%) of 3.44 as a yellow semi solid. ¹H-NMR (CDCl₃) δ:1.95 (d, 6H), 2.26 (s, 12H), 2.37 (dd, 2H), 2.86 (m, 2H), 3.74 (m, 2H), 8.02 (s, 4H) ppm.

**Attempted synthesis of 1,4-bis-(2-methyl-4-oxo-4-phenyl-butyryl)-benzene**

To a solution of 3.44 (900 mg, 3 mmol) and benzaldehyde (640 mg) in DMF (35 ml) was added NaCN (50 mg, 1 mmol), the mixture stirred at RT for 4 days, and poured into water (150 ml) and acidified with HCl. The resulting solid was collected and dried. This afforded (400 mg, 62%) of 1,4-bis-(2-methyl-acryloyl)-benzene (3.45) as a white solid, mp 92.4-93.4°C. ¹H-NMR (CDCl₃) δ:2.05 (s, 6H), 5.63 (s, 2H), 5.96 (s, 2H), 7.72 (s, 4H) ppm. ¹³C-NMR (CDCl₃) δ:18.3 (q), 128.1 (s), 128.8 (d), 140.4 (s), 143.5 (s), 197.4 (s) ppm.

**Thiophene-2,5-dicarbaldehyde (3.46)**

To a mixture of thiophene (3.1 g, 37 mmol), TMEDA (11.1 ml, 74 mmol) in hexane (15 ml) was added n-Buli (1.6 M, 46 ml). This mixture was refluxed for 35 minutes, cooled below 0°C and after addition of THF (75 ml) to -60°C, DMF (7.4 ml) was then added and the temperature allowed to reach RT. The turbid mixture was poured into HCl/H₂O and extracted with CH₂Cl₂ (3x75 ml). The organic layers were combined and washed with water, a NaHCO₃ solution, brine and dried (Na₂SO₄). After evaporation of the solvent, the product was crystallized from water giving 3.5 g (71 %) of 3.46 as white crystals, mp: 116.3-117.3°C (lit²³: 109-112). ¹H-NMR (CDCl₃) δ:7.8 (s, 2H), 10.0 (s, 2H) ppm. ¹³C-NMR (CDCl₃) δ:135.1 (d), 148.8 (s), 183.3 (d) ppm.

**1,4-Bis-(3-dimethylaminopropionyl)-benzene (3.48)**

A mixture of 1,4-diacetylbenzene (3.37) (3.2 g, 20 mmol) and dimethyl(methylene)ammonium chloride (3.47) (4.6 g, 50 mmol) in acetonitrile 50 ml was stirred at 30°C for 3h. After cooling to RT, the resulting solid was collected and recrystallized from EtOH/water. This afforded 5.8 g (84%) of 3.48.2 HCl as a white
solid. mp: 141-142.4°C (d). $^1$H-NMR (D$_2$O) 6: 2.90 (s, 12H), 3.52 (t, 4H), 3.61 (t, 4H), 7.99 (s, 4H) ppm. $^{13}$C-NMR (D$_2$O) 6: 36.0 (t), 45.6 (q), 55.2 (t), 131.1 (d), 141.7 (s) ppm. The free Mannich base was obtained by dissolving the salt in water, addition of ammonia and extraction with CH$_2$Cl$_2$ (3x70 ml). The organic layers were washed with water, brine and dried (Na$_2$SO$_4$). Evaporation of the solvent afforded the free base as a white solid. mp: 85-87°C.

**Di-(2-ketopropyl)sulfide (3.50)**

A solution of Na$_2$S.9H$_2$O (120 g, 0.5 mol) in H$_2$O (300 ml) was added in 50 min to a refluxing solution of chloroacetone (3.49) (93 g, 1 mol) in EtOH (450 ml). The mixture was refluxed for another 30 min and the EtOH evaporated. The aqueous phase was extracted with CHCl$_3$ (2x150 ml), the combined organic layers washed with water, brine and dried (MgSO$_4$). Evaporation of the solvent gave an orange oil which was dissolved in 150 ml EtOH. Cooling to -20°C gave 58 g (40%) of 3.50 as white crystals mp: 45.4-47.1°C. $^1$H-NMR (CDCl$_3$) 6: 2.3 (s, 6H), 3.4 (s, 4H) ppm. $^{13}$C-NMR (CDCl$_3$) 6: 28.1 (q), 41.4 (t), 202.4 (s) ppm.

