*Novel polythiophenes bearing fused redox-active components.*

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# Novel Polythiophenes Bearing Fused Redox-Active Components

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A thesis submitted in partial fulfilment of the
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for the degree of Doctor of Philosophy

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# ABSTRACT

This thesis is mainly concerned with the preparation of a range of novel poly(thiophene)s incorporating fused redox active substituents. Confirmation of the structure of the monomer units was carried out by NMR ($^{1}$H and $^{13}$C), mass spectral analysis, C,H,N analysis and where applicable, single crystal X-ray structural determination. Electrochemical studies on a number of the systems synthesised was also investigated, and voltammetric measurements were made using cyclic voltammetry.

The novel fused TTF-thiophene monomer 2,5-dibromothieno[3,4-*d*]-1,3-dithiole-2-ylidine-4,5-bis(hexylsulfanyl)-1,3-dithiole has been prepared and polymerised using Yamamoto methodology. The resulting polymer exhibits significant electrical conductivity in the neutral state and is the first example of an annelated TTF-thiophene polymer.

The development of terthiophene and bithienyl furan derivatives bearing the synthetically versatile 1,3-dithiole-2-thione functionality is also described, and conversion to a tetrathiafulvalene derivative via a phosphite mediated coupling reaction has been investigated. However, electropolymerisation of this system was unsuccessful which highlights unfavourable interactions arising between the two redox units. Synthesis of analogous terthiophene derivatives bearing a fused dithiino spacer group between the polythiophene chain and the 1,3-dithiole-2-thione moiety is also discussed.

A series of bis-substituted alkylsulfanyl terthiophene derivatives have been synthesised which can be electrochemically polymerised; a hexylsulfanyl derivative can also be polymerised chemically. Preliminary photoinduced absorption studies show that an ethylene bridged derivative exhibits interesting properties, which has been studied in collaboration with the Johannes Keppler University, Linz, Austria.

A polythiophene bearing a fused quinoxaline moiety has been prepared and electropolymerised to form polymer films which are capable of molecular recognition of transition metal cations. This is the first example of a conducting polymer which is able to detect selectively and reversibly $Hg^{2+}$ and $Ag^{+}$ ions in aqueous and organic media.

# ACKNOWLEDGEMENTS

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# CHAPTER 1

# INTRODUCTION

## 1.1 ORGANIC CONDUCTORS

### 1.1.1 INTRODUCTION

The concept that certain organic compounds in the solid state could conduct electricity and exhibit the electrical properties of a metal was first implied in the early part of this century.[1] Although the majority of organic compounds are electrical insulators in the ground state, there is an increasing number of materials that have been synthesised in which electrical conductivity has been observed.

Work in this field has been based mainly around the areas of conjugated polymers and charge-transfer complexes.

This thesis is primarily concerned with the synthesis of conjugated (polythiophene)s bearing fused redox active components, leading towards highly electroactive species.

### 1.1.2 REQUIREMENTS FOR CONDUCTIVITY

The movement of electrons (or ions) is essential for a material to conduct electricity. When a large number of atoms or molecules are brought together in the formation of a polymeric system or crystalline solid, an energy band occurs if there is sufficient interaction of atomic or molecular orbitals (figure 1). The occupancy of these bands is critical if the material is to exhibit metallic properties. Valence electrons (arising from the highest occupied molecular orbital [HOMO]) are responsible for electron conduction, and their mobility throughout the solid determines the efficiency of conduction within the material.

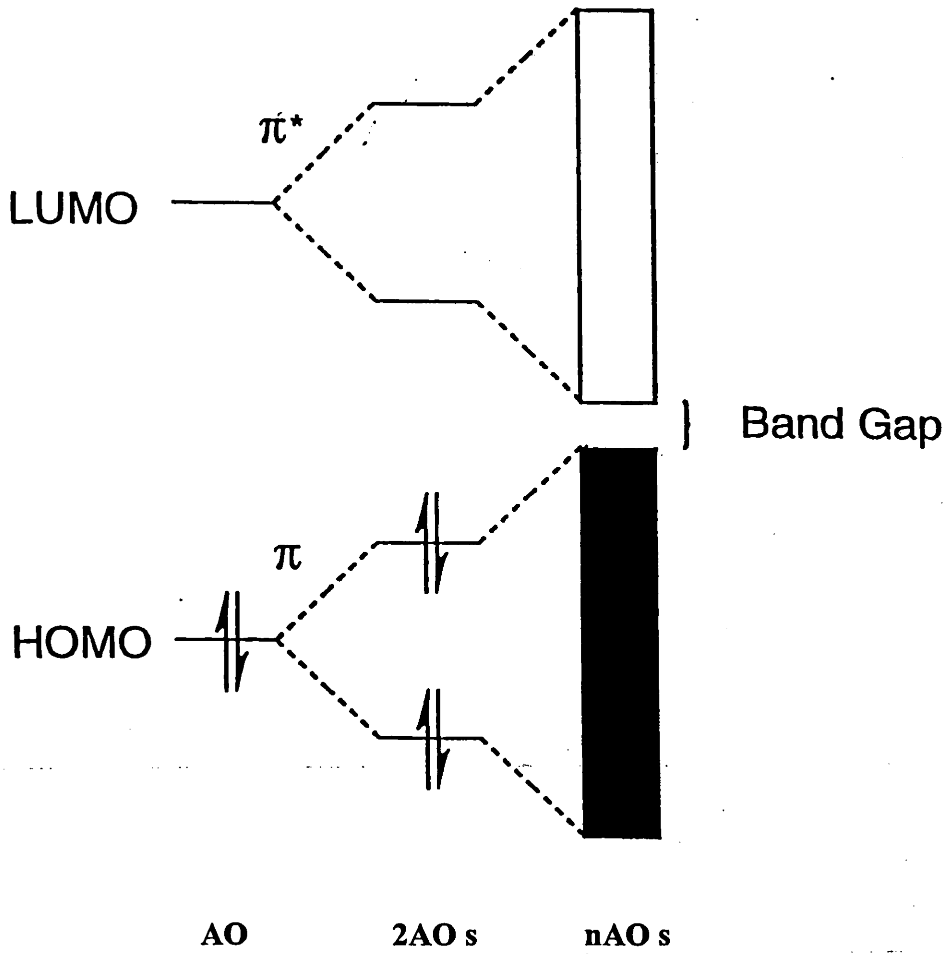


**Figure 1 : Formation of electronic bands upon interaction of atomic orbitals**

Upon excitation, electrons are promoted from the valence band across an energy gap (bandgap **Eg**) to the conductance band, the lowest unoccupied molecular orbital (LUMO). During relaxation, the electron falls back to the HOMO and emits energy equal to **Eg**.

The conducting and optical properties of conjugated organic polymers are dictated by the degree of bandgap separation within the material. Variation of the band energy in the neutral form is a major goal in the synthesis of conducting materials,[2] as this determines the optical and redox properties of such systems.

Too large an energy gap results in the material existing as an electrical insulator (e.g. diamond, **Eg** 4 eV). As the gap decreases, thermal excitation of electrons becomes possible and the material behaves as an intrinsic semiconductor (semi-conducting materials possess an energy gap of < 2 eV). Metallic behaviour is observed when the energy gap is negligible and the partially filled bands make it possible for a large number of electrons to be promoted easily into higher energy states within the band (figure 2).

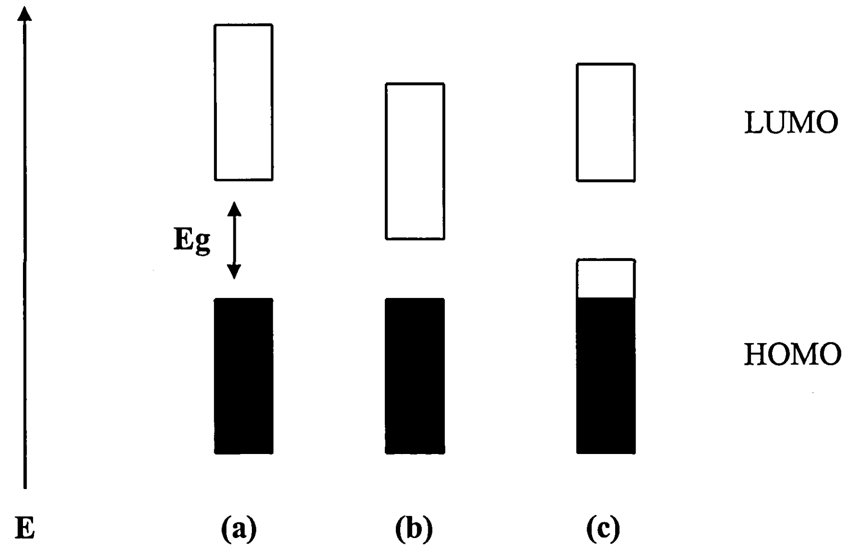


**Figure 2: Band diagrams for (a) an insulator (b) a semiconductor and (c) a metal**

Conductivity within organic and inorganic materials is temperature dependent. For metallic species, this is dominated by the interaction of electrons with lattice vibrations. Fewer vibrations arise when the temperature is lowered resulting in an increase in molecular orbital overlap, hence conductivity increases. An opposite effect is observed for semiconducting and insulating materials. The mobility of charge carriers within a semiconductor is the key to its conducting properties. As the temperature is lowered, fewer electrons can be promoted across the gap due to a lowering of energy. A decrease in the number of charge carriers results, hence a reduction in conductivity is observed. An increase in temperature induces a Boltzmann-type factor:

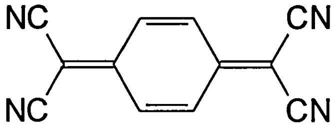
$$n \alpha e^{-Eg/kT}$$

where n = number of charge carriers which will increase if Eg is not greater than kT. In this instance, an increase in temperature leads to an increase in conductivity as a result of thermal excitation.

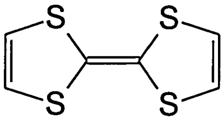
## 1.2 CHARGE TRANSFER COMPLEXES

Charge transfer (CT) complexes are formed by the interaction of a donor and an acceptor molecule through the partial transfer of an electron (systems of this nature usually form crystalline solids of alternating donor and acceptor stacks within the crystal lattice, and possess very interesting electrical properties).

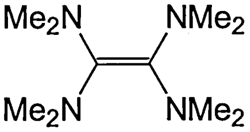
In the early 1960's, Melby and co-workers reported the synthesis and properties of the powerful electron acceptor 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ)[3] **(1)**. A series of charge transfer systems were prepared, including metal-TCNQ complexes and a wide range of salts of TCNQ with alkylammonium, aromatic and heterocyclic cations. These complexes showed semiconductor characteristics ($\sigma$ rt $\approx 10^{-5}\ \Omega^{-1}\ \mathrm{cm}^{-1}$), thus providing the first examples of organic materials exhibiting electrical conductivity.[4] The synthesis of the electron donor tetrathiafulvalene **(2)** was first reported in 1970 by Wudl *et al.*[5] This was developed with the intention of synthesising a more efficient reducing agent than tetrakis(dimethylamino)ethylene **(3)**.



**TCNQ (1)**



**TTF (2)**



**(3)**

Although TTF proved to be a poorer donor than **(3)**, due to the greater electron withdrawing nature of the sulfur atoms compared to the nitrogen atoms with respect to the double bond, the system afforded more stable radical cations than those derived from (3).

The cyclic voltammogram of TTF shows two reversible oxidation peaks at $E^{1/2} = +0.34$ V and $E^{1/2} = +0.71$ V (in acetonitrile vs. Ag/AgCl) which is due to sequential formation of radical cation and dication species (figure 5).

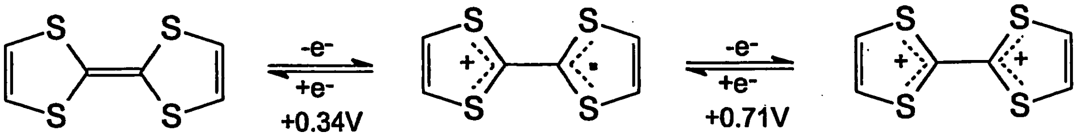


**Figure 3: Redox behaviour of TTF**

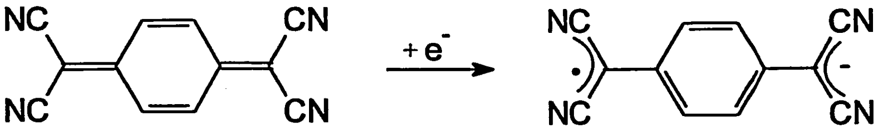


**Figure 4: Radical ion formation of TCNQ**

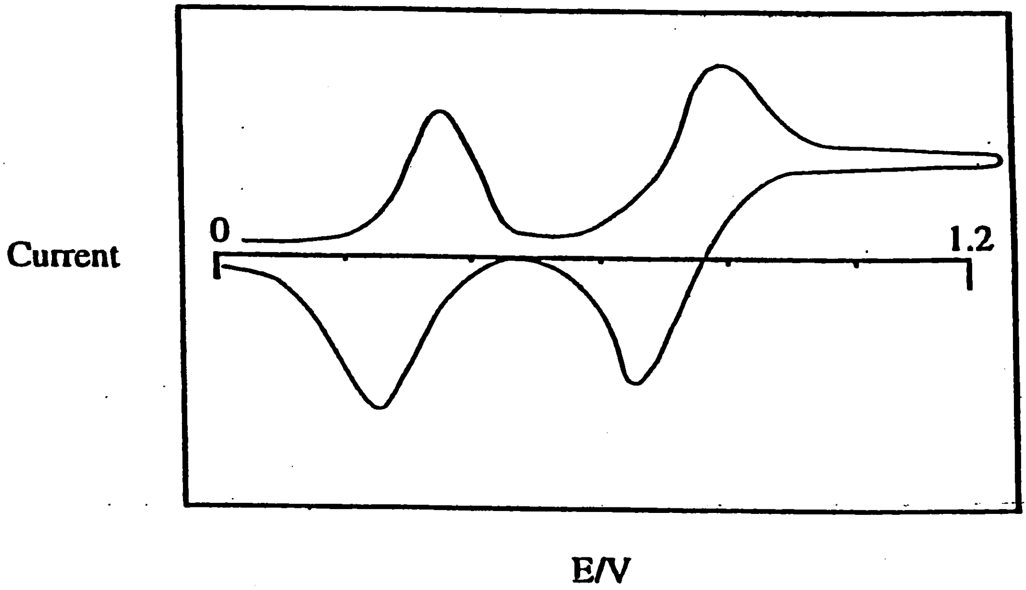


**Figure 5: Cyclic voltammogram of TTF**

The transfer of an electron from a donor species to a neutral acceptor molecule (e.g. TCNQ) results in the formation of the corresponding radical anion (figure 4). During this process, the energy level of the HOMO increases to form a partially filled band. Electrons can then be easily promoted to the LUMO, hence conduction arises. In a donor species, the loss of an electron lowers the energy level of the LUMO, and again conductivity occurs as a result of electron promotion (figure 6).

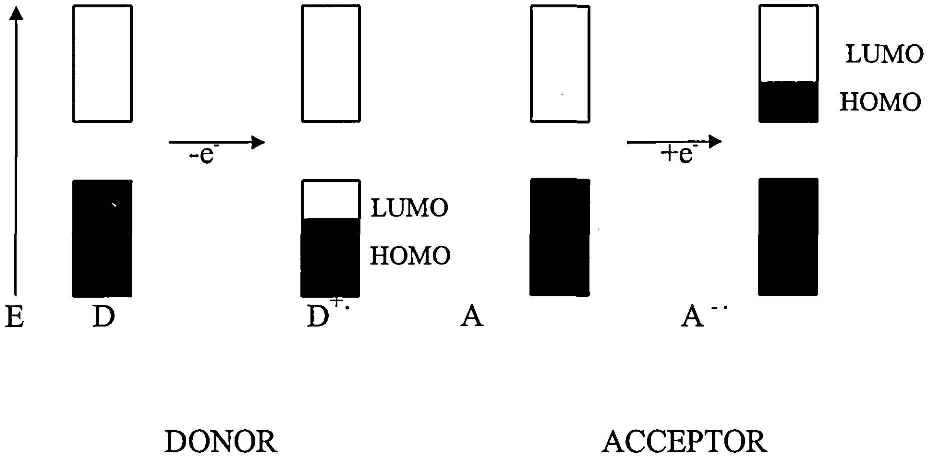


**Figure 6: Band diagram for Charge-Transfer complex formation**

In 1972, the chloride salt of TTF was reported[5] (figure 7). This interesting new donor was found to be an organic semiconductor exhibiting a conductivity value of 0.2 $\Omega^{-1}$ $cm^{-1}$ at room temperature,[6] and in 1973 the charge transfer complex $TTF^{+\cdot}$ -$TCNQ^{-\cdot}$ was reported by Ferraris and co-workers.[7] The complex was found to exhibit metallic characteristics at room temperature with a conductivity value of 500 $\Omega^{-1}$ $cm^{-1}$. Thus, synthetic organic 'metals' had become a reality. The crystal structure[8] of the complex shows a 1:1 stoichiometry with the radical cations of TTF and the radical anions of TCNQ aligning in segregated stacks (figure 8). Within these stacks, the molecules are arranged in such a way that an efficient intermolecular overlap is ensured and intrastack interactions arise with the exocyclic C-C double bond lying over the ring of its adjacent molecule in the stack, resulting in extensive π-interactions.