**2,5-Diacetyltiolaphene (3.52)**

A suspension of glyoxal trimer dihydrate (14.4 g) in ethanol (250 ml) was refluxed for 1 h affording monomeric glyoxal (3.51) and to the clear solution) of sulfide 3.50 (25 g, 171 mmol was added. To this solution a NaOEt solution (freshly prepared from Na (4.3 g) in EtOH (250 ml)) was added dropwise. The solvent was evaporated and water added. This dark colored mixture was extracted with CHCl$_3$ (2x150 ml). The organic layers were washed with water, brine and dried (MgSO$_4$). Evaporation of the solvent and chromatography (silica, CH$_2$Cl$_2$/pentane 1:1) gave 14.1 g (49%) of 3.52 as a slightly yellow solid, mp 170.1-172.6°C (lit$^{39}$: 171.5-172°C) $^1$H-NMR (CDCl$_3$) 6: 2.2.5 (s, 6H), 7.7 (s, 2H) ppm. $^{13}$C-NMR (CDCl$_3$) 6: 26.9 (q), 131.9 (d), 148.9 (s), 190.7 (s) ppm.

**[2,2’]-Bithienyl (3.54)**

To a solution of thiophene (16 ml, 200 mmol) in ether (100 ml) was added n-Buli (2.2 M, 90 ml) over a period of 0.5 h. After the spontaneous reflux had subsided, the mixture was stirred for an additional 0.5 h and cooled to -90°C. Anhydrous CuCl$_2$ (28 g, 208 mmol) was added at once, and the mixture was allowed to warm up. The temperature rose rapidly from -60°C to 0°C, and at RT the mixture was poured into cold diluted HCI (200 ml). The layers were seperated, and the aqueous phase extracted with ether (2x 100 ml). The combined organic layers were washed with water, brine and dried (Na$_2$SO$_4$). The solvent was evaporated and the residue distilled (kugelrohr, 90°C Imm Hg). This afforded 10.1 g (76%) of 3.54 as a off-white solid. mp: 32-33°C. (lit: 33°C$^{53}$)

**5,5'-Diacetyl-[2,2']-bithienyl (3.55)**

A mixture of [2,2’]-bithienyl (3.54) (4.7 g, 28 mmol) in acetic anhydride (60 ml) was heated to reflux, and 4 drops of H$_3$PO$_4$ (85%) were added. The resulting dark mixture was refluxed for an 1 h, poured into ice-

---

water (300 ml) and extracted with CH$_2$Cl$_2$ (3 x 100 ml). The combined organic layers were washed with water, a NaHCO$_3$ solution, brine and dried (Na$_2$SO$_4$). Most of the solvent was evaporated and the residue filtered (silica, CH$_2$Cl$_2$). The resulting solid was recrystallized from dioxan to give 2 g (28%) of 3.55 as a yellow solid, mp: 230-232°C (lit$^4$ 233.5-234°C). The motherlqour contained the monoacylated derivative, which was purified by distillation (kugelrohr) to give 1.26 g (22%) of the monoacylated product.

$5,5'$-Bis-(3-dimethylaminopropionyl)-[2,2']-bithienyl (3.56)

A mixture of $5,5'$-diacetyl-[2,2']-bithienyl (3.55) (1.6 g, 6.4 mmol), NHMe$_2$.HCl (1.05 g, 12.8 mmol), paraformaldehyde (385 mg) and HCl (conc, 0.3 ml) in DMF (200 ml) was stirred at 90°C for 6 h. After cooling to RT the solid was collected, washed with acetone and dried. This afforded 2.23 g (80%) of 3.56 as a yellow solid. The free Mannich base was obtained by dissolving the salt in water, addition of ammonia and extraction with CH$_2$Cl$_2$ (3x70 ml). The organic layers were washed with water, brine and dried (Na$_2$SO$_4$).

$^1$H-NMR (CDCl$_3$) $\delta$:2.22 (s, 12H), 2.69 (t, 4H), 2.99 (t, 4H), 7.02 (d, 2H), 7.57 (d, 2H).

$^{13}$C-NMR (CDCl$_3$) $\delta$: 37.2 (t), 45.3 (q), 54.3 (t), 125.8 (d), 132.5 (d), 143.7 (s), 191.4 (s).

2,5-Dibromo-3-dodecylthiophene (3.57)

3-dodecylthiophene (3.15) (20 g, 80 mmol) was dissolved in a mixture of CH$_2$Cl$_2$ (50 ml) and HOAc (50 ml) and cooled to 15°C. Br$_2$ (25.6 g, 160 mmol) in HOAc (50 ml) was added and the reaction mixture was stirred at 15°C for two days. It was poured into H$_2$O (500 ml) and the layers separated. The aqueous layer was extracted with CH$_2$Cl$_2$ (3x150 ml) and the combined organic layers were washed with H$_2$O, a NaHCO$_3$ solution, H$_2$O and brine. Drying (Na$_2$SO$_4$), evaporation of the solvent and distillation (kugelrohr) gave 30 g (91%) of 3.57 as a colorless oil. (bp: 170°C 0.05 mbar). $^1$H-NMR (CDCl$_3$) $\delta$:0.90 (t, 3H), 1.28 (m, 18H), 1.55 (m, 2H), 2.5 1 (t, 2H), 6.78 (s, 1H) ppm. $^{13}$C-NMR (CDCl$_3$) 6: 14.2 (q), 22.7 (t), 28.9 - 29.7 (t), 31.9 (t), 107.9 (s), 110.3 (s), 130.9 (d), 142.9 (s) ppm. Anal. calcd. for C$_{16}$H$_{26}$Br$_2$S: C 46.84, H 6.39, Br 38.95, S 7.81, found: C 46.85, H 6.35, Br 38.98, S 7.82.

2,5-Diacetyl-3-dodecylthiophene (3.58)

A solution of 2,5-dibromo-3-dodecylthiophene 3.57 (10.2 g, 25 mmol) in THF (200 ml) was cooled to -40°C and to the white suspension n-BuLi (1.6 M, 32 ml) was added. The mixture was warmed up to -30°C giving a yellowish slurry and kept at this temperature for 30 min. After cooling to -60°C freshly prepared CuCl (5 g) was added. The mixture was warmed up to 0°C changing to dark yellow and clear. AcCl (5 ml) was added and at 15°C the mixture was poured into ice-water and extracted with hexane (4x75 ml). The combined organic layers were washed with H$_2$O, a NaHCO$_3$ solution, H$_2$O, brine and dried (Na$_2$SO$_4$). The solvents were evaporated and the residue crystallized from hexane (100 ml cooling to -25°C) and MeOH affording 5.2 g (63%) of 3.58 as a yellow solid. mp: 51.9-53.2°C $^1$H-NMR (CDCl$_3$) $\delta$:0.85 (t, 3H), 1.23 (m, 18H), 1.58 (m, 2H), 2.54 (s,3), 2.56 (s,3), 2.93 (t, 2H), 7.50 (s, 1H) ppm. $^{13}$C-NMR (CDCl$_3$) $\delta$:14.0 (q), 22.5 (t), 26.8 (q), 29.2-30.1 (t, 29.7 (q), 31.8 (t), 134.9 (d), 140.8 (s), 144.7 (s), 150.4 (s), 190.8 (s), 191.3 (s) ppm. Anal. calcd. for C$_{20}$H$_{32}$O$_2$S: C 71.38, H 9.58, S 9.53, found: C 71.44, H 9.60, S 9.62.
5,5'-Diaetyl-3-dodecyl-[2,2'-]bithienyl (3.61)

A mixture of 3-dodecyl-[2,2'-]bithienyl (3.60) (5 g, 15 mmol), acetic anhydride (50 ml) and 85% H₃PO₄ (0.5 ml) was kept at 90°C for 3.5 h. The mixture was poured into H₂O (150 ml) and extracted with ether (3×100 ml). The combined organic layers were thoroughly washed with water, a NaHCO₃ solution, water, brine and dried (Na₂SO₄). the solvent was evaporated and the residue dissolved in hexane (75 ml). Cooling to -25°C gave 3.9 g of a yellow solid. This was chromatographed (silica) with hexane-ether (3:1) to give 300 mg of the mono acylated product and hexane-ether (1:1) giving the product. Recrystallization from hexane afforded 3.4 g (54%) of 3.61 as yellow crystals, mp: 64-67.1°C. ¹H-NMR (CDCl₃) δ:0.84 (t, 3H), 1.24 (m, 18H), 1.62 (m, 2H), 2.53 (s, 3H), 2.56 (s, 3H), 2.76 (t, 2H), 7.2 (d, 1H), 7.49 (s, 1H), 7.61 (d, 2H) ppm. ¹³C-NMR (CDCl₃) δ:13.9 (q), 22.5 (t), 26.4 (q), 29.1-29.4 (t), 30.1 (t), 31.7 (t), 127.4 (d), 132.5 (d), 134.8 (d), 137.8 (s), 141.9 (s), 142.1 (s), 143.1 (s), 144.4 (s), 190.1 (s), 190.2 (s) ppm. Anal. calcd. for C₂₆H₃₅O₃S₂: C 68.85, H 8.19, S 15.32, found: C 68.76, H 8.14, S 15.27.

To a mixture of 5,5'-diacetyl-3-dodecyl-[2,2']-bithienyl (3.61) (3 g, 14.4 mmol), dimethylamine.HCl (1.17 g, 14.4 mmol) and paraformaldehyde (431 mg, 14.4 mmol) in DMF (10 ml) was added 3 drops of HCI (conc). The solution was stirred at 70-80°C overnight and cooled. The solid was collected and washed with ether and acetone yielding 1.7 g (40%) of 3.62 as an instable yellow solid. ¹H-NMR (D₂O) (all peaks are broad) δ:0.75, 1.15, 2.70, 3.20, 6.96, 7.22, 7.51 ppm.