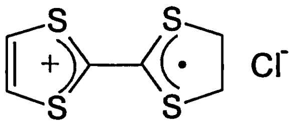


Figure 7: Chloride salt of TTF

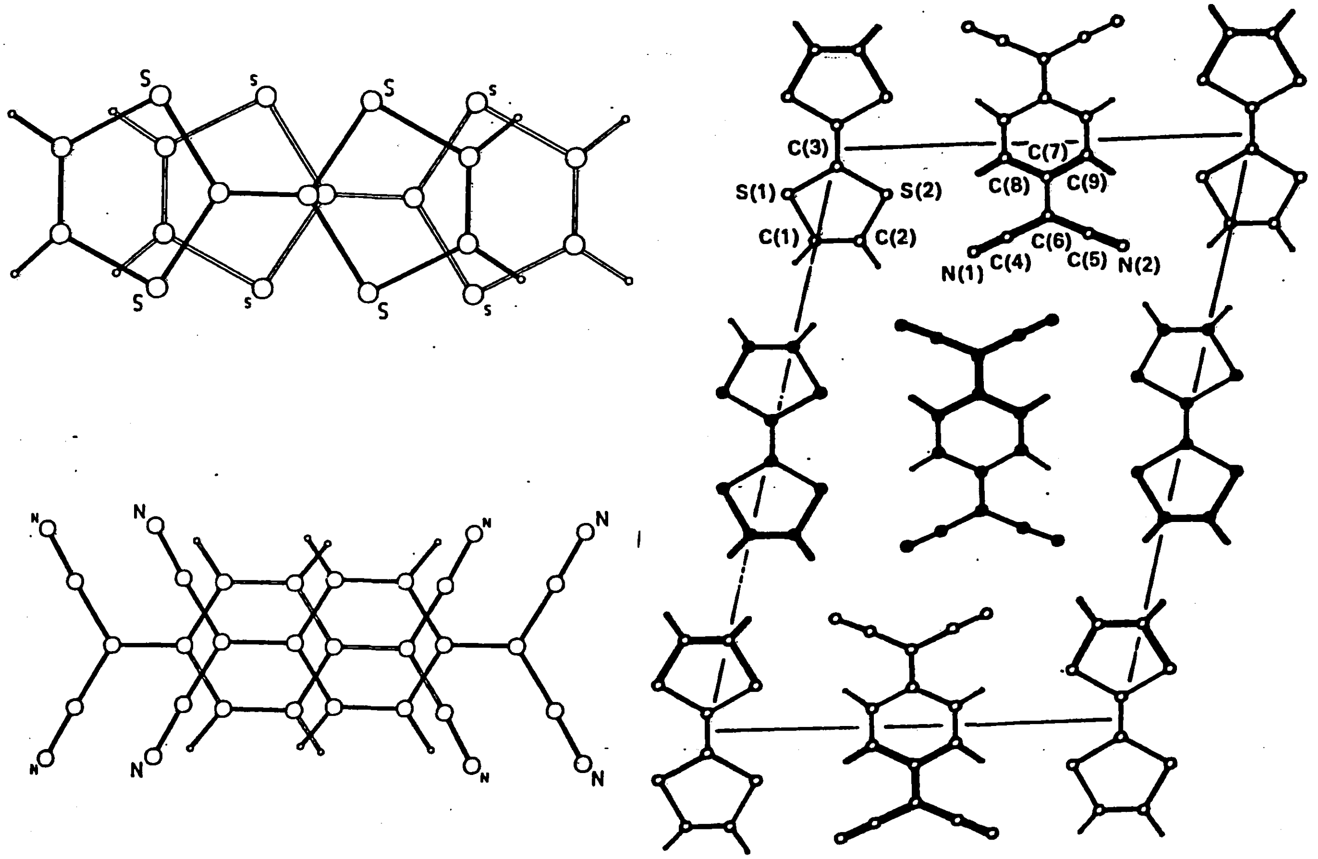


Figure 8: X-Ray crystal structure of TTF-TCNQ

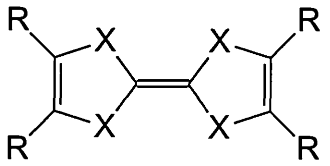
X-ray scattering techniques[9] and infra-red analysis[10] show that only 0.59 electrons are transferred from each TTF molecule to TCNQ, and metallic conductivity is observed between both stacks due to the formation of partially filled electron bands as a result of incomplete charge transfer. This charge transfer salt was metallic down to 54 K, and was known as the first true organic metal. On further cooling, the complex undergoes a series of phase transitions (at 53, 47 and 38 K).[11] These transitions were first considered by Peierls[12] and Fröhlich[13] in the mid-1950's, who predicted that a one-dimensional metal could not support long range order and would be unstable to lattice distortions. Charge transfer complexes can be either single chain conductors (where the anion is a closed shell species i.e. $PF_6^-$), or two chain conductors, as is observed for

TTF-TCNQ. The complexes formed contain stacks of molecules that are open shell radicals. Partially filled bands form which are capable of anisotropic (one-dimensional) conductivity along the direction of the stacks. Whenever radicals are present, there is always a driving force for dimerisation, and spin pairing may arise. This results in the emergence of a gap (Peierls gap) which separates bonding and antibonding energy levels. Metallic conductivity is reduced and the complex becomes either semiconducting or insulating. As dimerisation occurs, formation of a charge density wave becomes apparent. Alternating zones of high and low charge density results and a 'wave' is formed.

This phenomenon is commonly known as the Peierls distortion, and is restricted to one dimensional systems such as TTF-TCNQ which, as observed, eventually results in an insulating state at reduced temperatures.

Since the discovery of TTF in 1970, many analogous π-donor systems have been synthesised by the derivatisation of TTF with varying substituents along with replacement of sulfur by other chalcogens.

Tetraselenafulvalene (TSF) **(4)**[14] and tetratellurafulvalene (TTeF) **(5)**[15] exhibit higher conductivity values upon complexation with TCNQ (700-800 $\Omega^{-1}$ $cm^{-1}$ for TSF, and 2000 $\Omega^{-1}$ $cm^{-1}$ for TTeF), compared to that of TTF-TCNQ ($\sigma$ rt. = 500 $\Omega^{-1}$ $cm^{-1}$), although the synthesis of these derivatives is much more chemically demanding. This increase in conductivity may be assigned to an improvement in donor π-interactions, promoted by the increasingly diffuse p and d orbitals of the selenium and tellurium atoms, resulting in enhanced delocalisation throughout the molecule.



**(4) TSF, R = H, X = Se**

**(5) TTeF, R = H, X = Te**

**(6) TMTTF, R = Me, X = S**

**(7) TMTSF, R = Me, X = Se**

**(8) TMTTeF, R = Me, X = Te**

Extending the σ-bond framework of these systems with methyl groups afforded tetramethyl-TTF[16] **(6)** and tetramethyl-TSF[17] **(7)**. The analogous derivative of tetratellurafulvalene **(8)** was reported in 1985[18] but there have been no further developments concerning this system reported in the literature.

Bechgaard *et al*[19] synthesised a series of salts of TMTSF through the variation of anion species. These have the general formula $(TMTSF)_2X$ (where X = $PF_6^-$, $AsF_6^-$, $FSO_3^-$, $ReO_4^-$, and $ClO_4^-$), and in 1980 the first organic superconductor $(TMTSF)_2^{+}PF_6^-$ was synthesised which showed superconductivity at 0.9 K, 12 Bar.

A structural feature of the Bechgaard salts is the 'zig zag' stacking arrangement of the TMTSF moiety in sheets separated by anions with inter and intrastack contacts of selenium atoms. The structure of $(TMTSF)_2^+PF_6^-$ shows a pseudo two dimensional structure (figure 9), rather than one-dimension as is observed for TTF-TCNQ. The salts also have the advantage in that Peierls distortion is more likely to be suppressed; spin density wave instabilities dominate the low temperature properties within these systems.

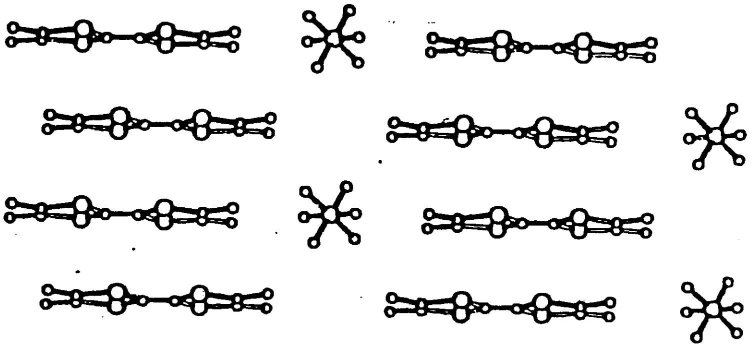
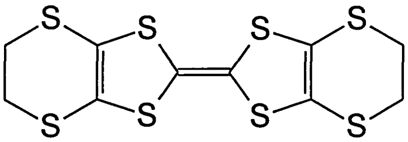
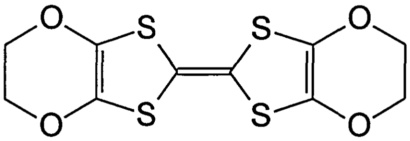


**Figure 9: X-Ray crystal structure of $(TMTSF)_2^+PF_6^-$**

Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) **(9)** was first synthesised in 1977,[20] and a number of salts have been prepared from this donor system, with several proving to be superconductors (conductors with zero resistance) at ambient pressure. Examples include $\beta(BEDT\text{-}TTF)_2I_3$[21] where superconductivity was observed at 1.4 K at ambient pressure, and $(BEDT\text{-}TTF)_2IBr_2$[22] which possesses a $T_c$ (critical temperature that the material undergoes the transition to a superconducting state) of 2.6 K under similar conditions.



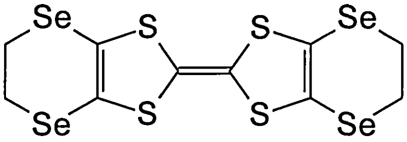
**BEDT-TTF (9)**



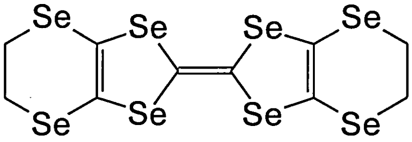
**BEDO-TTF (10)**

The oxygen analogue of BEDT-TTF, BEDO-TTF **(10)** was reported in 1990 by Wudl *et al*[23] through the substitution of the two peripheral sulfur atoms by oxygen. The charge transfer complex $(BEDO\text{-}TTF)_3Cu_2(NCS)_3$[24] formed from this donor possessed a $T_c$ of 12.5 K which, although inferior to BEDT-TTF salts, was the first organic superconductor containing oxygen.

Selenium analogue donors were reported in the mid 1980's, however complexes formed from BEDS-TTF **(11)**[25] and BEDS-TSF **(12)**[26] did not exhibit superconducting properties.



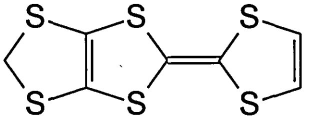
**BEDS-TTF (11)**



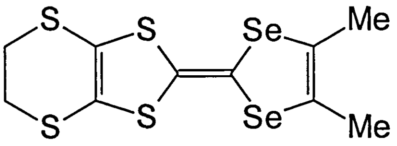
**BEDS-TSF (12)**

Unsymmetrical donor systems have also been synthesised. MDT-TTF[27] **(13)** was reported in 1988 by Papavassiliou *et al* and DMET[28] **(14)** was reported by Kikuchi and co-workers in the same year.

Both donors form superconducting salts, for example $(MDT\text{-}TTF)_2AuI_2$[29] ($T_c$ at 4.5 K) and $(DMET)_2AuBr_2$[28] ($T_c$ of 1.9 K) at ambient pressure illustrating that symmetry is not necessary in order for a species to be superconducting. In fact, the symmetrical donors of these systems are simply charge transfer materials.

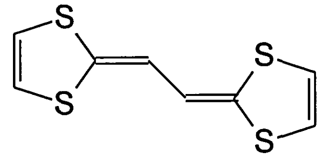


**MDT-TTF (13)**

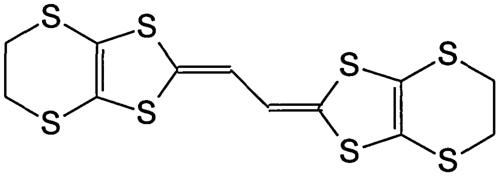


**DMET (14)**

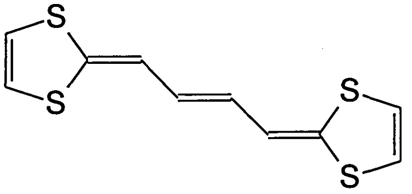
Vinylogous tetrathiafulvalene π-electron donors have also been prepared. The idea behind the introduction of a spacer group between the two 1,3-dithiole rings in TTF was to reduce the intramolecular coulombic repulsion of the dication state.[30] Ethanediylidene-2,2′-bis(1,3-dithiole) **(15)** was prepared by Yoshida and co-workers in 1983[31].



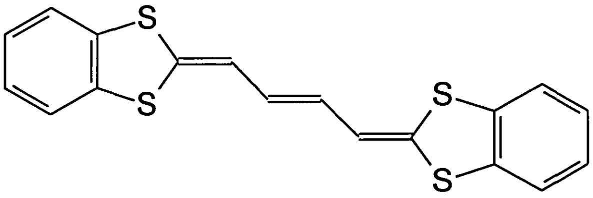
**(15)**



**(16)**



**(17)**



**(18)**

The BEDT vinylogue **(16)** was prepared concurrently by three different groups.[32]

The redox behaviour of these systems has been studied by cyclic voltammetry and is summarised in table 1. These derivatives of TTF display lower first and second ionisation potentials than their parent molecules.

|  | $E1^{1/2}$ | $E2^{1/2}$ | ΔE |
|---|---|---|---|
| **TTF**[a] | 0.34 | 0.71 | 0.37 |
| **(15)**[a] | 0.20 | 0.36 | 0.16 |
| **BEDT-TTF**[b] | 0.59 | 0.99 | 0.40 |
| **(16)**[b] | 0.48 | 0.71 | 0.23 |
| **(17)**[a] | 0.22 | ....... | ....... |
| **(18)**[a] | 0.47 | ....... | ....... |

**Table 1: Cyclic voltammetry data for TTF (1), BEDT-TTF (9) and donors (15) - (18). Pt electrode vs. Ag/AgCl, supporting electrolyte $Et_4NClO_4$, 0.1M, 20°C in (a) $CH_2Cl_2$ (b) $CH_3CN$**

The results obtained confirm that the insertion of C $sp^2$ derived spacer groups into the central bonds of these systems promotes the formation of the dication state at lower potentials. However, the introduction of a second pair of $sp^2$ carbon atoms did not lead to a further reduction in the redox values. A single two electron oxidation was observed for **(17)**[33] and **(18)**[34] at + 0.22 V and + 0.47 V respectively, where the dithiole rings act independently of each other resulting in a single redox process.

In summary, many symmetrical, unsymmetrical and 'stretched' tetrachalcogenafulvalenes have been synthesised which form highly conducting charge transfer materials. The presence of substituents attached to these donor systems determines the redox behaviour of these materials, with a number exhibiting superconducting properties at low temperatures.

## 1.3 CONDUCTING POLYMERS

### 1.3.1 INTRODUCTION

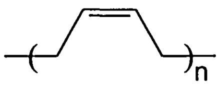
The synthesis of electrically conducting organic polymers has become a major challenge within the field of materials chemistry, and systems of this nature are being incorporated into a variety of commercial applications such as batteries, chemical and biological sensors and light emitting diodes.[35]

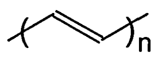
An ideal conducting polymer should be an ordered, linear system assembled from repeating units consisting of delocalised $\pi$-electrons such that there is no interruption of conjugation. Processability of polymers is a problem within the field of organic conductors, due to the insolubility of the materials produced. However, many polymeric systems have been prepared which are soluble, processable and exhibit high conductivities. The polymers synthesised contain extensive $\pi$-delocalisation within the conjugated backbone in the hope that a narrow bandgap separation will be achieved.

A brief outline follows of some of the conjugated polymeric systems that have been synthesised to date.

### 1.3.2 POLYACETYLENE

Polyacetylene **(19)** is the simplest of the conjugated polymers and has served as a model in the development of both the physical and electronic properties of many electrically conducting systems. Polyacetylene can exist in two isomeric forms; (a) *cis* and (b) *trans*. The *cis* isomer can be prepared at low temperatures, but at room temperature or above, this isomerises to the more thermodynamically stable *trans* form. In its pure state, polyacetylene exhibits a room temperature conductivity of $10^{-7}$-$10^{-5}$ $\Omega^{-1}$ $cm^{-1}$ [36]. Polyacetylene was first prepared in 1958 by Natta *et al* via the polymerisation of acetylene in hexane with an $Al(Et)_3$ or $Ti(OPr)_4$ initiator[37] which formed a linear, high molecular weight polyconjugated polymer of high crystallinity and regular structure.



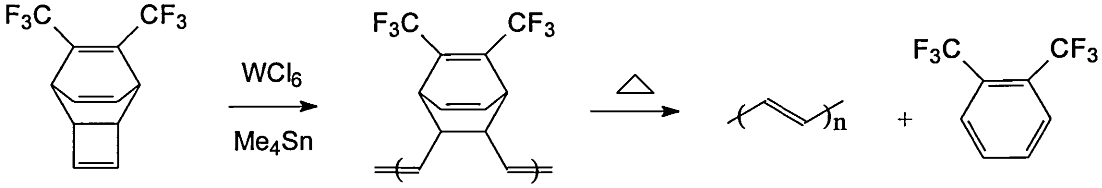


***cis* polyacetylene** **(19)** ***trans* polyacetylene**

Polyacetylene was initially considered of little interest due to its infusibility and insolubility, along with its susceptibility to rapid atmospheric degradation. However, in the early 1970's, a new phase in the development of polyacetylene began. Shirakawa and co-workers[38] developed a simple method based on Natta's work for the preparation of the polymer, involving polymerisation of acetylene at the surface of a high concentration of initiator in an inert solvent. Upon oxidative doping of **(19)** with halogens or $AsF_6$, the material exhibited significant electrical conductivity ($10^2\,\Omega^{-1}\,cm^{-1}$).[39]

Although high conductivity values were observed, the preparation of polyacetylene via this route resulted in the polymer containing impurities from the polymerisation catalysts employed. In order to remedy this, synthesis via a soluble precursor polymer was developed.

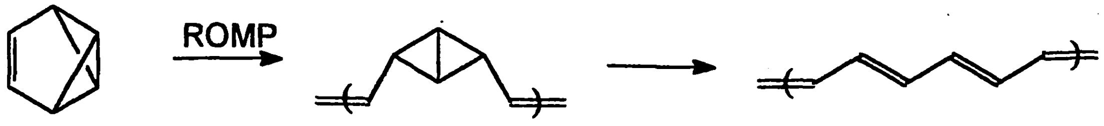
In 1985, the Durham route to polyacetylene was reported by Feast *et al.*[40] This synthetic route incorporates a ring opening metathesis polymerisation of 7,8-bis(trifluoromethyl)tricyclo[4.2.2.0]deca-3,7,9-diene **(20)**. The reaction takes place in the presence of a tungsten or tin initiator to form soluble precursor **(21)**, which undergoes thermal conversion to produce polyacetylene,[41] with the evolution of 1,2-bis(trifluoromethyl)benzene **(22)** (scheme 1).



**(20)** **(21)** **(19)** **(22)**

**Scheme 1: Durham route to polyacetylene**

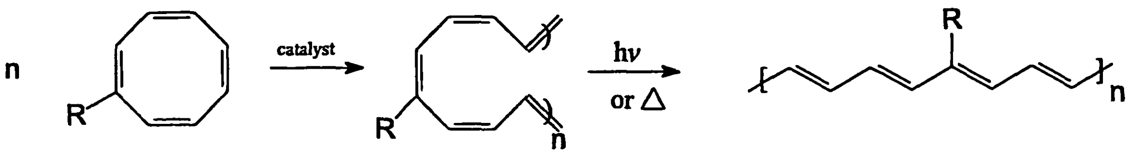
Another synthetic route devised by Swager and co-workers[42] involved a ring opening metathesis polymerisation (ROMP) of benzvalene **(23)** with subsequent catalytic isomerisation to polyacetylene. The production of volatile by-products is avoided in this route, and a polymer of low crystallinity is produced (scheme 2).



**(23)** **(24)** **(19)**

**Scheme 2: Swager's route to polyacetylene**

However, in general, polyacetylene is insoluble, infusible and a generally intractable material irrespective of the synthetic methods employed. In order to isolate a soluble polyacetylene, monosubstituted derivatives have been prepared. Conductivity values for such systems are lower than for polyacetylene itself (before doping $10^{-15}\ \Omega^{-1}\ \mathrm{cm}^{-1}$, after doping $10^{-5}$ -$10^{-3}\ \Omega^{-1}\ \mathrm{cm}^{-1}$)[43] and a lower polymer conjugation length is observed. Grubbs and co-workers demonstrated the synthesis of a substituted polyacetylene derivative **(25)** by the ring opening metathesis polymerisation of cyclooctatriene derivatives leading to systems that were both soluble and highly conjugated[44] (scheme 3).