5,5'-Bis-(3-dimethylamino-propionyl)-3-dodecyl-[2,2'-]bithienyl (3.62)

To a mixture of 5,5'-diacetyl-3-dodecyl-[2,2']-bithienyl (3.61) (3 g, 7.2 mmol), dimethylamine.HCl (1.17 g, 14.4 mmol) and paraformaldehyde (431 mg, 14.4 mmol) in DMF (10 ml) was added 3 drops of HCl (conc). The solution was stirred at 70-80°C overnight and cooled. The solid was collected and washed with ether and acetone yielding 1.7 g (40%) of 3.62 as an instable yellow solid. 'H-NMR (D₂O) (all peaks are broad) δ:0.75, 1.15, 2.70, 3.20, 6.96, 7.22, 7.51 ppm.

5,5''-Diaetyl-3'-dodecyl-[2,2'';5',2'']-terthienyl (3.63)

A solution of 3'-dodecyl-[2,2'';5',2'']-terthienyl (3.11) (12 g, 29 mmol), acetic anhydride (7.5 g) and 85% H₃PO₄ (0.25 ml) was heated at 100°C for 1 h. The mixture was poured into water and extracted with CH₂Cl₂ (3×200 ml). The organic layers were washed with water, a NaHCO₃ solution, brine and dried (Na₂SO₄). The solvent was removed, the residue dissolved in MeOH and filtered over Al₂O₃ Chromatography (Al₂O₃, CH₂Cl₂) and crystallization from MeOH afforded 5 g (35%) of 3.63 as a yellow solid. mp: 90.4-90.8°C. ¹H-NMR (CDCl₃) δ:0.88 (t, 3H), 1.26 (m, 18H), 1.67 (m, 2H), 2.56 (s, 3H), 2.57 (s, 3H), 2.79 (t, 2H), 7.17 (m, 3H), 7.59 (d, 1H), 7.64 (d, 1H) ppm. ¹³C-NMR (CDCl₃) δ:14.0 (q), 22.6 (t), 26.4 (q), 26.5 (q), 29.2 (t), 29.3 (t), 29.4 (t), 29.5 (t), 30.1 (t), 31.8 (t), 124.3 (d), 126.3 (d), 128.5 (d), 130.7 (s), 132.6 (d), 133.1 (d), 142.4 (s), 142.6 (s), 143.3 (s), 143.7 (s), 144.6 (s), 190.0 (s), 190.2 (s) ppm. HRMS calcd. for C₂₈H₃₆O₂S₃: 500.188, found: 500.189.

5,5''-Bis-(3-dimethylamino-propionyl)-3''-dodecyl-[2,2'';5',2'']-terthienyl (3.64)

A mixture of 5,5''-diacetyl-3''-dodecyl-2,2'',5',2''-terthienyl (3.63) (3 g, 6 mmol), dimethylamine.HCl (1 g, 12.2 mmol), paraformaldehyde (380 mg, 12.2 mmol), HCl (conc, 0.5 ml) in DMF (50 ml) was heated at
100°C overnight. The mixture was cooled and the resulting solid was collected and washed with ether giving 2.9 g (70%) of 3.64 as a red solid. $^1$H-NMR (MeOD) δ: 0.63 (t, 3H), 1.01 (m, 18H), 1.40 (m, 2H), 2.54 (t, 2H), 2.71 (s, 12H), 3.05 (m, 8H), 7.05 (d, J=4.3 Hz, 1H), 7.08 (s, J=3.8 Hz, 1H), 7.11 (d, J=4.3 Hz, 1H), 7.67 (d, 1H), 7.21 (d, J=3.8 Hz, 1H) ppm. The free Mannich base was obtained by dissolving the salt in water, addition of ammonia and extraction with CH$_2$Cl$_2$ (3x70 ml). The organic layers were washed with water, brine and dried (Na$_2$SO$_4$). $^1$H-NMR (CDCl$_3$) δ: 0.87 (t, 3H), 1.26 (m, 18H), 1.67 (m, 2H), 2.29 (s, 12H), 2.77 (m, 6H), 3.07 (dt, 4H), 7.17 (m, 3H), 7.63 (d, 1H), 7.67 (d, 1H) ppm. $^{13}$C-NMR (CDCl$_3$) δ: 14.0 (q), 22.6 (t), 29.2 (t), 29.3 (t), 29.4 (t), 29.5 (t), 30.2 (t), 31.8 (t), 37.2 (t), 37.3 (t), 45.3 (q), 54.2 (t), 124.3 (d), 126.3 (d), 128.6 (d), 130.8 (s), 132.1 (d), 132.6 (d), 135.3 (d), 142.5 (s), 143.2 (s), 143.7 (s), 144.6 (s), 191.4 (s), 191.6 (s) ppm.

Pol-y-1,4-(phenyl-1,4-diyl)butane-1,4-dione (3.65)

1,4-Bis-(3-dimethylaminopropionyl)-benzene (3.48) (5.4957 g, 21.513 mmol, freshly prepared from the hydrochloride salt) and terephthaldehyde (2.8856 g, 21.315 mmol, recrystallized from water) were dissolved in DMF (80 ml). To the solution was added sodium cyanide (200 mg) and the dark colored mixture was stirred at RT overnight. After the addition of more DMF (50 ml) the viscous reaction mixture was stirred at 55°C for two days, during which time the product precipitated, and poured into water (400 ml). The resulting solid was collected and was with water, EtOH, CH$_2$Cl$_2$ and ether and dried. This afforded 5 g (81%) of 3.65 as a yellow solid. mp: > 250°C. IR (KBr) cm$^{-1}$: 1680 (s), 841 (m). $^{13}$C-NMR δ: 32.4 (t), 129.4 (d), 138.5 (s), 197.5 (s) ppm.

Poly-1,4-(1-H-pyrrol-2,5-diyl) phenylene (3.66)

Polyketone 3.65 (1.0 g) was heated with NH$_3$ in an autoclave for 16 h at 250°C and 9 bar. The apparatus was cooled and the NH$_3$ evaporated, affording 3.66 as a dark solid. IR (KBr) cm$^{-1}$: 1604 (m), 835 (m), 771 (m).

Poly-1,4-(thiophen-2,5-diyl)phenylene (3.67)

A mixture of polydiketone 3.65 (1.0 g), LR (2 g) and o-dichlorobenzene (30 ml) was refluxed for 2 days, and cooled. The resulting dark solid was collected and washed with EtOH, water and stirred overnight in 20% NaOH to remove last traces of LR. Washing with water, EtOH, CHCl$_3$ and acetone afforded 900 mg (90%) of 3.67 as a black solid. IR (KBr) cm$^{-1}$: 1595, (m), 832 (m).

Poly-5-(4-oxo-4-thiophene-2,5-diyl-butyryl)-5’-(4-oxo-butyryl)_[2,2’] -bithienyl (3.68)

As described for 3.65 with dialdehyde 3.46 (202.9 mg, 1.4482 mmol), bis mannich base 3.56 (527.9 mg, 1.4482 mmol), NaCN (10 mg, 0.2 mmol) in DMF (30 ml) and 4 days at RT, affording 600 mg (95%) of 3.68. IR (KBr) cm$^{-1}$: 1649 (s), 781 (m).
Poly(thiophen-2,5-diyl) (3.69)

As described for 3.67 with polydiketone 3.68 (450 mg), LR (1 g) in dichlorobenzene (50 ml). This afforded 400 mg (90%) of 3.69 as a dark brown-black colored solid. IR (KBr) cm⁻¹: 1026 (m), 789 (s).

Poly-1-(4-oxo-4-thiophene-2,5-diyl-butryrl)-4-(4-oxo-butyryl)phenylene (3.70)

As described for 3.65 with Mannich base 3.48 (1.1690 g, 5.4 mmol), dialdehyde 3.46 (757.2 mg, 5.4 mmol), NaCN (50 mg, 1 mmol) in DMF (30 ml), 3 days at RT and 1 night 70°C. Pouring into water gave an emulsion that upon the addition of HCl afforded 1.53 g (90%) 3.70 as a yellow brown solid. IR (KBr) cm⁻¹: 1678 (s), 1662 (s), 991 (w).

Poly-1,4-([2,2';5',2'']-terthiophen-5,5''-diyl)phenylene (3.71)

As described for 3.67 with polydiketone 3.70 (1.06 g), LR (2.5 g) and dichlorobenzene (100 ml), 60 h Reflux afforded 1 g (95%) of 3.71 as a brown solid. IR (KBr) cm⁻¹: 1659 (w), 1643 (w), 785 (s).

Poly-1,4-(3'-dodecyl-[2,2';5',2'']-terthiophen-5,5''-diyl)-butane-1,4-dione (3.72)

As described for 3.65 with dialdehyde 3.12 (2.1612 g, 4.572 mmol), Mannich base 3.64 (2.8115 g, 4.572 mmol), NaCN (40 mg, 0.8 mmol) in DMF (100 ml), 3 days at RT afforded 4.3 g (90%) of 3.70 as a red solid. IR (KBr) cm⁻¹: 2920 (s), 2849 (s), 1651 (s), 1435 (s), 1061 (m), 796 (m), 779 (m).

Poly-2,5-(3'-dodecyl-[2,2';5',2'']-terthiophen-5,5''-diyl)-1-H-pyrrole (3.73)

A mixture of polydiketone 3.72 (1 g), NH₄OAc (3 g) in dichlorobenzene (50 ml) was refluxed for 3 days. During the reaction NH₄OAc (1 g) was added daily (necessary due to the evaporation of some NH₃). The mixture was cooled, the solid collected and washed with EtOH and plenty of water, than again with EtOH and CHCl₃ affording 900 mg (90%) of 3.73 as a purple black solid with a green metallic luster. IR (KBr) cm⁻¹: 2918 (s), 2847 (s), 1578 (s), 1425 (s), 791 (s), 764 (s).