**(25)** **(19)**

**Scheme 3 : Grubbs route to polyacetylene**

Doped polyacetylene can now be produced which is essentially as conducting as copper, with conductivity values as high as 8000 $\Omega^{-1}\ \mathrm{cm}^{-1}$, the highest room temperature conductivity obtained for any organic material.[45]

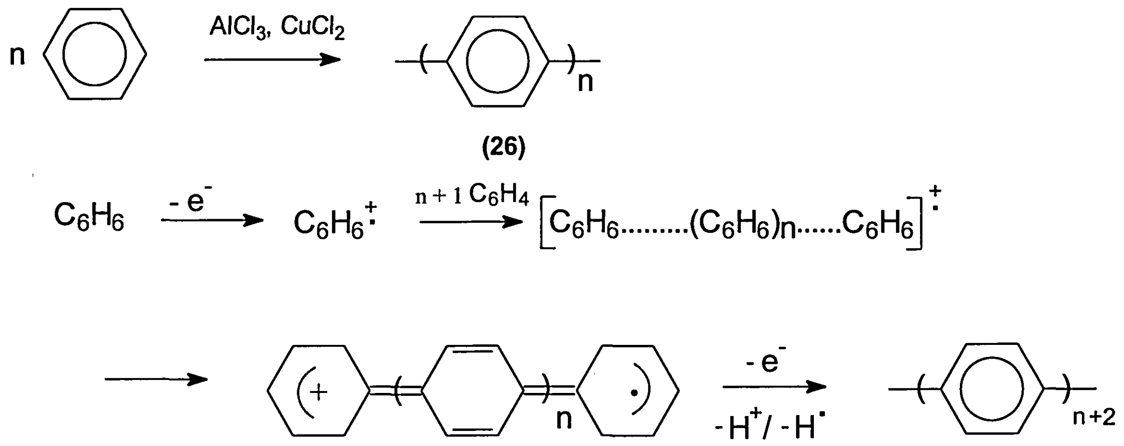
The rigidity of the backbone of polyacetylene holds the key to its high conductivity and has therefore been the basis of the design of a large number of conducting polymers which have been synthesised over the last 20 years.

### 1.3.3 POLY(PHENYLENE)S

Poly(phenylene) **(26)** represents the simplest of the polyaromatic hydrocarbons and is an insoluble, intractable, rigid rod polymer. In its pristine form, poly(*p*-phenylene) exhibits a conductivity value of $10^{-12}$ $\Omega^{-1}$ $cm^{-1}$, and upon doping with $AsF_5$, this dramatically increases to 500 $\Omega^{-1}$ $cm^{-1}$.[46]

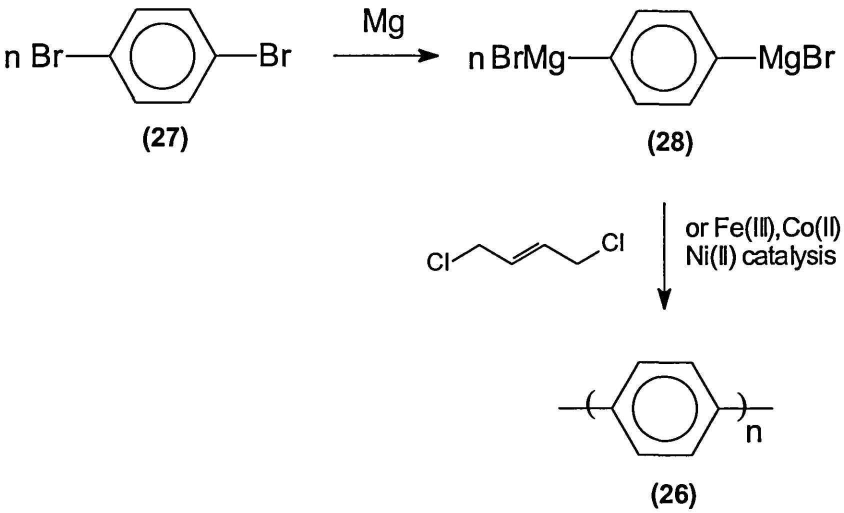
The preparation of polyphenylenes is based mainly around four synthetic routes; (a) oxidative coupling, (b) organometallic coupling, (c) dehydrogenation of polycyclohexylenes and (d) cycloaddition reactions.

In 1963, Kovacic and Kyriakis[47] reported the synthesis of poly(*p*-phenylene), which was achieved by the oxidative coupling of benzene in the presence of the Lewis acid catalyst $AlCl_3$, and oxidant $CuCl_2$ at 25-35 °C (scheme 4). The process is thought to occur via a one electron oxidation of benzene to form its radical cation, followed by reaction with several benzene molecules to form an oligomeric radical cation. A further oxidation process follows with the loss of two protons resulting in aromatisation of the terminal rings, with subsequent oxidative rearomatisation of the dihydro structures by $CuCl_2$ to yield the polymer.[48]



**Scheme 4: Oxidative coupling of benzene to form PPP (26)**

The preparation of poly(phenylene)s via a Grignard coupling reaction was reported in the early 1970's by Kovacic and co-workers.[49] This method incorporates the synthesis of a mono-Grignard reagent from dihalobenzene **(27)** with subsequent polymerisation in the presence of an organometallic or organic promoter,[50] and has been used in the synthesis of a range of *para* and *meta* substituted PPPs [51] (scheme 5).



**Scheme 5: Grignard route to PPP (26)**

Poly(*p*-phenylene) can also be prepared from diester derivatives of 5,6-dihydroxy-1,3-cyclohexadiene. The reaction proceeds via a radical process using AIBN or benzoyl peroxide, with subsequent pyrolysis of the polycyclohexylene derivative formed to PPP.[39,52] 1,4-Cycloaddition reactions between a bis-cyclopentadiene and a bis-acetylene have also been used in the synthesis of high molecular weight polymers with equal *para* and *meta* substitution.[49,53]

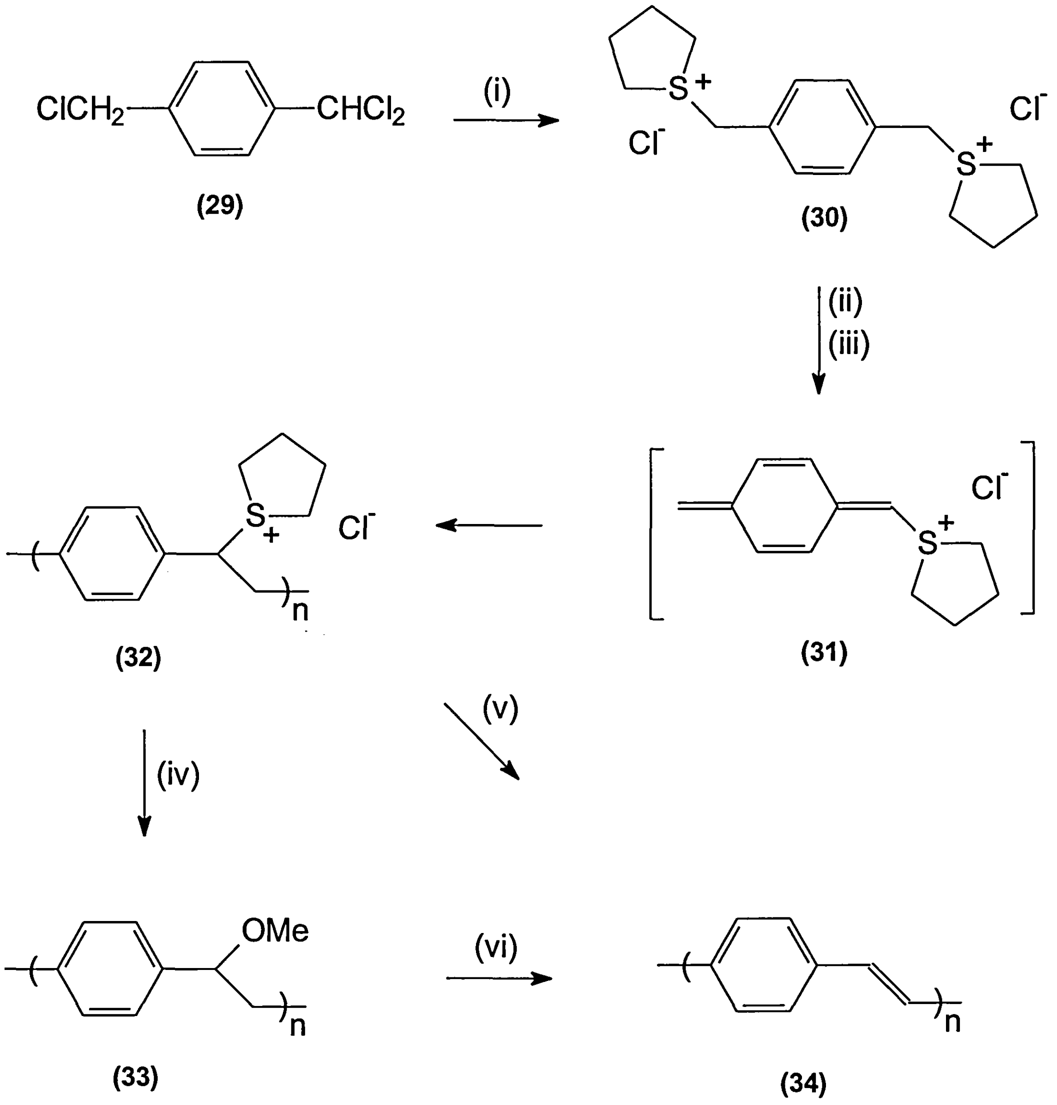
Again, as with the majority of organic conducting polymers, poly(*p*-phenylene) is insoluble, and therefore its processability has proved problematic, which has resulted in the majority of these compounds existing as oligomeric systems rather than as polymers.[46] Improvement in the solubility of poly(*p*-phenylene) has been resolved by substitution of the aromatic ring with flexible side chains.[54] Metal catalysed coupling reactions via Suzuki methodology have been adopted to aromatic monomers which has opened the way to high molecular weight polymers.[55]

### 1.3.4 POLY(PHENYLENE VINYLENE)S

Poly(phenylene vinylene)s (PPVs) are structurally analogous to both polyphenylene and polyacetylene, and a number of synthetic approaches have been adopted in the development of these systems. In 1990, Burroughes and co-workers[56] discovered that PPV exhibited excellent electroluminescent properties and could be incorporated into light emitting devices (LED's).

PPV **(34)** is an insoluble, intractable and infusible polymer when synthesised directly from a monomer unit, rendering its processability difficult.

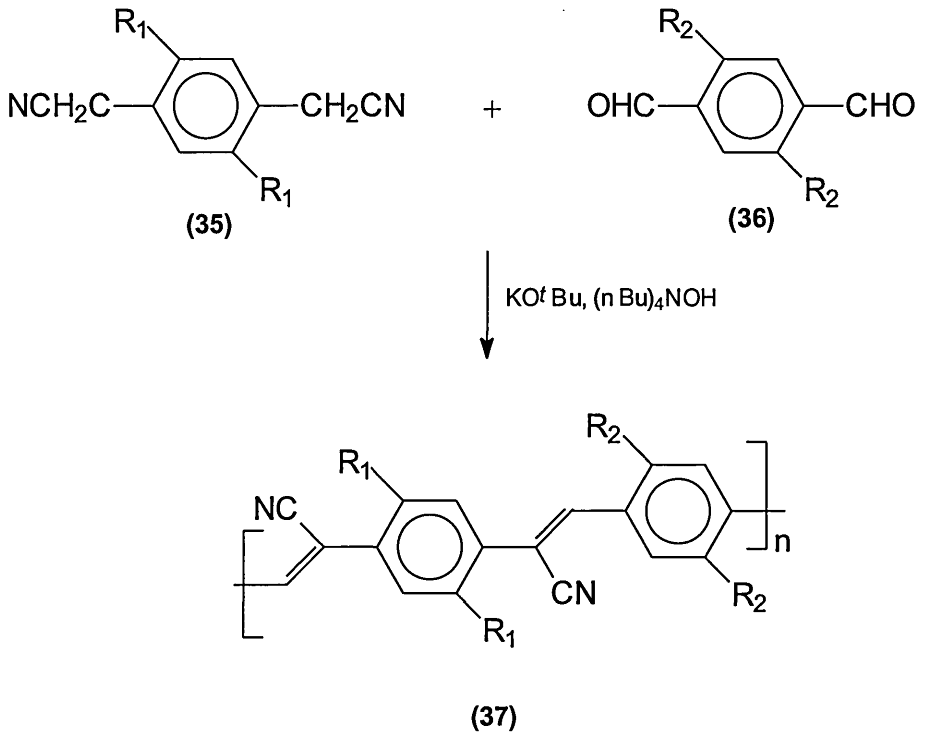
The standard synthetic route to PPV[57] was reported by Wessling and Zimmerman[58] in the 1960's and is summarised in scheme 6. Synthesis involves initial treatment of 1,4-bis(dichloromethyl benzene) **(29)** with tetrahydrothiophene to afford the bis-sulfonium salt **(30)**. Aqueous sodium hydroxide initiates the polymerisation in a methanolic solution to afford the quinodimethane intermediate **(31)**, which is then neutralised with aqueous hydrochloric acid to give precursor polymer **(32)**. This is then converted into PPV upon heating thin films under vacuum to 180-300 °C, or is converted to polymer **(33)** by treatment with refluxing methanol, followed by heating at 200 °C in gaseous HCl to afford PPV **(34)**.



**Scheme 6: Standard synthesis of PPV (34)**

**Reagents and conditions:** (i) Tetrahydrothiophene, MeOH, 65 °C (ii) NaOH, MeOH/$H_2O$ or $Bu_4NOH$, MeOH, 0 °C (iii) neutralisation (HCl), dialysis ($H_2O$) (iv) MeOH, 50 °C (v) 180 - 300 °C, vacuum, 12 h (vi) 220 °C, HCl (g)

Due to the versatility of the aromatic ring system to structural modifications, a number of functionalised PPV's have been synthesised. Cyano substituted PPV **(37)** has been prepared by a Knoevenagel condensation reaction between diacetonitrile **(35)** and dialdehyde **(36)** (scheme 7).[59] This route to PPV's has also been adapted for the synthesis of heteroaromatic cyanopolymers.



$\mathbf{R = C_6H_{13}O\text{-}}$

**Scheme 7: Knoevenagel condensation synthesis of cyano substituted PPV (37)**

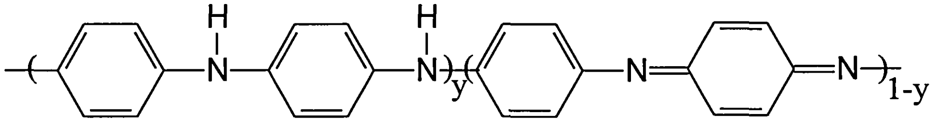
Research into PPV derivatives is still widely studied due to the potential of such materials as electroluminescent components of LED's. Substitution with cyano groups (and presumably other electron withdrawing species) on the aromatic ring or vinylene moiety of PPV lowers the HOMO and LUMO energies which increases the electron affinity of the polymer, thus improving the efficiency of the polymer. Poly[2,5-bis(hexyloxy)-1,4-phenylene-(1-cyanovinylene)] (CN-PPV) is a red fluorescent material and systems of this type undergo various colour changes over a wide range of wavelengths, depending on the nature of the substituents and have been used in the fabrication of the first polymer based IR-emitting LED's.[60]

### 1.3.5 POLYANILINE

Polyaniline **(38)** and its derivatives have attracted much attention over the last decade, and have become regarded as having high potential in many commercial applications such as secondary batteries, molecular sensors and electrochromic displays to name a few.[61] It is an environmentally stable conducting polymer and exhibits excellent properties (electrical, optical), and is probably the oldest known synthetic organic polymer,[62] although shows poor solubility in water and organic solvents.

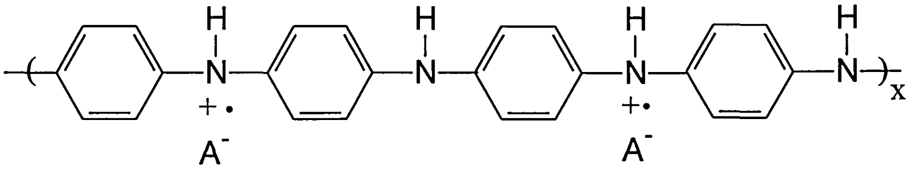
The synthesis of polyaniline was first reported in 1862,[63] and in 1912 was described as existing in 4 oxidation states.[64]

The oxidation level of polyaniline synthesised by either electrochemical or oxidative chemical polymerisation can be summarised by the general formula:



***Emeraldine* Polyaniline (38)**

where y = 1, 0.5, or 0 corresponds to the ***Leucoemeraldine*** (fully reduced), ***Emeraldine*** (half oxidised) ***Nigraniline*** and ***Pernigraniline*** (fully oxidised) forms of polyaniline respectively. The most widely studied state of polyaniline is the emeraldine form since upon doping with protonic acids it is the form that exhibits the highest conductivity (5 $\Omega^{-1}$ $cm^{-1}$) and was the first conducting polymer whose electronic properties can be reversibly controlled by protonation.[65]



**Protonated form of polyaniline**

Most of the interest in polyaniline and its derivatives has been established since 1980 and there has been extensive development in this area of conducting polymer research.

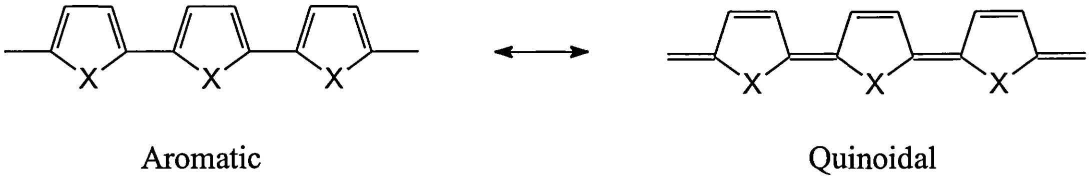
The solubility of polyaniline has been improved by the incorporation of sulfonic acid groups on the benzene ring of the monomer units. Sulfonated polyaniline shows improved environmental stability and increased solubility in aqueous media, and was the first reported 'self-doping' conjugated polymer,[66] with a conductivity of 0.1 $\Omega^{-1}$ $cm^{-1}$. The system also brings about new acid-base chemistry within the polymer, which can be altered externally by chemical or electrochemical methods. Protonation of the parent emeraldine base structure leads to an emeraldine salt which causes a reorganisation of the electronic structure of the polymer resulting in a polaronic metal.[67]

Various polyaniline derivatives have been prepared and research into this area is still widely studied, with aims of synthesising pure polymers in a known oxidation state and molecular weight with a known degree of doping.[68]

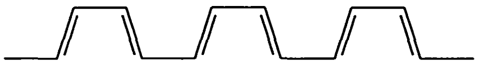
## 1.3.6 POLY(THIOPHENE)S

### 1.3.6.1 INTRODUCTION

The study of conjugated poly(thiophene)s is a major area within conducting polymeric systems, and has attracted much interest over the last 20 years. Poly(heterocycles) **(39)** can be viewed with a structure analogous to that of *cis* poly(acetylene) **(40)**, with stabilisation of the system due to the presence of a heteroatom.[69] This class of conducting polymer differs from $(CH)_x$ because, (a) they can exist in two limiting mesomeric forms, aromatic and quinoidal, therefore their nondegenerate ground state is related to the non-energetic equivalence of the two forms, (b) they have higher environmental stability and (c) they have greater structural versatility.



**(39)** X = S, O, NH



**(40)**

A major development in the synthesis of polyheterocycles was reported in 1979 by Diaz *et al,*[70] where a highly conducting form of polypyrrole (X = NH) was synthesised by the electrochemical polymerisation of pyrrole. This method of polymerisation was then adopted to other heterocyclic compounds such as thiophene.[71]

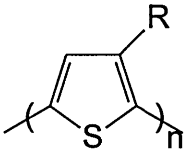
Poly(thiophene) (X = S) can be synthesised by either chemical or electrochemical methods. Several approaches have been employed in the synthesis of poly(thiophene)s, including oxidative coupling of lithiated derivatives,[72] Grignard coupling of 2,5-halothiophenes[73] and $NiCl_2$(dppp) coupling methods of Grignard compounds have also been used with an appropriate dibromothiophene.[74] Electrochemical methods of polymerisation can be achieved via an anodic or cathodic route. The cathodic route to polythiophene can be achieved by the electroreduction in acetonitrile of the complex (2-bromo-5-thienyl)triphenylnickel bromide.[75] The disadvantage of this route is that the polymer formed is in its neutral insulating form, limiting attainable film thickness due to its rapid passivation of the electrode. Polythiophene synthesised by an anodic electrochemical method presents several advantages including the absence of a catalyst, therefore reducing the amount of impurities in the polymer. Also, this method results in direct grafting of the polymer onto the electrode surface with easy control of film thickness by deposition charge and the possibility to perform in situ characterisation. However, a disadvantage of polythiophene is its insolubility, hence poor processability results, which has been overcome by functionalisation by a variety of substituents.