Poly-(3''-dodecyl-[2,2';5',2'';5'',2''']-quarthiophen-5,5'''-diyl) (3.74)

As described for 3.67 with polydiketone 3.72 (1 g), LR (2 g) in dichlorobenzene (50 ml) and 3 days reflux. This afforded 1 g of 3.74 as a purple black solid with a green metallic luster. The dichlorobenzene layer had a purple color (maximum 550 nm) but is after one reprecipitation from EtOH no longer soluble. IR (KBr) cm⁻¹: 2918 (s), 2849 (s), 1452 (m), 787 (s).

2-(Thiophen-2-yl)-2-methyl-[1,3]dioxolane (3.77)⁴⁴

A mixture of 2-acetyltiophene (3.76) (35.5 g, 132 mmol), ethylene glycol (89 g), p-TsOH (150 mg) in benzene (300 ml) was refluxed. The reaction was monitored by ¹H-NMR and continued until the acetyl signal had disappeared. This required a reaction time of 4 days. The mixture was cooled, 5% NaOH (100 ml)
was added and the layers separated. The organic phase was washed with water, brine and dried (Na$_2$SO$_4$). Evaporation of the solvent and recrystallization from pentane afforded 35.9 g (75%) of 3.77 as a white solid. mp: 31-32°C (lit$^{[44]}$ 32-33°C).

**5-Acetyl-thiophene-2-carbaldehyde (3.78)$^{[44]}$**

A solution of 3.77 (10 g, 59 mmol), n-BuLi (1.6 M, 40 ml), TMEDA (9 ml) in THF (350 ml) was stirred at -60°C for 3 h, cooled to -80°C and DMF (14 ml) was added. The mixture was allowed to reach RT overnight. Water (50 ml) was added and the THF evaporated. The aqueous phase was extracted with ether (4x50 ml) and the combined organic phases washed with brine and dried (MgSO$_4$). The solvent was evaporated and the oily residue stirred in HCl-water for 3 h. The resulting solid was collected and recrystallized from pentane-EtOAc, affording 8.3 g (91%) of 3.78 as a yellow solid. mp: 105.4-106.4°C (lit$^{[44]}$ 103-104°C).

**2-(3-Dodecyl-thiophen-2-yl)-2-methyl-[1,3]dioxolane (3.80)**

A mixture of 3-dodecylthiophene (3.15) (14 g, 56 mmol), 85% H$_3$PO$_4$ (1 ml) and acetic anhydride (80 ml) was kept at 70°C for 4.5 h. The resulting dark mixture was cooled to RT and poured into water and extracted with ether (3x150 ml). The combined organic layers were washed with water, a NaHCO$_3$ solution brine and dried (Na$_2$SO$_4$). The ether was evaporated and the crude compound, consisting of the 2- and the 5-acetyl-3-dodecylthiophene (3.77) was dissolved in benzene (150 ml). Ethylene glycol (10 ml) and p-TsOH (0.5 g) were added and the reaction mixture was refluxed overnight with azeotropic water removal by means of a Dean Stark trap. After cooling it was poured into a NaHCO$_3$ solution. The layers were separated and the aqueous phase extracted with ether (2x100 ml). The combined organic layers were washed with brine and dried (Na$_2$SO$_4$). Removal of the solvents and crystallization from hexane (cooling to -25°C) gave 6.6 g (35%) of 3.80 as a solid. $^1$H-NMR (CDCl$_3$) $\delta$: 0.89 (t, 3H), 1.28 (m, 18H), 1.58 (m, 2H), 1.75 (s, 3H), 2.69 (t, 2H), 3.93 (m, 2H), 4.04 (m, 2H), 6.86 (d, 1H), 7.08 (d, 2H) ppm. $^{13}$C-NMR (CDCl$_3$) $\delta$: 13.9 (q), 22.6 (t), 27.3 (q), 28.3 (t), 29.2 (t), 29.4 (t), 29.5 (t), 29.6 (t), 30.8 (t), 31.8 (t), 64.6 (s), 107.7 (d), 122.6 (d), 129.9 (d), 138.6 (s) ppm. The mother liquor mainly consisted of the other isomer that rapidly hydrolysed. $^1$H-NMR (CDCl$_3$) $\delta$: 0.91 (t, 3H), 1.29 (m, 18H), 1.62 (m, 2H), 1.78 (s, 3H), 2.56 (t, 2H), 4.02 (m, 4H), 6.82 (s, 1H), 6.90 (s, 1H) ppm.