### 1.3.6.2 FUNCTIONALISED POLY(THIOPHENE)S

Functionalised polythiophene derivatives have attracted much attention over the last two decades, due to the insolubility and processability of polythiophene. Incorporation of various substituents onto the polythiophene backbone has led to a wide variety of soluble polymeric systems with high conductivity and improved processability.

Introduction of alkyl groups at the 3-position of the thiophene ring has lead to enhancement of conductivity, solubility and the synthesis of environmentally stable systems with good mechanical properties. A series of solution processable poly(3-alkylthiophene)s were reported by Elsenbaumer *et al* in 1987.[76] Highly conductive and stable polymers were formed, irrespective of the alkyl chain length of the substituents. Although conductivity values were lower for the doped polymers than that for polythiophene itself (10-20 $\Omega^{-1}$ cm$^{-1}$), improved processability was observed which is a major challenge in the synthesis of conducting polymers. The polymeric systems synthesised were soluble in common organic solvents and were both environmentally and mechanically stable.

In 1987, Bryce *et al* synthesised a number of long chain 3- substituted polythiophene derivatives **(41)**.[77] Electropolymerisation of monomer units afforded flexible polymers which were typically stable up to 210 °C with conductivity values ranging from 11-95 $\Omega^{-1}$ $cm^{-1}$. A series of 3-substituted polythiophene monomer units with ether and amide linkages and alkoxy substituents were also prepared by the same group. Conductivity values obtained for the doped polymers with various substituents are summarised in table 2.[77]



**(41)**

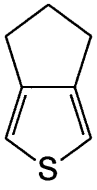
| **R** | **$\sigma_{rt}$ ($\Omega$ $cm^{-1}$)** |
|---|---|
| $CH_2OMe$ | 0.31 |
| $CH_2O(CH_2)_2OMe$ | 51 |
| $CH_2O(CH_2)_2O(CH_2)_2OMe$ | 1050 |
| $CH_2NHC(O)(CH_2)_{10}Me$ | 200 |
| $O(CH_2)_2O(CH_2)_2OMe$ | 0.05 |

**Table 2: Conductivity values for 3-substituted poly(thiophene)s (41)**

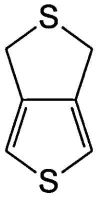
Although the introduction of alkyl substituents at the 3-position resulted in enhancement of conductivity, this attributed to an increase in the number of 2,4′ couplings between thiophene moieties upon polymerisation which interrupt conjugation along the polymer backbone. The inductive effect of alkyl groups also lowered the oxidation potential of the monomer which in turn lead to a less reactive radical cation during electropolymerisation.[78]

The synthesis of polymeric systems incorporating substitution at both the 3- and 4- positions was developed with the aim of producing polymers with greater stereoregularity by preventing any 2,4′ coupling processes. However, this approach is limited by steric hindrance to planarity by the alkyl chains in the conjugated system of the resulting polymer, hence a loss of conjugation results.[79]

The synthesis of polymers of cyclopenta[c]thiophene[80] **(42)** and thieno[c]thiophene[81] **(43)** was reported by Roncali in 1987.[82] It was envisaged that these systems would reduce steric hindrance to conjugation in the polymer compared to poly(3,4-dialkylthiophenes). Even so, these systems did not lead to an expected improvement in the conductivity values.



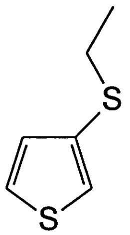
**(42)**



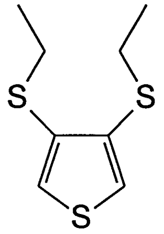
**(43)**

The conductivity observed for polycyclopenta[c]thiophene was 10-20 $\Omega^{-1}$ cm$^{-1}$ [80] which although higher than the conductivity for poly(3,4-dimethylthiophene) (0.5 $\Omega^{-1}$ cm$^{-1}$), it is lower than for poly(3-methylthiophene) films (450 - 500 $\Omega^{-1}$ cm$^{-1}$).[83] Electropolymerisation of thieno[c]thiophene **(43)**[81] proved to be difficult due to the presence of the sulfide functionality. This is more easily oxidised than the thiophene ring and it was suggested that this could capture the radical cations produced by oxidation of the thiophene ring, thereby acting as a radical scavenger, in turn hindering the polymerisation process.

Synthesis of ethylmercapto substituted derivatives of thiophene was reported by Ruiz and co-workers in 1989.[84] Brief reports on the synthesis of mercapto substituted polythiophenes were published by Elsenbaumer[85] and Tanaka[86]; however, relatively low conductivities were observed in both cases for the doped polymers (10$^{-1}$ $\Omega^{-1}$ cm$^{-1}$).



**(44)**



**(45)**

Polymers of 3-(ethylmercapto)thiophene **(44)** (PEMT) and 3,4-bis(ethylmercapto)thiophene **(45)** (PBEMT) are both soluble in common organic solvents and are semiconducting in the oxidised state (up to $10^{-3}$ $\Omega^{-1}$ $cm^{-1}$). Chemical polymerisation of these systems was achieved via a nickel catalysed Grignard coupling of 2,5-dihalogenated derivatives[87] of the ethylmercapto monomer.[73,88] However, electropolymerisation of the monomers resulted in no formation of precipitated or deposited polymer film on the electrodes.

The neutral states of both polymers are soluble in common organic solvents and insoluble in more polar solvents (MeOH, acetone) which shows similarities to previously reported 3-substituted thiophene polymers.

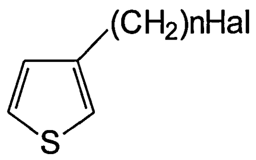
PEMT has a resulting bandgap value of approximately 2 eV which is comparable to that of polythiophene. The presence of two relatively bulky ethylmercapto substituents in the bis- derivative resulted in a polymeric system with an increased bandgap. Both polymers in the neutral form are insulators with conductivity values in the region of $10^{-12}$-$10^{-13}$ $\Omega^{-1}$ $cm^{-1}$. Upon doping with various oxidants, the conductivity increases by several orders of magnitude, which is summarised in table 3.[84]

| | Conductivity $\Omega^{-1}$ $cm^{-1}$ | | |
|---|---|---|---|
| | **$NOPF_6$** | **$Br_2$** | **$I_2$** |
| **PEMT (44)** | $2 \times 10^{-5}$ | $1 \times 10^{-5}$ | $1 \times 10^{-3}$ |
| **PBEMT (45)** | $2 \times 10^{-7}$ | | |

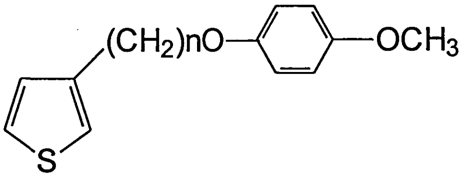
**Table 3: Conductivity Values for mercapto substituted poly(thiophene)s**

These systems show lower values than for poly(alkyl)substituted polythiophenes.[84] This may be due to a positive charge localisation onto the sulfur atom in the ethylmercapto derivatives.

Synthesis of a 3-alkylthiophene containing a terminal halogen substituent **(46)** was reported by Bäuerle *et al* in 1990.[89] Systems of this nature can be used as key building blocks in the preparation of functionalised 3-alkylthiophenes.[90]



**(46)**

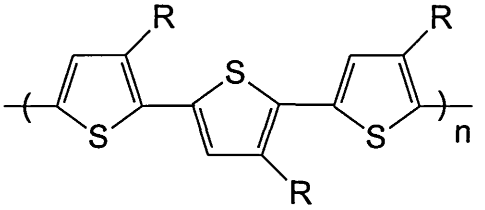


**(47)**

Preparation of substituted thiophene **(46)** was achieved via an ether cleavage of **(47)** with a hydrogen halide in acetic anhydride.[91]

A problem in the synthesis of 3-alkylthiophene derivatives is the random regiospecificity of coupling of thiophene moieties resulting in a mixture of polymeric structures. Polymerisation of 3-alkylthiophenes may result in three types of coupling of the thiophene ring. These are (a) head to tail, **(HT)** and, (b) head to head **(HH)** and (c) tail to tail **(TT)**. Polymers with **HH** or **TT** linkages have been found to contain a number of defects which in turn has reduced the conductivity of the polymer. Head to tail coupling is favoured as a more conjugated system is formed.

Control of this regioregularity and order in the polymer results in increased conjugation within the polymer which leads to enhancement of electrical properties, and systems with a highly ordered structure were reported by McCullough *et al.*[92] Poly(3-dodecylthiophene) **(48)** was synthesised with almost exclusive head to tail coupling.

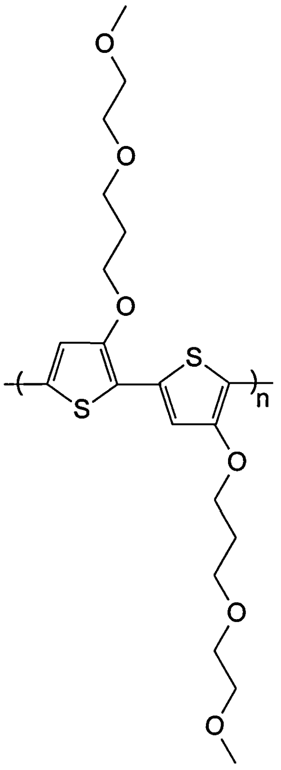


**(48)** **R = $C_{12}H_{25}$**

Conductivity values of 600 - 1000 $\Omega^{-1}$ $cm^{-1}$ were observed for the iodine doped polymer which are much greater than those observed for polymers synthesised by other chemical or electrochemical methods. This polymeric system consists of 91% head to tail regiospecificity and is also thermally stable to 370 °C.

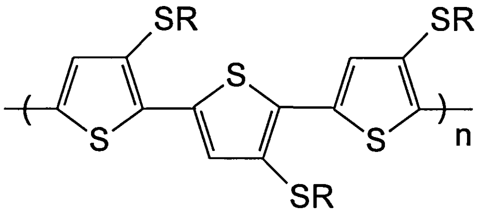
The first completely regioregular HT poly(3-alkylthiophene) was reported by Chen and Reike[93] using highly reactive zinc,[94] providing a means of synthesising poly(3-alkylthiophenes) with a wide range of functional groups. Regioregular poly(butylthiophene)s were synthesised via a chemoselective zinc insertion of a 2,5-dibromo derivative to yield quantitatively the 2-(bromozincio)-5-bromothiophene. Polymerisation was achieved via a palladium (0) or nickel coupling reaction and the resulting polymer possessed a bandgap value of 1.7 eV and a conductivity of $10^{-6}$ $\Omega^{-1}$ $cm^{-1}$ for the neutral polymer which significantly increases to 1350 $\Omega^{-1}$ $cm^{-1}$ upon iodine doping. A decrease in the bandgap results from an increase in conjugation of the thiophene backbone which is probably reflected by the degree of planarity between thiophene units in the polymer backbone.

A range of poly(3-substituted)thiophenes were reported by McCullough *et al* resulting in regioregular homogenous polythiophenes with enhanced conductivity. Poly(3-(2,5,8-trioxanonyl)thiophene **(49)** possessed an average conductivity of 500 $\Omega^{-1}$ $cm^{-1}$ and is almost exclusively 100% HT regiospecific.[95]



**(49)**

The synthesis of regioregular mercaptothiophene **(50)** derivatives was reported by Reike *et al* in 1995.[96] Preparation of the regiorandom derivative was previously reported by Ruiz and co-workers.[84]

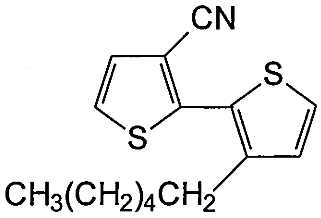


**(50)**

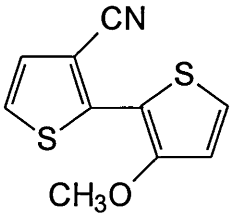
This polymeric system was obtained with > 90% regiospecificity with doped polymer films exhibiting conductivity values of 450 - 750 $\Omega^{-1}$ cm$^{-1}$.

Within the polythiophene series of conducting polymers, ideal linkage of monomer units is via the 2- and 5- positions. Substitution at 3- and 4- positions has resulted in systems with steric effects giving rise to shorter chain lengths of the synthesised polymers. This has been overcome with the use of bithiophene derivatives as starting materials.

Although most of the research into functionalised polythiophene derivatives has involved mono-funtionalised polymers, the synthesis of a polymeric system incorporating both electron acceptor and electron donor moieties has been reported.[97]



**(51)**

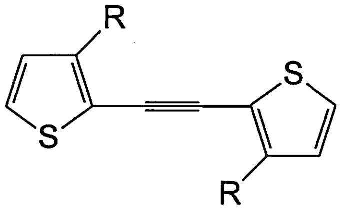


**(52)**

The synthesis of bithiophene monomers **(51)** and **(52)**[98] has resulted in systems with an asymmetric charge distribution due to the donating alkyl and alkoxy functionalities combined with the electron withdrawing properties of the cyano substituent.

The incorporation of these substituents along with the electrochemical behaviour of bithiophene resulted in the stereoregular α-α′ coupling between bithienyl moieties by the control of the antagonistic effect of the substituents. The presence of electron donating groups decreases the oxidation potential and increases the stability of the corresponding radical cation, while electron withdrawing substituents have an opposite effect, increasing the oxidation potential of the monomer units resulting in enhanced reactivity of the resulting radical cation. This results in a system where the electron accepting effects of the cyano substituent is neutralised by the efficient electron donating capability of the alkyl or alkoxy substituent on the neighbouring thiophene moiety. Systems of this nature exhibit characteristics that can be finely tuned through subtle chemical modifications of the monomer unit which open the possibility of molecular engineering of organic multiple-well structures, an area of potential interest.[99]

The incorporation of acetylenic spacer groups into the polythiophene backbone **(53)** was recently reported by Ng *et al.*[100] This functionality can act as rigid conjugative spacer groups linking two bithiophene moieties through the 2,2′ positions in the same plane. A maximum degree of delocalisation is expected due to diminished steric effects resulting in a more planar conformation.[101]



**(53)**

A number of derivatives were prepared with varying alkyl chain lengths. These possess a rigid polymer backbone predominantly with α-α′ coupling. Conductivity values of the resulting iodine doped polymers are summarised in table 4.[100]

| **R** | **$\sigma\ \Omega^{-1}\ cm^{-1}$** | **Eg** |
|---|---|---|
| **H** | 1.5 | 1.8 |
| **$C_4H_9$** | 0.03 | 1.7 |
| **$C_6H_{13}$** | 0.002 | 1.9 |
| **$C_8H_{17}$** | 0.001 | 1.9 |
| **$C_{12}H_{25}$** | 0.0002 | 1.9 |

**Table 4: Conductivity and bandgap values for (53) with varying alkyl groups**

The highest conductivity value is observed for the unsubstituted polymer, which decreases as the alkyl chain length increases. These results are consistent with those obtained by Kaeriyama *et al.*[102] With an increase in chain length, the rate of iodine absorption decreases although the duration of the doping process was the same for each derivative. Significant steric hindrance towards dopant molecules inhibits charge carrier formation during doping, hence a reduction in conductivity is observed.

## 1.4 LOW BANDGAP POLYMERS

The synthesis of conducting materials possessing a narrow bandgap (**Eg** <1.5 eV) in their neutral state has attracted much attention over the last decade and remains a desired goal within the field of electroactive materials.

A number of strategies have been adopted in the tailoring of molecules or macromolecules in order that systems of this nature possess near metallic properties. The synthetic principles that have been adopted in the search for low bandgap materials include:

(a) Increasing the quinoidal character of the π-conjugated system at the expense of its aromatic character,

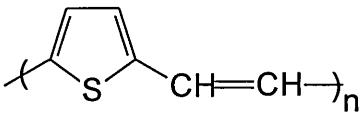
(b) Minimisation of rotational and vibrational disorder through rigidification of the conjugated polymer structure,

(c) Introduction of alternate donor and acceptor moieties along the polymer chain.

A reduction in the bandgap leads to an increased number of charge carriers as a result of an enhanced population of electrons in the conductance band leading to intrinsic conductivity. Stabilisation of the doped state occurs as a result of the lower oxidation potential associated with a reduced bandgap.

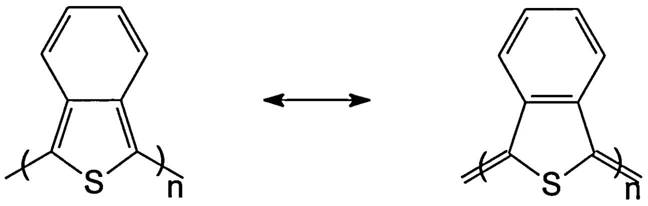
Poly(thiophene) derivatives have been the major interest and a number of systems have been prepared which possess a narrow bandgap value because of their ease of preparation and their stability to atmospheric exposure, compared to polyacetylene or poly(paraphenylene).

In 1987, Saito *et al* prepared a system based on both thiophene and polyacetylene[103] resulting in poly(2-5-thienylenevinylene) **(54)** which has a bandgap value of 1.8 eV. This system was originally synthesised by Kossmehl in 1969[104] but only in powder form. Saito synthesised stable films of the system which were conducting upon iodine doping (60 $\Omega^{-1}$ cm$^{-1}$, in neutral state $10^{-13}$ $\Omega^{-1}$ cm $^{-1}$ at room temperature).



**(54)**

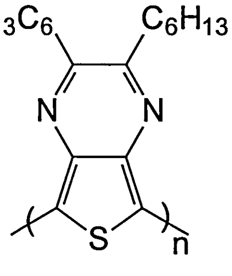
A major breakthrough in the synthesis of low bandgap polymers was reported in 1984 by Wudl *et al,*[105] who successfully reduced the bandgap of polythiophene from 2.0 eV to 1.1 eV by the fusion of a benzene ring into each thiophene unit, based on the synthesis of the monomer isothianaphthene, described by Cava *et al* in 1971.[106]



**(55)**

Poly(isothianaphthene) **(55)**, a blue-black polymer which becomes transparent upon doping[107] exhibits a conductivity value of 50 $\Omega^{-1}$ $cm^{-1}$. The strategy adopted involved the tailoring of monomer units in order to increase the quinoid character of the resulting π-conjugated system at the expense of its aromatic character.[108] The higher resonance energy of the benzene moiety (1.56 eV vs. 1.26 eV for thiophene) results in the tendency to retain aromatic character in the six membered ring, thus imposing a quinoid geometry on the polythiophene backbone resulting in a reduced bandgap. Unfortunately, poly(isothianaphthene) was found to be insoluble, hence processability was difficult.

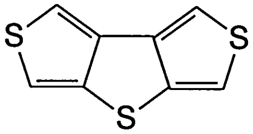
The synthesis of poly(2,3-dihexylthieno[3,4-*b*]pyrazine **(56)** was reported in 1992 by Pomerantz *et al.*[109]



**(56)**

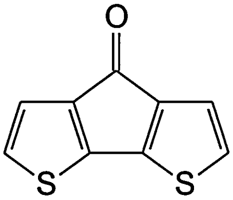
Based on poly(isothianaphthene), the presence of alkyl groups within the system enhanced the solubility of the material in common organic solvents, and hence improved its processability.[110] The resulting polymer possessed a bandgap value of 0.95 eV with a doped film conductivity of $3.6 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$.

Poly(dithieno[3,4-*b*:3',4'-*d*]thiophene was synthesised in 1988[111] from the monomer unit dithieno[3,4-*b*:3',4'-*d*]thiophene **(57)**, reported in 1971.[112] This novel transparent conducting polymer exhibited a doped conductivity of $1.0\ \Omega^{-1}\ cm^{-1}$ at room temperature **(Eg** 1eV), and was the first example of a low bandgap electrically conducting polymer based on thienothiophenes.[113]

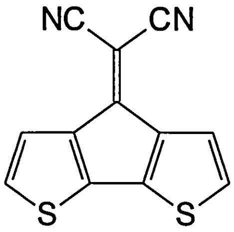


**(57)**

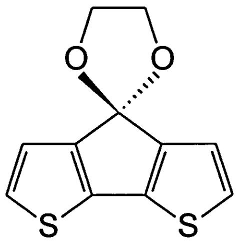
Bithiophene derivatives cyclopenta[2,1-*b*;3,4-*b'*]dithiophen-4-one **(58)** and 4-dicyanomethylene-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene **(59)** were synthesised with the introduction of electron withdrawing groups bridging the 4,4' positions resulting in polymeric systems with a bandgap value of 1.2 eV for PCDT**(58)** and 0.8 eV for PDCM **(59)**.[2] Introduction of electron withdrawing groups was shown to lower the energy of the LUMO, hence a reduction in the bandgap results.



**(58)**

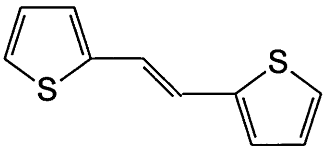


**(59)**

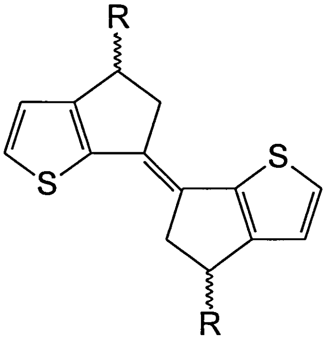


**(60)**

Rigidification of the conjugated backbone within the system was another strategy adopted in the search for processable low bandgap polymers. Poly(4,4-ethylenedioxy-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene **(60)** was synthesised by Roncali *et al* in 1994.[114] The grafting of a dioxolane moiety at the bridging $sp^3$ carbon atom to produce a rigid bithiophene resulted in a polymer with a bandgap of 1.2 eV.[52] Rigidification of thiophene rings with a bridging double bond as in compound **(61)** resulted in the synthesis of a poly(dithienylethylene) (DTE) which lowered the oxidation potential of the monomer, hence producing a system with a reduced bandgap of 1.8 eV.[115] Substituted bridged derivative **(62)**[116] further reduced the bandgap to 1.4 eV. Compared to poly(thiophene) the presence of double bonds with defined conformations reduces aromatic character of the π-conjugated backbone limiting the number of rotations and hence long range deviation from planarity. Extension of the rigidification approach suppresses rotation about the double bond, hence reducing the bandgap further.



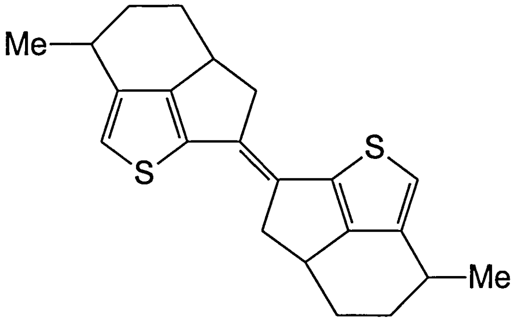
**(61)**



**(62)**

**R = H, alkyl**

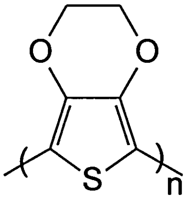
This structural modification resulted in a considerable decrease in the solubility of the system. In order to remedy this problem, a series of bridged DTE derivatives incorporating solubilising alkyl groups at various positions have also been synthesised.[117] These systems did not have an effect on the bandgap of the resulting polymers, they were merely introduced to aid solubility and hence increase the efficiency of the electropolymerisation process.



**(63)**

Compound **(63)** has recently been synthesised by Roncali *et al.*[118] An additional six membered ring incorporated into the system induces a deformation in the thiophene ring system. It is proposed that it is this functional deformity which is responsible for a further reduction of **Eg** compared to the simple bridged systems, allowing a significant decrease of steric hindrance associated with substituents on the 4,4′ positions of the thiophene ring.

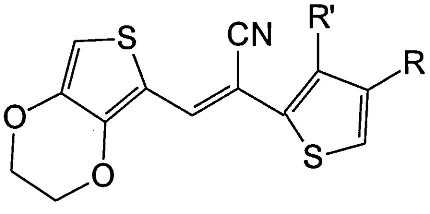
Poly(3,4-ethylenedioxythiophene) [PEDOT] **(64)** and its derivatives has attracted much attention over the last few years, due to its electrochromic properties and its stability in the oxidised form.[119]



**(64)**

This conducting polymer possesses a bandgap value of 1.6 eV and was synthesised by Pei and co-workers in 1994[119d] based on the monomer which was previously reported by Fager,[120] and Guha and Iyer.[121]

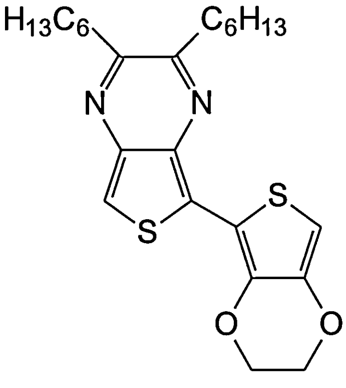
A number of systems have been prepared based on PEDOT, leading to low bandgap polymers with improved stability.



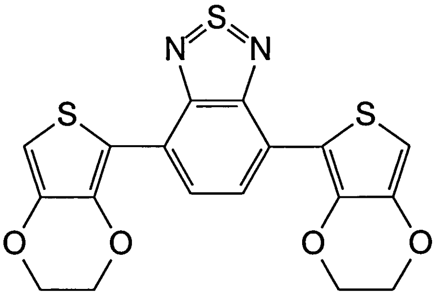
**(65) R,R′ = H**

**(66) R,R′ = -OCH$_2$CH$_2$O-**

1-Cyano-2-(2-[3,4-ethylenedioxythienyl])-1-(2-thienyl)vinylene **(65)** and 1-cyano-1,2-bis(2-[3,4-ethylenedioxythienyl])vinylene **(66)** undergo facile electrochemical polymerisation to afford polymeric systems with bandgap values of 1.3 and 1.1 eV respectively. These systems are quite stable and can undergo p- doping to the conducting form and can be reversibly reduced.[122]



**(67)**



**(68)**

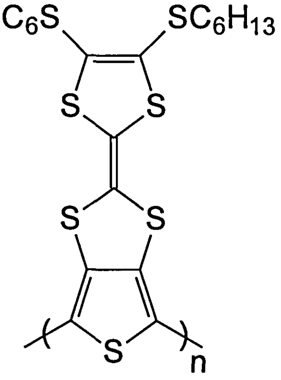
The synthesis of monomer unit **(67)** was reported in 1998,[123] and is derived from a bithiophenic precursor involving 3,4-ethylenedioxythiophene and thieno[3,4-*b*]pyrazine, combining a number of properties to achieve a polymeric system with a much reduced bandgap value. Solubility is improved by the hexyl chains, the stability of the polymer is enhanced by the presence of the particularly stable EDOT moiety, and the structure combines the superior polymerisability of bithiophenic structures over more conjugated ones.[124] This polymer has an optical bandgap of 0.36 eV, which is to date, the lowest ever reported for a conjugated polymer.

Derivative **(68)** has also been synthesised based on EDOT with median quinoid acceptor benzothiadiazole, showing enhanced stability under redox cycling.[125] Electropolymerisation of this system leads to a material possessing an electrochemical bandgap value of 1.3 eV.

In summary, the development of conjugated polymers exhibiting 'metallic' conductivity has become a focal interest within the field of organic conductors. Most of the interest in this area has evolved over the last two decades and a wide variety of systems have been prepared and, in particular, polythiophene has emerged as a prototype for materials of this nature, due to its stability and structural versatility.

# CHAPTER 2

## Synthesis of Poly(2-[4,5-bis(hexylsulfanyl)1,3-dithiol-2-ylidine]thieno[3,4-*d*]-1,3-dithiole) - A Novel Fused TTF-Thiophene Polymer



**(69)**

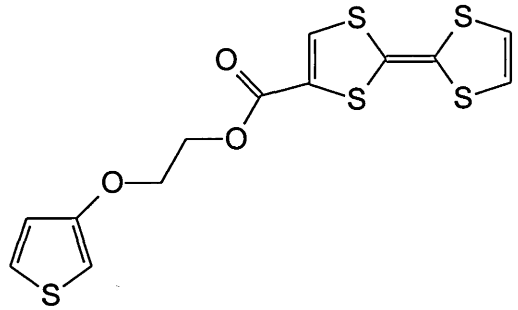
### 2.1 INTRODUCTION

The incorporation of redox mediators into conjugated polymers has received interest over the last decade and examples have been reported where polythiophene has been derivatised by substituents such as viologens,[126] quinones,[127] and ferrocene.[128] The association of tetrathiafulvalene and conducting polymers[129] is of growing interest and has become an exciting area of conducting materials, resulting in fascinating new electrode components.

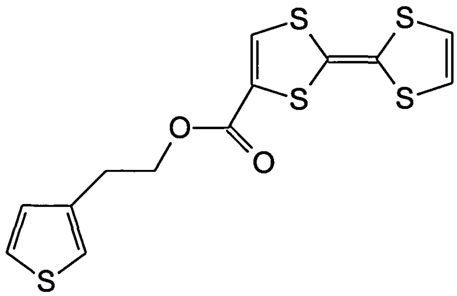
The synthesis of polythiophene/TTF derivatives results in the co-existence of two different charge transport mechanisms (π-electron transfer in mixed valence TTF stacks and polaron/bipolaron conduction in the main chain of conjugated polythiophenes), contributing to the development of new species with hybrid conduction of both technological and fundamental interest.[129]

Such a combination of individual classes of organic 'metals' could lead to increased dimensionality within such systems, with the strong propensity of TTF to self assemble into regular π-stacks when covalently attached to a conjugated polymer backbone.[127,130] This may also enhance the processability of tetrathiafulvalene based conductors and lead to increased charge storage capacity of the resulting conducting polymer.

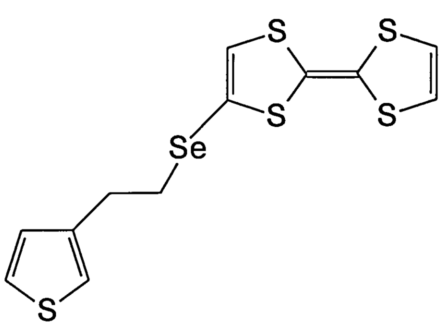
In 1991, Bryce and co-workers[131] reported the first examples where TTF was covalently linked to a thiophene monomer via spacer groups. Compounds **(70), (71),** and **(72)** were synthesised, however, polymerisation by electrochemical methods of the monosubstituted thienyl derivatives was only observed for **(71),** where the grafting of TTF was through an ester functionality. The unsuccessful electropolymerisation of these systems was believed to be due to steric hindrance between the TTF groups and the thiophene moiety as a result of too short a spacer group, leading to a distortion of the polymer backbone.



**(70)**

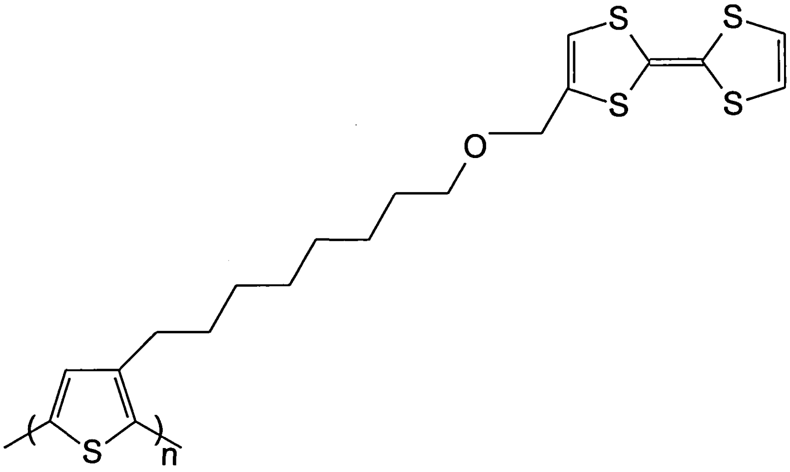


**(71)**



**(72)**

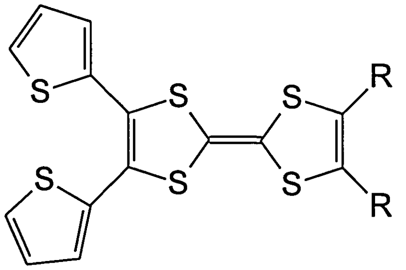
In 1993, Roncali *et al*[129b] reported the earliest examples of oligomeric thiophene/TTF systems with substitution at the 3-position of the thiophene ring. Compound **(73)** was synthesised, where an oxadecyl functionality was employed as spacer group between the redox centre and the conjugated polythiophene moiety in order to minimise steric interactions whilst preserving conjugation within the polymer backbone.



**(73)**

Electropolymerisation of this system in nitrobenzene occurred through the formation of an unusual donor-acceptor complex between the solvent and TTF, which lowers the oxidation potential of the thiophene moiety and decreases the ability of TTF to scavenge the thiophene radical cations, thus allowing deposition of a unique polymeric material, where the resulting electroactive polymer retained the electrochemical features of both polythiophene and TTF. Broad anodic waves were observed at + 0.70 V and + 1.15 V corresponding to the TTF moiety, with a subsequent peak at + 1.30 V. This wave corresponds to the oxidation of the deposited polythiophene backbone, which although difficult to distinguish at the experimental scan potential (+ 2.0 V), could be intensified if the anodic peak potential was raised to + 2.20 V.

In 1997, Charlton *et al* reported the synthesis of a series of thiophene functionalised TTF derivatives **(74)** where the redox centre was linked directly to two thiophene moieties at the 2-position of the thiophene ring.[132]



**(74)**

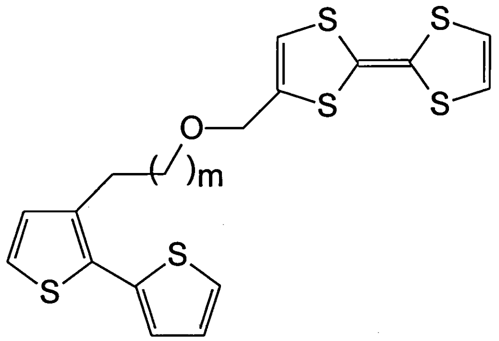
**R = 2-Thienyl, H, $S(CH_2)_2CN$,**
**R-R = $S(CH_2CH_2)S$**

It was envisaged that a soluble conducting polymeric system would form upon electropolymerisation. Cyclic voltammetry of the monomer revealed typical features of TTF, with two reversible waves corresponding to the sequential formation of $TTF^{+\cdot}$ and $TTF^{2+}$ species, although higher oxidation potentials were observed than for the parent TTF as a result of the electron withdrawing nature of the grafted thiophene groups. However, electropolymerisation of compound **(74)** was unsuccessful: although diffusion of a dark blue species (characteristic of the nature of the radical cation of thiophene) was observed, along with deposition of material at the working electrode, further voltammetric studies confirmed that this was not of a polymeric nature. It seemed likely that the potential required to oxidise the TTF moiety to the dication species renders the thiophene first oxidation potential too high to polymerise, hence the electropolymerisation of this system was unsuccessful.

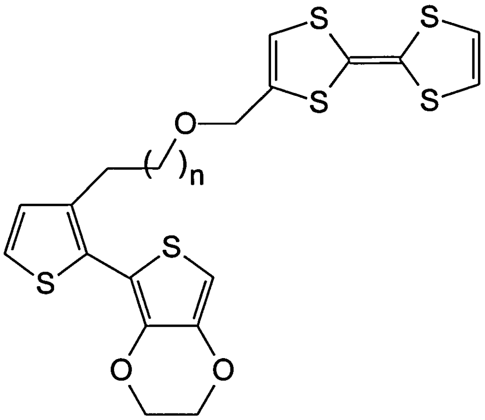
It was concluded that one of the key barriers to efficient electropolymerisation of systems of this nature lies in the difference in the oxidation potentials of tetrathiafulvalene compared to that of thiophene (+ 0.40 V[133] and + 2.07 V[71] respectively vs. SCE). The potential required to form the radical cation of thiophene becomes consumed by the oxidation of the TTF moiety, along with radical cations of thiophene becoming depleted by neutral TTF species.

In 1998, Roncali and co-workers[123] reported the synthesis and electropolymerisation of TTF derivatised bithiophenic precursors. The idea behind attaching TTF to bithiophene was to reduce the oxidation potential of the thiophene moiety, resulting in the facile electropolymerisation of the system.

Compound **(75)** and EDOT derivative **(76)** were synthesised. Electrochemistry of the resulting polymers revealed that the bithiophene moiety does not experience any steric or electronic effects from the attached TTF group. The cyclic voltammogram of **(75)** showed two reversible oxidation waves at + 0.38 V and + 0.86 V corresponding to $TTF^{+\cdot}$ and $TTF^{2+}$ species respectively, along with an irreversible oxidation wave at + 1.32 V which is identical to that of free bithiophene. A lower oxidation potential was observed for EDOT derivative **(76)** (+ 1.18 V) which is intermediate between the values obtained for bithiophene and the dimer of EDOT (+ 0.85 V).[129] Repetitive scanning over the third oxidation potential of both derivatives **(75** and **76)** in nitrobenzene resulted in electropolymerisation of the systems, forming highly electroactive TTF derivatised polythiophenes, rendering them interesting materials for electrochemical applications.[130]



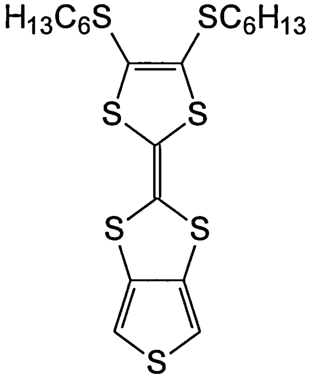
**(75)**



**(76)**

Synthesis of novel tetrathiafulvalene-thiophene monomer **(77)** was reported in 1997 by Skabara and Müllen[129e], consisting of a fused TTF-thiophene derivative with both 2- and 5- positions free on the thiophene ring, which could suggest a more ideal system for successful electropolymerisation. The novel thiophene monomer was designed to incorporate a tetrathiafulvalene unit, expected to be beneficial towards the electronic behaviour of the bulk polymer due to the highly redox active nature and self-assembling abilities of this system. It was envisaged that the quinoid state of the resulting polymer would be stabilised due to 'rearomatisation' of the TTF moiety, resulting in a lowering of **Eg** within the system.

The solubility of the system would also be enhanced due to the presence of two solubilising hexylsulfanyl chains per monomer unit.