**5-Acetyl-4-dodecyl-thiophene-2-carbaldehyde (3.81)**

To a solution of LDA (16 mmol) in THF (60 ml) at -70°C was added of the ketal 3.80 (4.45 g, 13 mmol). The temperature was kept below -20°C for 2 h cooled to -70°C and DMF (2 ml) was added. The mixture allowed to reach RT, hydrolysed with a NH$_4$Cl solution and the layers were separated. The aqueous phase was extracted with ether (3x50 ml), the combined organic layers were washed with water, brine and dried (Na$_2$SO$_4$). The solvents were evaporated and the residue was dissolved in acetone (100 ml). After 2N HCl (100 ml) was added the mixture was refluxed for 3 h. The acetone was evaporated and ether (100 ml) was added. The layers were separated and the aqueous layer was extracted with ether (2x50 ml). The combined organic layers were washed with water, a NaHCO$_3$ solution, brine and dried (Na$_2$SO$_4$). The solvent was removed and the residue crystallized from hexane affording 1.75 g (42%) of 3.81 as a yellow solid. mp: 52-
53.7°C. \(^1^H\text{-NMR (CDCl}_3\) δ: 0.85 (t, 3H), 1.25 (m, 18H), 1.59 (m, 2H) 2.55 (s, 3H), 2.97 (t, 2H), 7.61 (s, 1H), 9.93 (s, 1H) ppm. \(^1^3^C\text{-NMR (CDCl}_3\) δ: 6:13.9 (q), 22.5 (t), 29.2-29.9 (t), 29.7 (q), 138.1 (d), 141.4 (s), 143.7 (s), 150.2 (s), 183.3 (d), 191.4 (s) ppm. HRMS calcd. for C\(_{19}\)H\(_{30}\)O\(_2\)S: 322.197, found: 322.197.

5-Bromo-4-dodecyl-thiophene-2-carbaldehyde (3.83)

To a mixture of diisopropylamine (4 ml, 29 mmol) in THF (75 ml) at -20°C was added n-BuLi (2.5M, 11 ml). After cooling to -70°C 2-bromo-3-dodecylthiophene (3.82) (9 g, 27 mmol) was added and the mixture was kept between -70 and -40°C for 1.5 h. It was recooled to -75°C and DMF (4 ml) was added. The temperature was raised to -5°C and the reaction was quenched with a saturated NH\(_4\)Cl solution. The layers were separated and the aqueous phase extracted with ether (2x100 ml). The combined organic layers were washed with brine and dried (Na\(_2\)SO\(_4\)). Evaporation of the solvents gave 8.6 g (91%) of 3.83 of 95% purity (based on \(^1^H\text{-NMR}) which was used without further purification.

\(^1^H\text{-NMR (CDCl}_3\) δ: 0.84 (t, 3H), 1.23 (m, 18H), 1.57 (m, 2H), 2.55 (t, 2H), 7.42 (s, 1H), 9.71 (s, 1H) ppm. \(^1^3^C\text{-NMR (CDCl}_3\) δ: 13.9 (q), 22.5 (t), 28.9 (t), 29.1 (t), 29.2 (t), 29.3 (t), 29.4 (t), 31.7 (t), 121.7 (s), 136.5 (d), 143.7 (s), 181.4 (s) ppm.

A mixture of aldehyde 3.83 (8.2 g, 23 mmol), ethyleneglycol (5 ml) and p-TsOH in benzene (70 ml) was refluxed overnight with azeotropic water removal by means of a Dean-Stark trap. The cooled mixture was poured into a NaHC\(_2\)O solution and the layers were separated. The aqueous phase was extracted with ether (2x100 ml) and the combined organic layers were washed with water, brine and dried (Na\(_2\)SO\(_4\)). Removal of the solvents and crystallization from pentane with the aid of decolorizing charcoal afforded 8.5 g (93%) of 3.84 as white crystals. mp: 26.1-26.9°C. \(^1^H\text{-NMR (CDCl}_3\) δ: 0.95 (t, 3H), 1.32 (m, 18H), 2.52 (t, 2H), 3.95 (m, 4H), 5.89 (s, 1H), 6.78 (s, 1H) ppm. HRMS calcd. for C\(_{19}\)H\(_{31}\)BrO\(_2\)S: 402.123, found: 402.123.

4-(5-[1,3]Dioxolan-2-yl)-3-dodecyl-thiophen-2-yl)-4-oxo-butyric acid (3.85)