**(77)**

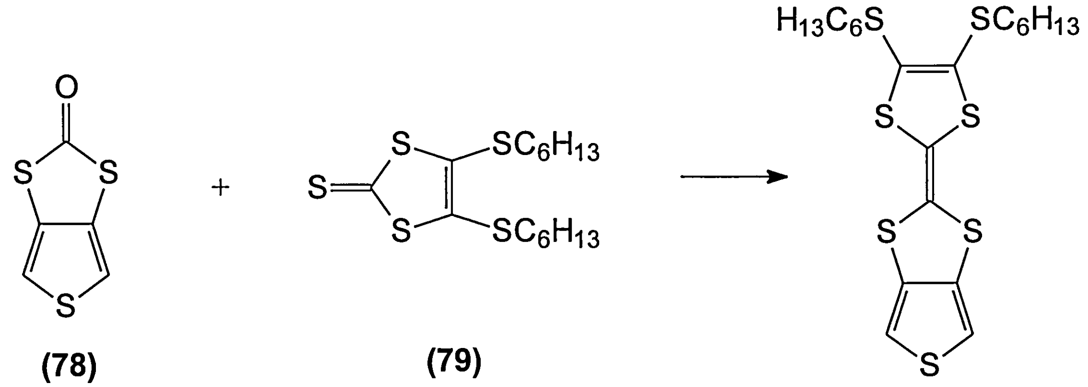
Electrochemistry of the system again showed the characteristic features of both tetrathiafulvalene and thiophene moieties, although slightly higher first oxidation potentials were observed than for the corresponding parent molecules (TTF $E_1$ + 0.46 V, $E_2$ + 0.83 V, thiophene $E_3$ + 2.18 V). However, electropolymerisation of compound **(77)** was unsuccessful and an unusual additional peak was observed at 1.36 V over the cathodic scan. It was suggested that this was due to side products resulting from reactions between the tricationic species formed upon oxidation and the solvent or anion used in the process, which has also been observed for derivatised thiophene monomers exhibiting high first oxidation potentials.[134]

Alternatively, it was suggested that stabilisation of the radical cation of the thiophene unit occurs through the TTF moiety, resulting in the dissolution of charged species away from the working electrode surface which may form soluble oligomers in solution, as observed for a number of alkylsulfanyl substituted thiophenes.[84] However, MALDI-TOF mass spectrometry of the solution gave evidence of only monomeric units rather than oligomeric/polymeric species.

The remainder of this chapter is concerned with the synthesis of halogenated derivatives of monomer unit **(77)**, along with the syntheses towards analogous derivatives of TTF. Chemical polymerisation of the 2,5-dibromo derivative is also described, adopting the use of Yamamoto polymerisation methodology, employing a nickel (0) catalyst.[135]

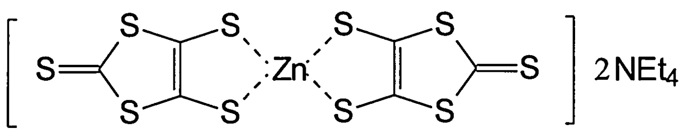
## 2.2 RESULTS AND DISCUSSION

Numerous synthetic pathways have been investigated towards polymeric system **(69)**. Initially, synthesis of monomer unit **(77)** was explored.[129e] The preparation of compound **(77)** was achieved via a coupling reaction between compounds **(78)** and **(79)** with triethyl phosphite (scheme 8).[136] The reagents were heated at 110 °C for 6 h, with subsequent purification upon cooling by column chromatography (silica, petroleum ether) to afford **(77)** in 20 - 30% yield. Compound **(79)** was prepared in 71% yield from the reaction of zinc complex **(80)** with 1-bromohexane in refluxing acetonitrile, which was prepared from carbon disulfide and sodium metal in dimethylformamide, with subsequent 'trapping' of the dithiolate species formed with zinc and ammonium salts.[137]



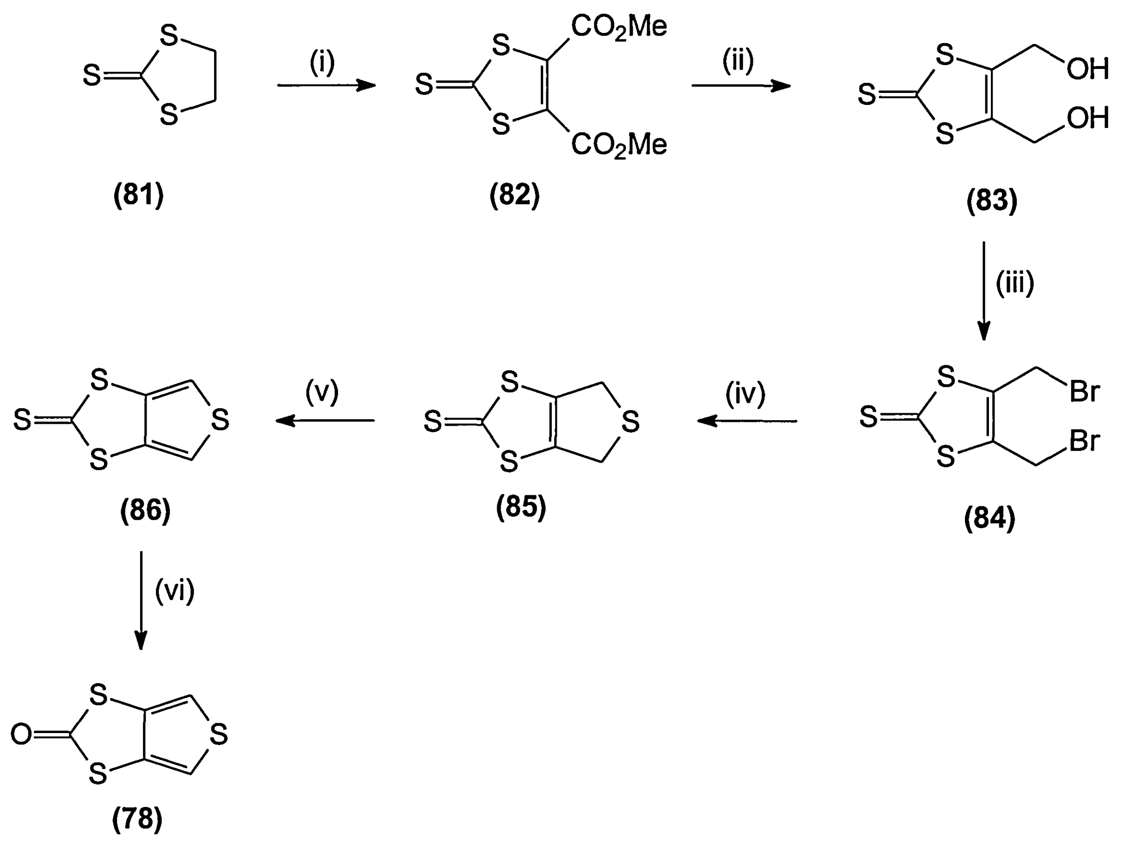
**(77)**

**Scheme 8:** Reagents and conditions (i) $POEt_3$, 110 °C, 6h



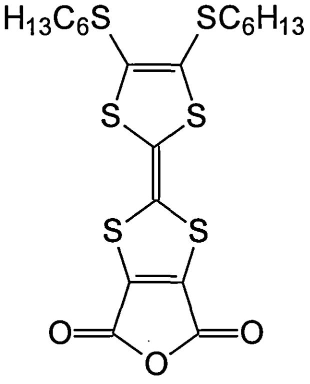
**(80)**

The synthetic route to compound **(78)** is summarised in scheme 9 and involves initial reaction of carbon disulfide with sodium hydroxide and 1,2-dibromoethane to afford **(81)** (60%).[138] Compound **(81)** was allowed to react with dimethylacetylene dicarboxylate (DMAD) in refluxing toluene to give diester **(82)**[139] in good yield (75%), which was subsequently reduced with sodium borohydride to afford 4,5-bis(hydroxymethyl)-1,3-dithiole-2-thione **(83)**[140] in 65% yield. Dibromide **(84)**[129e] was synthesised from diol **(83)** under mild brominating conditions ($PPh_3$, $CBr_4$, $CH_2Cl_2$), and was then reacted via a nucleophilic substitution ring closure with sodium sulfide to afford thioether **(85)**.[141] Aromatisation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) gave 3,4-substituted thiophene **(86)**[142] in 95% yield which was allowed to react with mercury (II) acetate in a mixture of 3:1 (v/v) dichloromethane:glacial acetic acid to afford thieno[3,4-*d*]-1,3-dithiole-2-one **(78)**.[143]

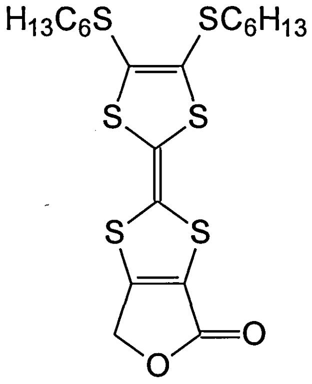


**Scheme 9:** Reagents and conditions (i) DMAD, toluene, reflux, 24h. (ii) $NaBH_4$, LiCl, THF, MeOH (iii) $CBr_4$, $PPh_3$, dichloromethane (iv) $Na_2S.9H_2O$, ethanol, THF (v) DDQ, toluene, reflux (vi) $Hg(OAc)_2$, dichloromethane: acetic acid (3:1 v/v), 2h.

Synthesis towards substituted cyclic anhydride **(87)** and lactone **(88)** was also investigated, since the reaction of these derivatives with $P_4S_{10}$ may lead to the isolation of a polymeric system, based on the reaction of phthalic anhydride and phthalide as a synthetic route to poly(isothianaphthene).[144]

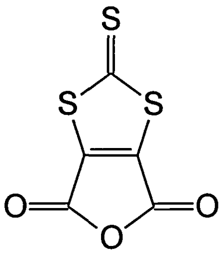


**(87)**

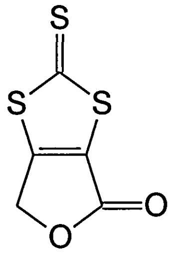


**(88)**

Preparation of half units **(89)** and **(90)** was studied by a number of synthetic pathways.



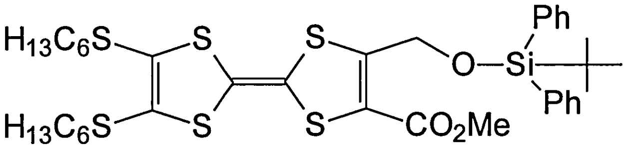
**(89)**



**(90)**

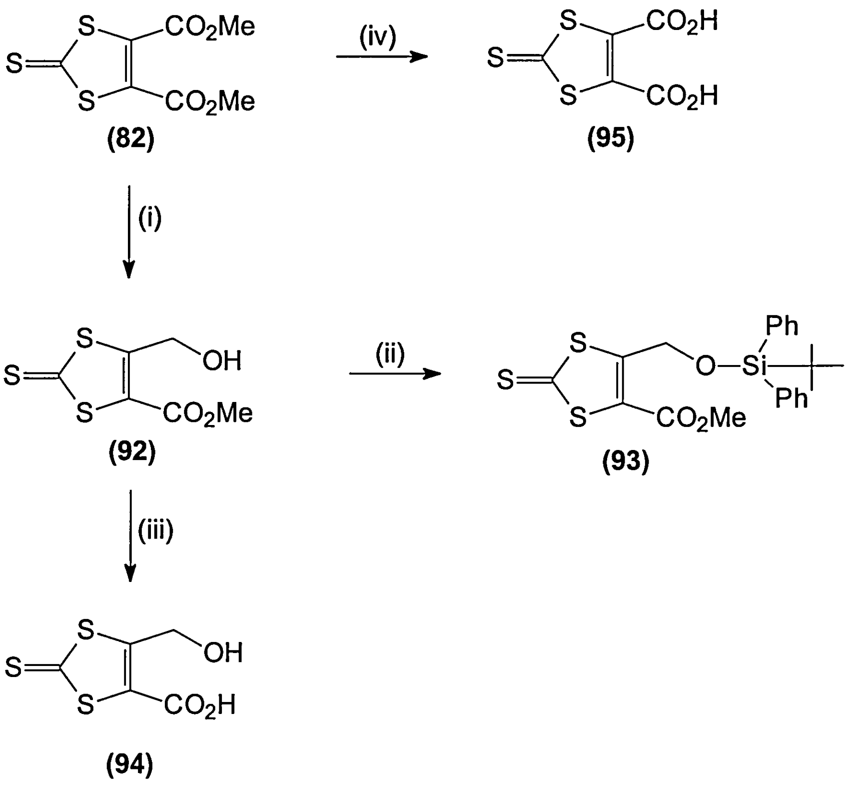
Partial reduction of compound **(82)** was achieved with sodium borohydride and lithium chloride in a solution of THF and methanol to afford **(92)**. The reaction time for this process was short (5 minutes) and a limited amount of sodium borohydride (0.5 molar equivalent) was used to increase the efficiency of the reaction (scheme 10). Compound **(92)** was synthesised in 56% yield along with a small amount of fully reduced diol **(83)**. Protection of the alcohol functionality with t-butyldiphenylsilyl chloride resulted in the isolation of compound **(93)** (71%). It was envisaged that deprotection of this system with tetra-n-butylammonium fluoride trihydrate at room temperature would result in subsequent ring closure to afford monomer unit **(90)**; however, this was unsuccessful and was thought to be due to attack of the thione by the deprotecting reagent. Cross coupling of protected alcohol **(93)** and

4,5-bis(hexylsulfanyl)-1,3-dithiole-2-thione **(79)** with triethyl phosphite at 110 °C afforded tetrathiafulvalene derivative **(91)**, which was confirmed by mass spectrometry (m/z (EI) 763). However, deprotection with tetra-n-butylammonium fluoride trihydrate was again unsuccessful and a new strategy was adopted.



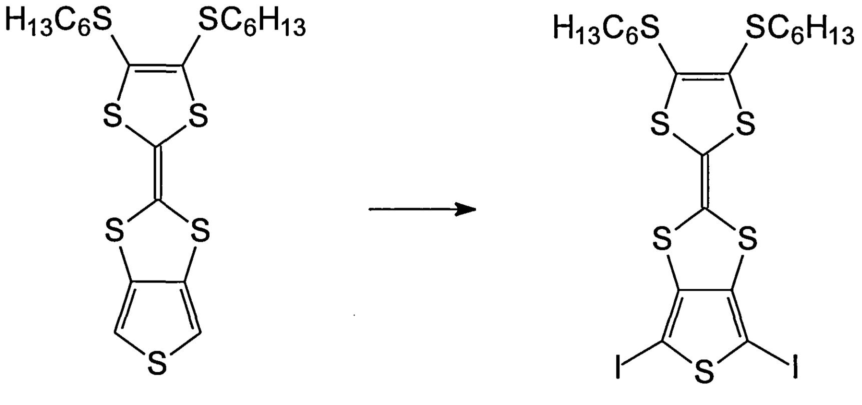
**(91)**

Conversion of mono-reduced alcohol **(92)** to its corresponding hydroxyacid **(94)** was achieved upon refluxing with hydrochloric acid and glacial acetic acid (scheme 10).[139] A similar strategy was adopted for the conversion of diester **(82)** to its corresponding diacid **(95)**.[143]



**Scheme 10 :** Reagents and conditions (i) $NaBH_4$, LiCl, THF, MeOH (ii) t-butyldiphenylsilyl chloride, imidazole, DMF (iii) c.HCl, $CH_3CO_2H$, reflux (iv) c.HCl, $CH_3CO_2H$, reflux, 2 h.

Ring closure of compound **(94)** was initiated by the addition of thionyl chloride. However, only a small amount of the desired product was obtained, which was indicated by mass spectrometry (m/z (EI) 190). Attempts at the dehydration of compound **(95)** to afford cyclic anhydride derivative **(89)** involved heating the starting material with glacial acetic anhydride. However, this resulted in decarboxylation of the system to afford vinylene trithiocarbonate, which was confirmed by mass spectrometry (m/z (EI) 134) and infrared analysis (absence of C=O str) mp 47 - 49 °C (Lit 50 - 51 °C).[145]

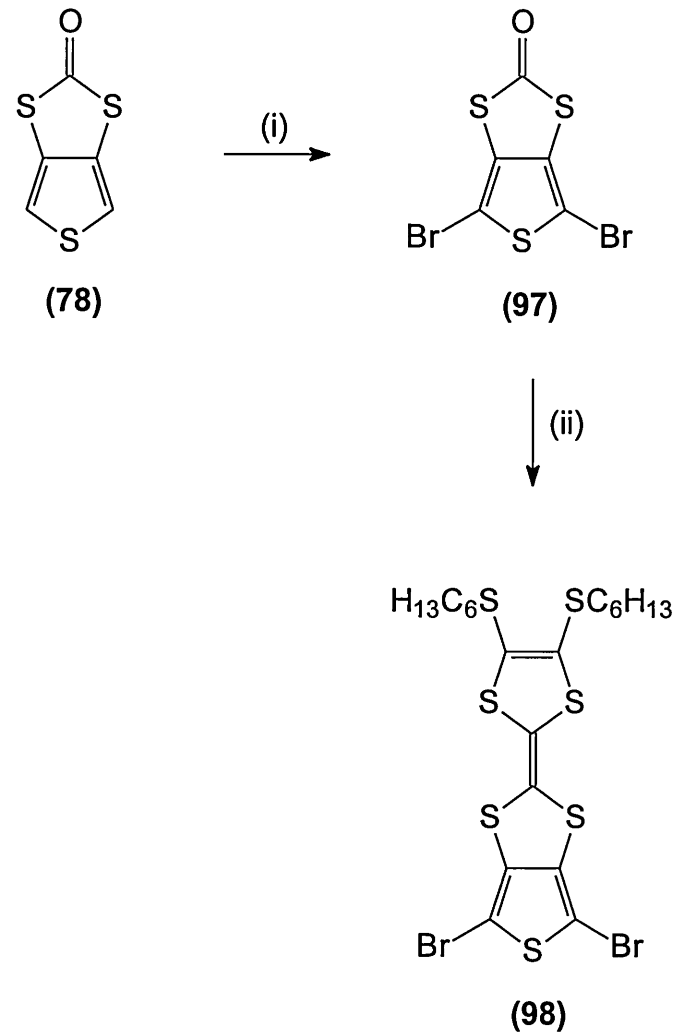


**(77)** **(96)**

**Scheme 11:** Reagents and conditions (i) LDA, -78 °C, 1h. (ii) $C_6F_{13}I$

Compound **(96)** was obtained in 88% yield by the reaction of **(77)** with lithium diisopropylamide monotetrahydrofuran under mild conditions ($N_2$, -78 °C) with subsequent addition of perfluorohexyl iodide (scheme 11). Chemical polymerisation of monomer unit **(96)**, adopting Ullman methodology,[146] by allowing a solution of **(96)** in dichloromethane to reflux with finely divided copper metal was unsuccessful, and starting materials were recovered from the reaction mixture.

Synthesis of 2,5-dibromo derivative **(97)** was achieved via bromination of compound **(78)** (scheme 12). This was allowed to reflux with an excess of bromine in chloroform for 2 h to afford **(97)** in good yield (79%). A cross coupling reaction of compound **(97)** with 4,5-bis(hexylthio)-1,3-dithiole-2-thione **(79)** in triethyl phosphite at 110 °C afforded **(98)** in 52% yield (scheme 12).



**Scheme 12 :** Reagents and conditions (i) $Br_2$, $CHCl_3$, (ii) **(79)**,$POEt_3$, 110 °C, 6 h.

Crystals of compound **(98)** were obtained by slow diffusion from dichloromethane/ acetonitrile. The single crystal X-ray structure of **(98)** is shown in figure 10. The structure shows a planar conformation, which differs from the structure obtained for the unsubstituted monomer.[142] The TTF molecules are aligned in stacks, and within each stack, a head to tail arrangement is adopted, and there are no significant close contacts between the atoms (closer than the Van der Waals radii of the corresponding elements).

Chemical polymerisation of the monomer unit was achieved via Yamamoto coupling methodology[135] and involved reaction of the monomer unit with zero valent nickel in the presence of cyclooctadiene, and 2,2′-bipyridyl in dimethylformamide.

Anhydrous conditions were employed and the reagents were allowed to stir at 60 °C in the absence of light for 48 h. A rigorous washing procedure was used upon reaction completion which afforded a dark purple solid in 95% yield. The bulk material exhibited poor solubility in common organic solvents and molecular weight determination was not possible.

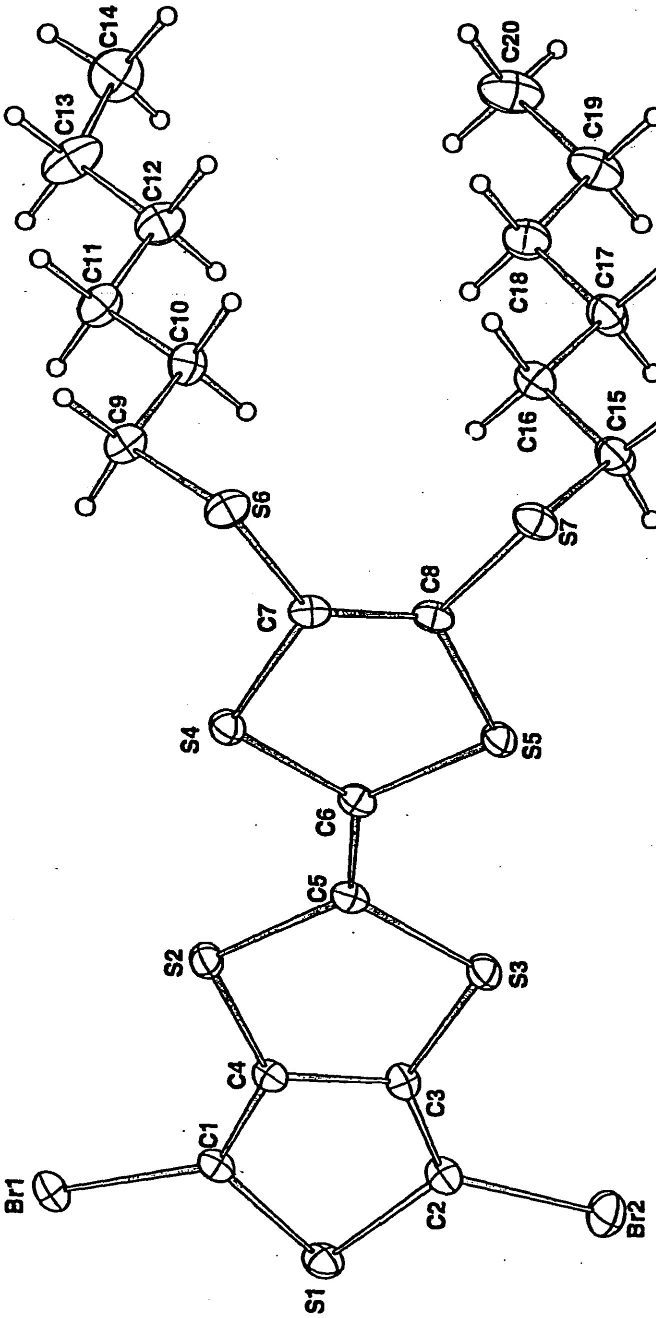
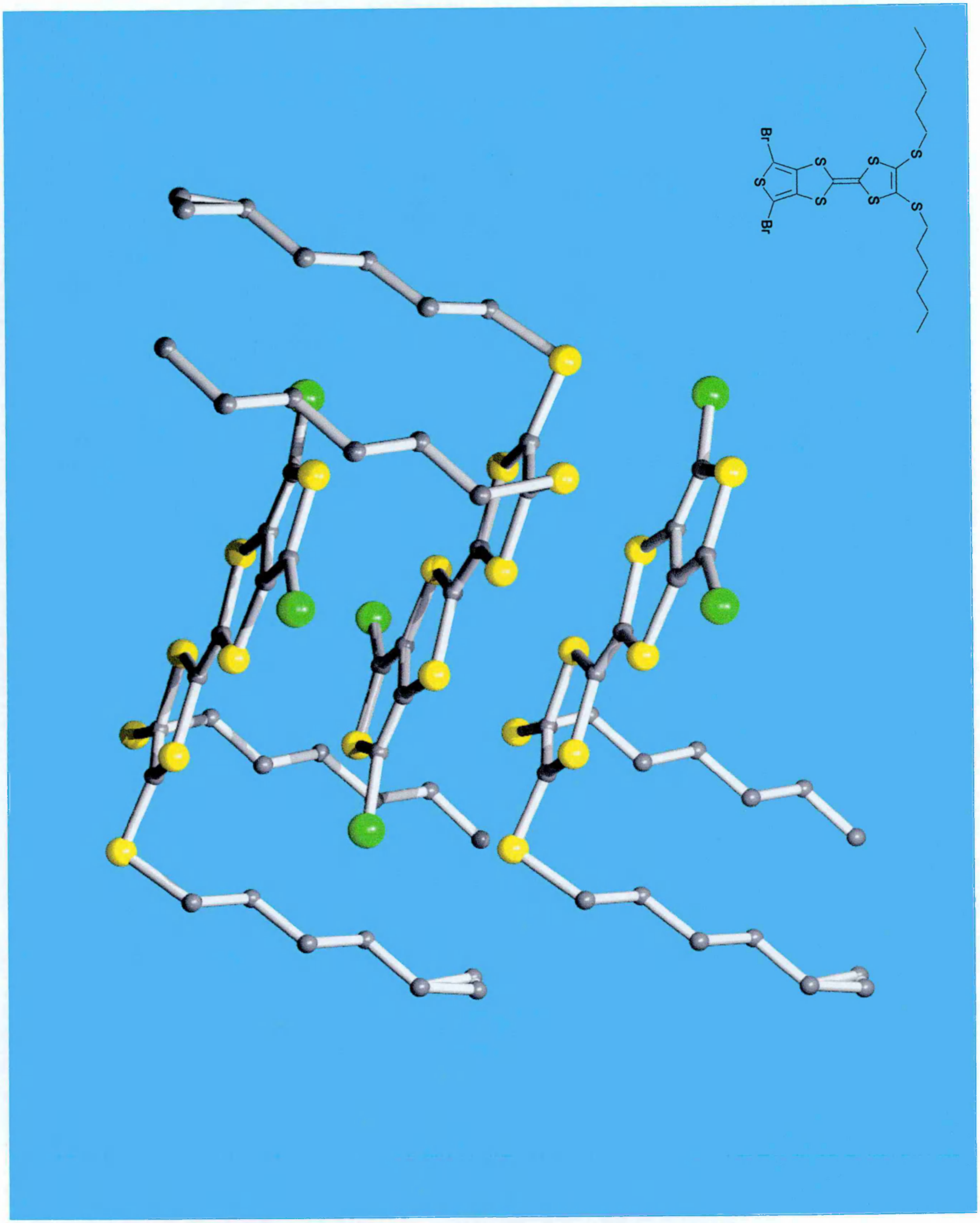


Figure 10: X-ray crystal structure of (98)


Br
S
S
S
S
S
S
S
S
Br

However, Soxhlet extraction of the resulting solid with dichloromethane afforded a purple solution which when evaporated and dried under reduced pressure resulted in the formation of a dark purple solid. Gel permeation chromatography of this soluble fraction in chloroform indicated that polymeric system **(69)** had been formed, with a thiophene chain length of up to *ca.* 14 monomer units with an average molecular weight of $M_w = 6852$ and a polydispersity of 6.218, which indicated that the fraction contained a number of short chain oligomers. Thermogravimetric analysis of the bulk polymer revealed an approximate 60% weight loss between 250 and 350 °C.

$^1$H NMR spectroscopy showed broad peaks in the aliphatic region which correspond to the hexylsulfanyl chains. The absence of aryl protons in the spectra indicate that the polymer is end-capped with bromine.

The bulk material was found to be almost completely soluble in *N,N'*-dimethylpropyleneurea (DMPU). The optical bandgap for **(69)** was estimated at 1.77 eV, which was determined by the electronic absorption spectra of the polymer. Two bands were observed at 272 and 560 nm from a thin film of the polymer (evaporation of a soluble sample onto a quartz slide). The conductivities of polymer films were 2-3 x $10^{-3}$ $\Omega^{-1}$ cm$^{-1}$, which is somewhat high for a neutral conducting polymeric system. An increase in conductivity compared to the neutral polymer was observed for the resulting films upon treatment of a solution of the polymer in DMPU with varying concentrations of TCNQ (0.1 $\Omega^{-1}$ cm$^{-1}$ derived from a 1:2 molar solution of polymer:TCNQ).

## 2.3 ELECTROCHEMISTRY

Cyclic voltammetry data was obtained from a polymer film of **(69)** which was deposited onto a gold disk working electrode by slow evaporation of a solution of the polymer in DMPU. Figure 11 shows the voltammogram obtained in acetonitrile. Three broad oxidation peaks are observed at + 0.59, + 0.78 and + 1.07 V. The corresponding reduction peaks for the system however are very broad, which makes the half-wave potentials difficult to estimate. The first and second oxidation peaks of the TTF moiety correspond to the peaks at + 0.59 and + 0.78 V, and the peak at + 1.07 V is likely to be due to the oxidation of the polythiophene chain, which shows that the electron donating sites of the system are retained by the TTF and polythiophene chain. The cyclic voltammogram of a solution of monomer **(98)** in dichloromethane shows two reversible oxidation waves at $E_1^{1/2} = +0.98$ V and $E_2^{1/2} = +1.34$ V, with the absence of a third oxidation. The differences in redox behaviour between the monomer and polymer is likely to be due to the electron withdrawing effect of the bromine atoms in the monomer unit.

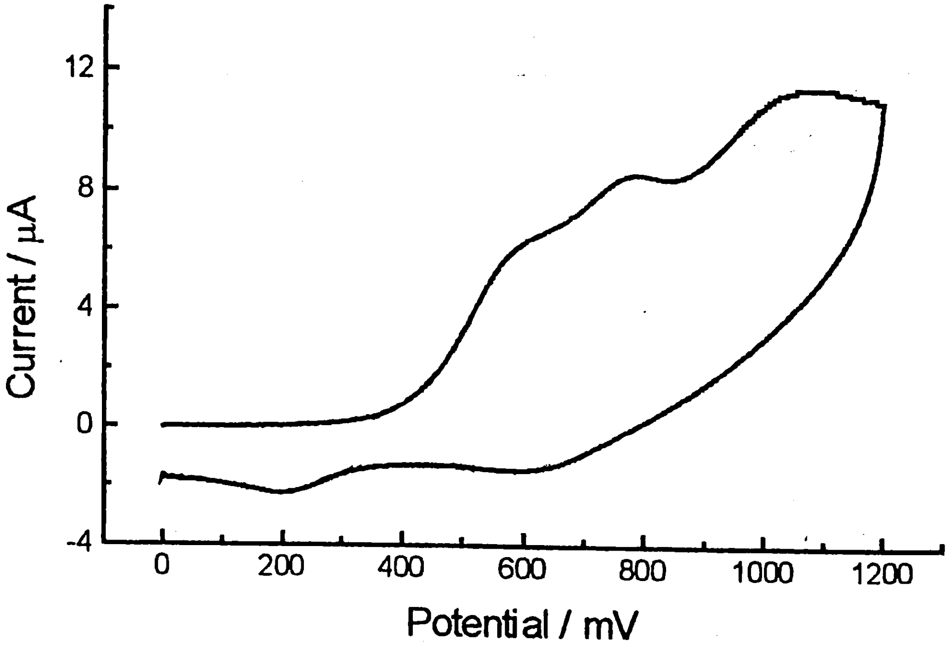


**Figure 11: Cyclic voltammogramm of (69)**

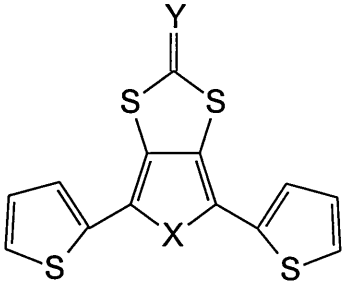
## 2.4 CONCLUSIONS AND FURTHER WORK

The incorporation of tetrathiafulvalene into conjugated polymers is an exciting and growing area of conducting materials. The synthesis of polymer **(69)** to the best of our knowledge, is the first example of an annelated TTF-thiophene polymer. The system exhibits significant electrical conductivity in the neutral state, which increases further upon doping with the electron acceptor TCNQ, has a reduced bandgap value compared to polythiophene and shows electrical activity.

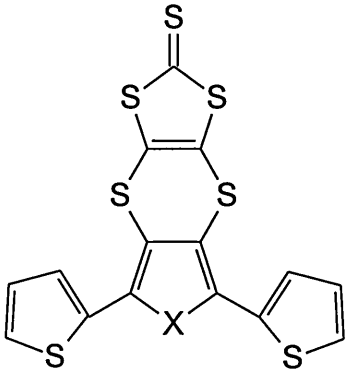
Further work in this area would involve investigation into improvement of the solubility of the system, along with detailed studies of the photophysical properties of the polymer and analogous fused TTF polythiophenes.

# CHAPTER 3

## Synthesis of Novel Terthiophene and Bithienyl Furan Derivatives



X = S, Y = S **(99)**
X = S, Y = O **(100)**
X = O, Y = S **(101)**

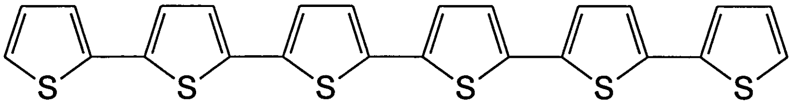


X = S **(102)**
X = O **(103)**

### 3.1 INTRODUCTION

Terthiophene systems play two main roles within the area of conjugated oligo- and poly(thiophene)s.[147] Firstly, unsubstituted 2,5″ derivatives can be used as effective trimers in oxidative polymerisation reactions, and they are also useful precursors to sexithiophenes, which are at present being investigated as useful components within field effect transistors (FET's).[148]

Oligothiophenes have become recognised as exciting materials for applications within the area of electronic devices. Among the higher oligomers, the hexamer of thiophene, α-sexithiophene (6T) is emerging as a promising organic material in FET's, diodes, optical converters and photovoltaic devices owing to its electrical conductivity and field effect mobility, photochromic properties and high efficiency of photon to electron conversion.[149]



**α-Sexithiophene**

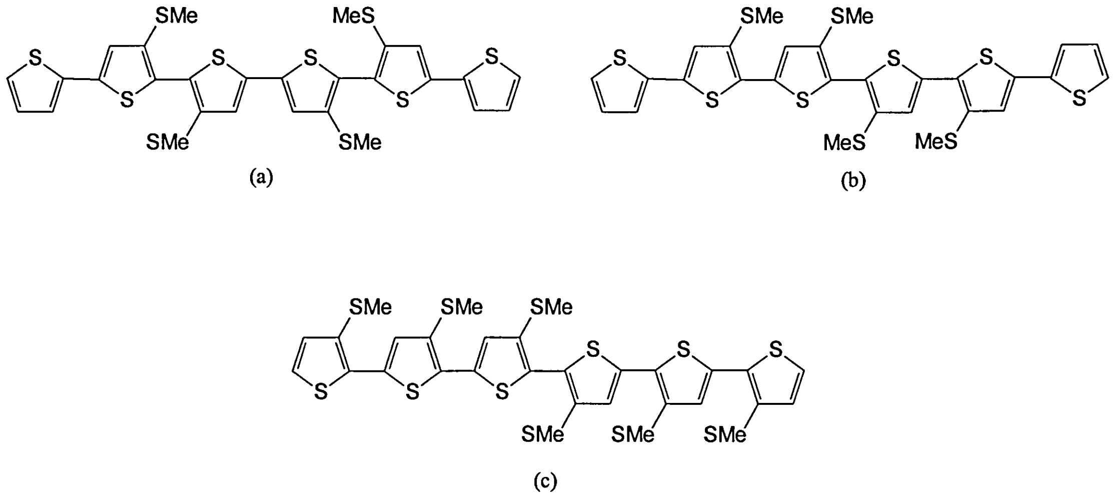
Although the majority of microelectronic devices are currently based on silicon, unsubstituted 6T is a p-type semiconducting material which can reach charge mobility values of the same order as Si (0.1 - 1.0 $cm^{-2} V^{-1} s^{-1}$) and achieve high ON/OFF ratios - essential parameters for thin film transistor applications.[150]

A disadvantage of α-6T is that it is practically insoluble in organic solvents, and requires rigorous purification, hence processability becomes difficult. It also suffers from instability due to the high reactivity of the α-C atoms on the terminal thiophene ring.[151]

Functionalisation of α-6T with long alkyl substituents has been reported. In 1995, a series of α,ω-sexithiophene derivatives were reported by Cava and Parakka,[151b] with the aim of obtaining more soluble and processable derivatives of sexithiophene. The synthesis was achieved via either an oxidative coupling of the corresponding substituted terthiophene with $FeCl_3$, or an organometallic methodology with the coupling of a brominated terthiophene derivative by the in-situ generation of a Ni (0) complex. However, despite the presence of long alkyl chains, the resulting α,ω-disubstituted sexithiophene derivative displayed surprisingly poor solubility in organic solvents, similar to the parent unsubstituted 6T, which was thought to be due to strong π-π intermolecular interactions between oligomeric thiophene units.

The synthesis of soluble and processable sexithiophene derivatives through substitution of alkyl chains on the β-position of the conjugated backbone was reported in the early 1990s.[152] However, this has resulted in a decrease in the degree of conjugation and carrier mobility caused by out of plane twisting of the thiophene rings.[152] A similar situation is observed for 3-polyalkylthiophenes where steric hindrance has caused a loss of electronic properties, unless the regiospecificity is controlled within the system.[152]

Although a loss of conjugation is observed for β-substituted derivatives, the same is not observed for alkylsulfanyl sexithiophene analogues. Barbarella *et al*[153] synthesised a series of sexithiophene derivatives functionalised by methylsulfanyl groups. Structures (a)-(c) were synthesised, with (b) exhibiting liquid crystalline properties. The loss of conjugation induced by β-substituents is compensated by the mesomeric effect of the electron lone pairs of the sulfur atoms on the S-methyl groups on the aromatic ring system, which are delocalised not only on the ring which they are attached to, but also on adjacent rings. This mesomeric effect predominates steric hindrance and is consequently an approach to synthesising soluble and processable sexithiophene derivatives. Methylsulfanyl 6T is capable of achieving a high degree of molecular organisation in the solid state, similar to unsubstituted 6T despite the presence of β-substituents.



**Methylsulfanyl 6T**

The investigation into the incorporation of strongly redox-active substituents fused onto thiophene monomers (in particular, the electron donor tetrathiafulvalene [129e,147]), has been a major target within this work. Systems of this nature represent highly redox active species with the added potential of exhibiting unusual electronic properties in addition to the properties of the conducting polymer backbone.[154]

Terthiophenes **(99)** and **(102)** have been prepared which are functionalised by a 1,3-dithiole-2-thione moiety, a synthetically versatile unit which is a well known precursor to tetrathiafulvalene.[155] Extension of the monomer unit with additional thiophene molecules will reduce any steric hindrance caused by substituents present on the central ring, which has hindered the polymerisation process in previous work. Also, the presence of a fused dithiino spacer group in **(102)** will reduce any unfavourable electronic effects caused by the 1,3-dithiole unit through 'dilution' due to the spacer group, leading to a more stable radical cation intermediate upon oxidation.