To a solution of acetal 3.84 (2 g, 5 mmol) in THF (10 ml) at -70°C was added n-BuLi (2.5M, 2 ml) and the temperature raised to -40°C. The mixture was cooled to -50°C and added to a mixture of succinic anhydride (3.27) (2 g, 20 mmol) in THF (20 ml) at -100°C. The temperature was allowed to reach RT overnight and poured into a NH\(_4\)Cl solution. The layers were separated and the aqueous phase extracted with ether (3x100 ml). The combined organic layers were washed with brine and dried (Na\(_2\)SO\(_4\)). Evaporation of the solvents and chromatography of the residue (silica, CHCl\(_3\)-EtOAc 9:1) gave 0.9 g (42%) of 3.85 as an off white solid. \(^1^H\text{-NMR (CDCl}_3\) δ: 0.86 (t, 3H), 1.23 (m, 18H), 1.75 (m, 2H), 2.74 (t, 2H), 2.92 (t, 2H), 3.14 (t, 2H), 4.05 (m, 4H), 6.05 (s, 1H), 7.03 (s, 1H) ppm. \(^1^3^C\text{-NMR (CDCl}_3\) δ: 6:13.9 (q), 22.5 (t), 27.9 (t), 29.1 (t), 29.3 (t), 29.4 (t), 29.9 (t), 303 (t), 31.7 (t), 35.7 (t), 65.1 (t), 99.6 (d), 129.7 (d), 134.3 (s), 145.9 (s), 150.7 (s), 178.5 (s), 190.9 (s) ppm. HRMS calcd. for C\(_{19}\)H\(_{32}\)O\(_2\)S: 324.211, found: 324.212.
This compound easily hydrolysed to afford 4-dodecyl-thiophene-2-carbaldehyde (3.87). $^1$H-NMR (CDCl$_3$) δ:0.85 (t, 3H), 1.25 (m, 18H), 1.60 (m, 2H), 2.61 (t, 2H), 7.34 (s, 1H), 7.56 (s, 1H), 9.83 (s, 1H) ppm. $^{13}$C-NMR (CDCl$_3$) δ:13.9 (q), 22.5 (t), 29.0 (t), 29.2 (t), 29.4 (t), 29.4 (t), 29.9 (t), 30.2 (t), 31.7 (t), 130.1 (d), 136.9 (d), 143.4 (s), 144.5 (s), 182.7 (d) ppm.

4-(3-Dodecyl-5-formyl-thiophen-2-yl)-4-oxo-butyric acid (3.88)

The acetal 3.85 was stirred in a water acetone HCl mixture for two h at RT. After most of the acetone was evaporated the aqueous phase was extracted with ether. The ether extracts were washed with water, brine and dried (Na$_2$SO$_4$). Evaporation of the solvent and crystallization from pentane gave 3.88 as a white solid. $^1$H-NMR (CDCl$_3$) δ:0.85 (t, 3H), 1.23 (m, 18H), 1.56 (m, 2H), 2.78 (t, 2H), 2.97 (t, 2H), 7.67 (s, 1H), 9.93 (s, 1H) ppm. $^{13}$C-NMR (CDCl$_3$) δ:14.0 (q), 22.5 (t), 27.8 (t), 29.2 (t), 29.3 (t), 29.5 (t), 29.9 (t) 30.1 (t), 31.8 (t), 36.1 (t), 138.1 (d), 140.5 (s), 143.8 (s), 150.7 (s), 178.4 (s), 183.4 (d), 191.6 (s) ppm. HRMS calcd. for C$_{21}$H$_{32}$O$_4$S: 380.202, found: 380.202.

3-Bromo-4-(3-dodecyl-5-formyl-thiophen-2-yl)-4-oxo-butyric acid (3.89)

To a hot solution of of the keto acid 3.88 (750 mg, 2 mmol) in CHC$_3$ (10 ml) was added 0.5 ml of a solution of Br$_2$ (400 mg) in CHC$_3$ (40 ml). After the color had disappeared, the rest of the bromine solution was added. After the reaction was completed (1 h) the mixture was poured into water, the layers separated and the aqueous phase extracted with CHC$_3$ (2x100 ml). The combined organic layers were washed with water (2x100 ml), brine and dried (Na$_2$SO$_4$). The solvent was evaporated and the oily residue treated with pentane giving 540 mg (60%) of 3.89 as an off white solid. mp 65.9-68.8°C. $^1$H-NMR (CDCl$_3$) δ:0.89 (t, 3H), 1.25 (m, 18H), 1.61 (m, 2H), 2.99 (m, 2H), 3.08 (dd, J=17.5 Hz, J=4.7 Hz, 1H), 3.52 (dd, J=15.4 Hz, J=9.4 Hz, 1H), 5.13 (dd, J=9.4 Hz, J=5.1 Hz, 1H), 7.65 (s, 1H), 9.97 (s, 1H), 10.92 (b, 1H) ppm. $^{13}$C-NMR (CDCl$_3$) δ:14.0 (q), 22.5 (t), 29.2 (t), 29.3 (t), 29.4 (t), 29.5 (t), 29.8 (t), 30.2 (t), 31.8 (t), 38.1 (t), 41.5 (d), 137.6 (s), 137.9 (d), 144.6 (s), 153.3 (s), 175.7 (s), 183.3 (d), 186.3 (s) ppm. HRMS calcd. for C$_{21}$H$_{31}$BrO$_4$S: 458.113, found: no exact mass could be determined, due to elimination of HBr, as indicated by the M/e 380 peak in the mass spectrum.