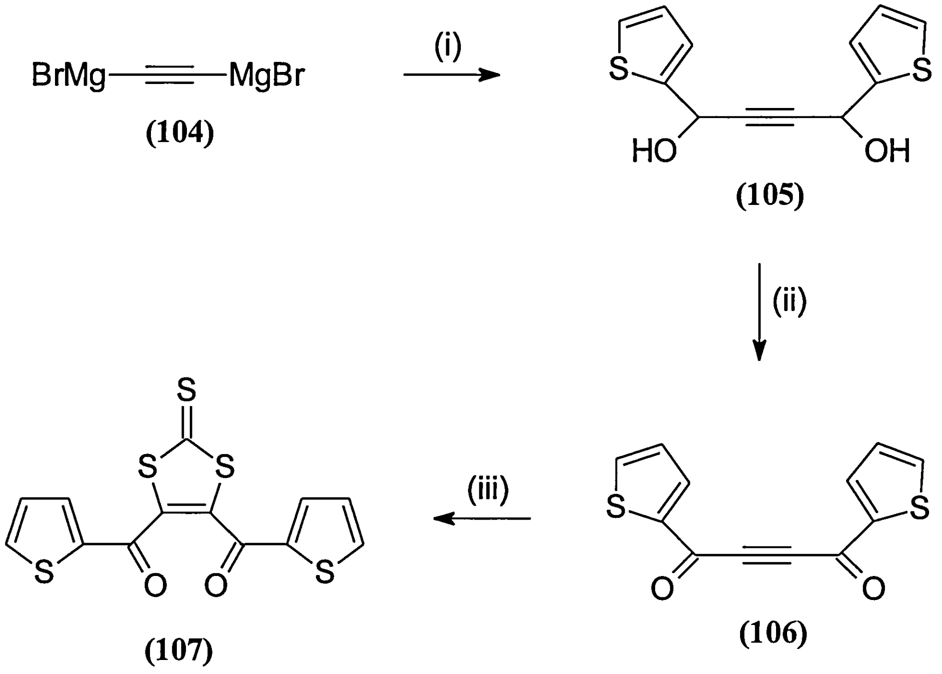
The synthesis of mixed heterocyclopentadiene co-oligomers[156] and copolymers[157] is also of interest. Theoretical studies of copolymers have shown that mixed repeating units with different bandgap values actually lowers the **Eg** of the resulting polymer,[158] and therefore can be used as a strategy for the tuning of the bandgap of conducting polymers.

The remainder of this chapter is concerned with the detailed synthesis and electrochemistry of terthiophenes **(99), (100)** and **(102)**.

Conversion to the tetrathiafulvalene derivative **(116)**, and synthesis towards a fused sexithiophene derivative is also discussed, along with the attempted polymerisation of monomer unit **(116/117)** by chemical and electrochemical methods.

## 3.2 RESULTS AND DISCUSSION

Terthiophenes **(99)** and **(102)** were obtained in 70% and 57% yields respectively, by the cyclisation of the corresponding diketones **(107)** and **(122)**. This was achieved by heating the diketones with phosphorus pentasulfide and sodium hydrogen carbonate in 1,4-dioxane.[159] Cyclisation of such systems under similar conditions has proved to be successful for both saturated and unsaturated diketones, as observed in the conversion of 2,3-dibenzoylnaphthalene to 1,3-diphenylnaphtho[2,3-*c*]thiophene.[160]



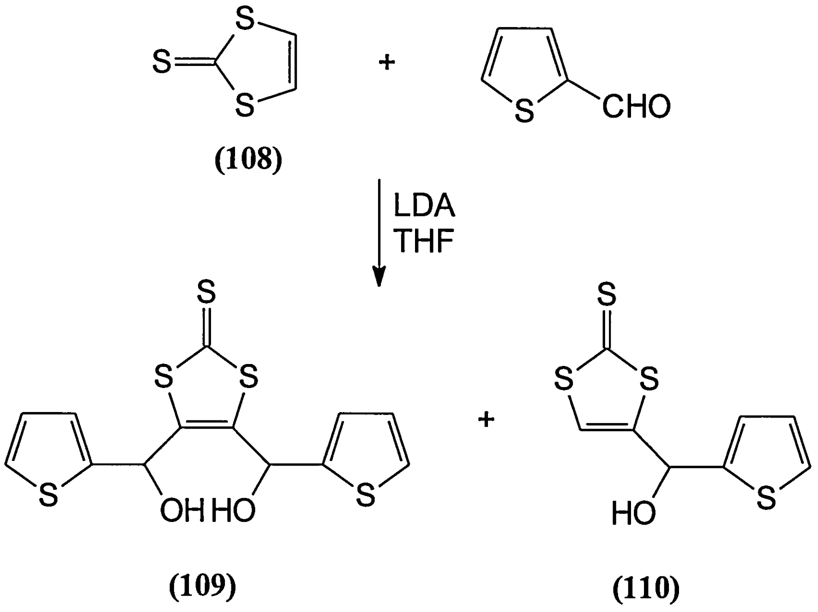
**Scheme 13:** Reagents and conditions (i) 2-thiophenecarboxaldehyde, THF (ii) $MnO_2$, $CH_2Cl_2$ (iii) **(81)**, toluene.

The synthetic pathway to diketone **(107)** has been explored by two routes. Initially, a cycloaddition reaction between ethylene trithiocarbonate **(81)**[161] and 1,4-bis(2-thienyl)but-2-yne-1,4-dione **(106)**, analogous to the synthesis of dimethyl-1,3-dithiole-2-thione-4,5-dicarboxylate[162] **(82)** resulted in the preparation of diketone **(107)** (Scheme 13). Synthesis of dithienoyl acetylene **(106)** involved oxidation of the corresponding diol **(105)** (previously reported as a by-product in the synthesis of monofunctionalised acetylene),[163] which in turn was obtained from the addition of 2-thiophenecarboxaldehyde to acetylene dimagnesium bromide[164] **(104)** (50% yield). The use of manganese (IV) oxide (10:1 w/w) was employed for the oxidation of diol **(105)**, since it was suspected that the acidic conditions employed in other oxidation processes, for example with $CrO_3$ would result in ring closure of the system to form the furan derivative via an acid catalysed rearrangement process.

Reaction efficiency of the oxidation process was dependent on the quantity of $MnO_2$ used in the reaction (~ 40% with $MnO_2$:diol 6:1w/w and 55% with 12:1w/w), but was independent of the solvent choice (dichloromethane, diethyl ether, benzene). Dichloromethane was chosen for convenience as this proved to be the best solvent in subsequent purification of diketone **(106)** by column chromatography. The optimum reaction time for the oxidation was very short (2 minutes) and decomposition of the product was observed with prolonged treatment with $MnO_2$.

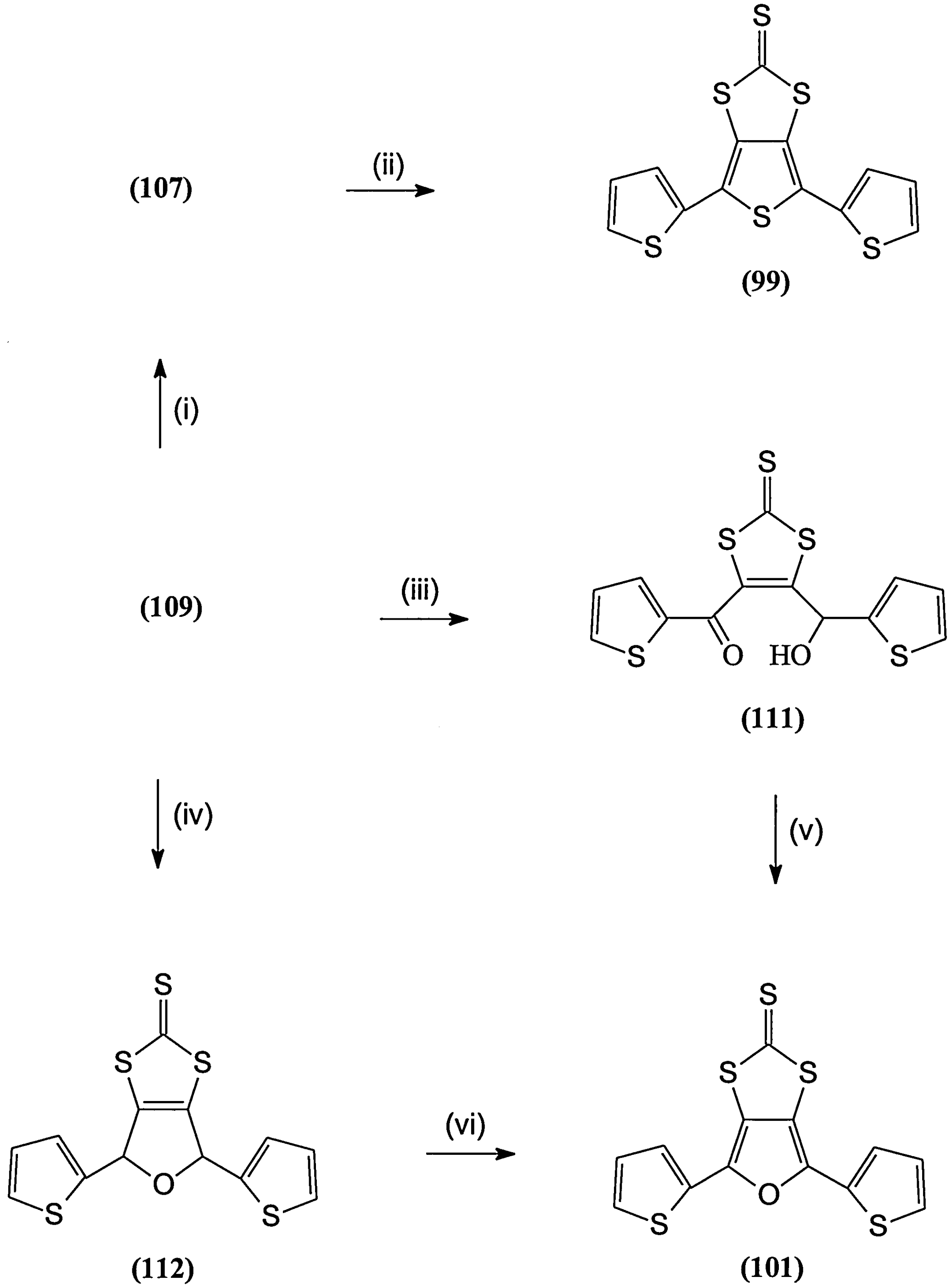
Although the yield obtained for the synthesis of diketone **(106)** was satisfactory (55%), its reaction with ethylene trithiocarbonate **(81)** to afford the diketone intermediate **(107)** resulted in a very poor yield (8%) and an alternative strategy was adopted in order to increase the efficiency of the synthesis of key intermediate **(107)**.

The synthetic route involved the oxidation of diol **(109)** which was obtained in good yield (82%), *via* the lithiation of vinylene trithiocarbonate **(108)**[139] (Fluka), with subsequent trapping of the carbanion species with 2-thiophenecarboxaldehyde (scheme 14). A step-wise process was adopted in the synthesis of **(109)**, such that one equivalent of reagents was allowed to react with **(108)** prior to the addition of the second equivalent of reagents. Attempts at a one step process to obtain the dilithio derivative of **(108)** were unsuccessful even under mild conditions (tetrahydrofuran, -60 °C), which predominantly led to the formation of monofunctionalised derivative **(110)**, even in the presence of a large excess of LDA. The formation of dilithiothiophenes[165] has proved to be favoured by using less polar solvents such as toluene and petroleum ether. However, this did not lead to an increase in the yield of **(109)**, and decomposition of the starting material was observed when using *n*-BuLi or by increasing the reaction temperature.



**Scheme 14**

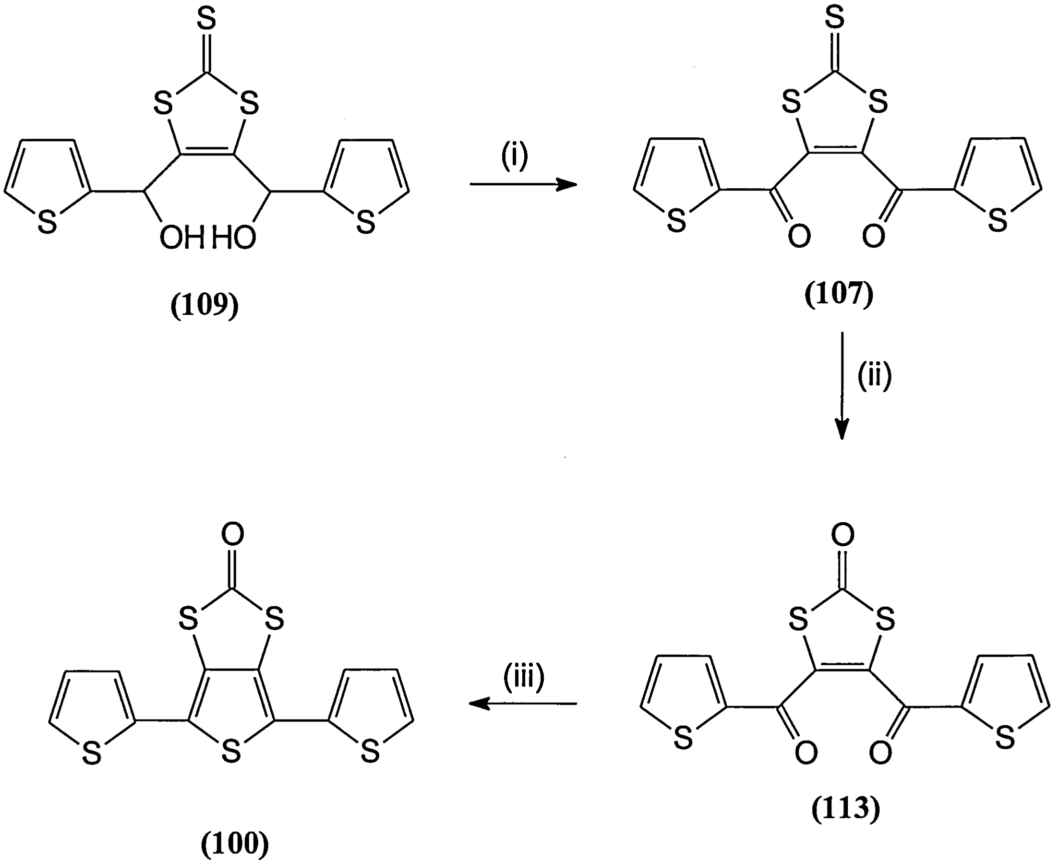
Synthesis of diol **(109)** resulted in the formation of diastereomers **109a** and **109b**, which were separated easily by column chromatography (silica, dichloromethane). The NMR spectra showed a normal splitting pattern for the methine proton in isomer a. This is due to coupling of the proton with the adjacent hydroxyl group ($J$ = 3.6 Hz). The same peak for isomer b appeared as a broad singlet ($W_{1/2}$ = 3 Hz). A trace amount of acid (or $CDCl_3$) was added to both isomers to quench the coupling of methine to hydroxyl protons. The resulting NMR spectra for each isomer showed methine doublets, due to interaction with 3 - H protons of the thiophene ring ($J$ = 0.8 Hz). The value of the coupling constant between methine and hydroxyl protons in isomer b does not exceed 2 Hz which suggests an unfavourable value for the H-C-O-H dihedral angle, which may be due to a dominant hydrogen bonded conformation of the molecule.



**Scheme 15:** Reagents and conditions (i) $MnO_2$, $CH_2Cl_2$ (ii) $P_2S_5$, $NaHCO_3$, 1,4-dioxane (iii) $MnO_2$, $CH_2Cl_2$, (iv) HBr, $CH_2Cl_2$ (v) HBr, $Me_2CO$ (vi) DDQ, toluene, reflux.

Oxidation of diol **(109)** was achieved using manganese (IV) oxide (scheme 15). The reaction efficiency increased with the quantity of manganese (IV) oxide used, and a quantitative yield was obtained using a ten-fold excess (by weight). Mono-oxidised derivative **(111)** was obtained in 50% yield with a limited amount of oxidising reagent (3:1 (w/w)) with **(107)** as a side product of the reaction. Under ambient conditions, this underwent slow conversion to the furan derivative **(101)**. The addition of acid (HBr or $HClO_4$) efficiently catalysed the reaction to give the corresponding furan **(101)** (89% yield).

Compound **(101)** was also synthesised by the aromatisation of the dihydrofuran **(112)** with DDQ, which was in turn obtained by the acid catalysed cyclisation of diol **(109)**. However, this synthetic route led to a lower overall yield (ca. 5%) than the previous method (45%), rendering it a much more inferior synthetic pathway to furan **(101)**.

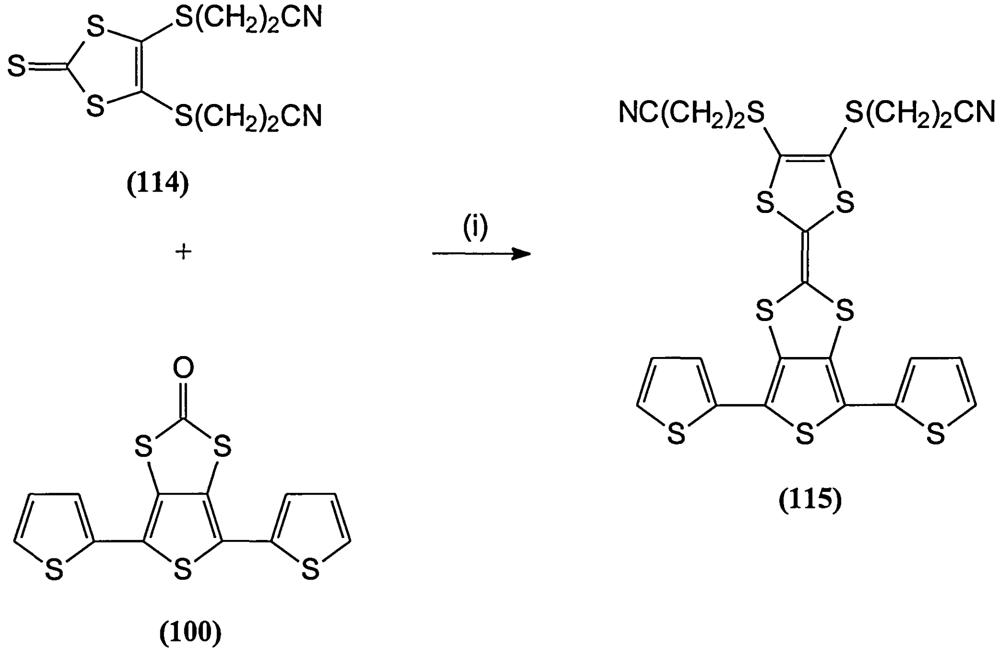


**Scheme 16:** Reagents and conditions (i) $MnO_2$ (ii) $Hg(OAc)_2$ (iii) $P_2S_5$, $NaHCO_3$, 1,4-dioxane.

The synthesis of tetrathiafulvalene derivative **(115)** was achieved via a cross coupling reaction of compounds **(100)** and **(114)** in triethyl phosphite. The reaction efficiency of the coupling process is increased if one of the half units is a carbonyl rather than a thione (usually the least soluble moiety - in this case, the terthiophene). It was therefore necessary to synthesise compound **(100)**. The transchalcogenation of **(99)** to afford compound **(100)** was inefficient due to the poor solubility of **(99)** in the reaction media used (dichloromethane : acetic acid) and low yields were obtained (20%). Solubility is the key to an efficient transchalcogenation reaction. The reaction involves stirring a solution of a starting material with $Hg(OAc)_2$ in a 3:1 v/v mixture of dichloromethane:glacial acetic acid. During the reaction, a solid precipitate is formed which is filtered upon reaction completion. The starting materials and product should therefore be soluble in the reaction media so as to maximise reaction yields. It was therefore necessary to convert compound **(107)** to its corresponding carbonyl before cyclisation with $P_2S_5$, which was achieved by treatment of **(107)** with mercuric acetate (scheme 16).[142] Diketone **(113)** is soluble in dichloromethane, and the reaction afforded **(113)** in 76% yield.

It was anticipated that ring closure of this system to afford the corresponding terthiophene with phosphorus pentasulfide may result in conversion of the carbonyl moiety back to the thione. In order to prevent this, a lower temperature was used in the cyclisation process (90 °C), and **(100)** was successfully synthesised in 63% yield. Mass spectrometry (m/z (EI) 338) and Infrared analysis (C=O, 1623 $cm^{-1}$) confirmed that the carbonyl functionality had remained intact under these reaction conditions.

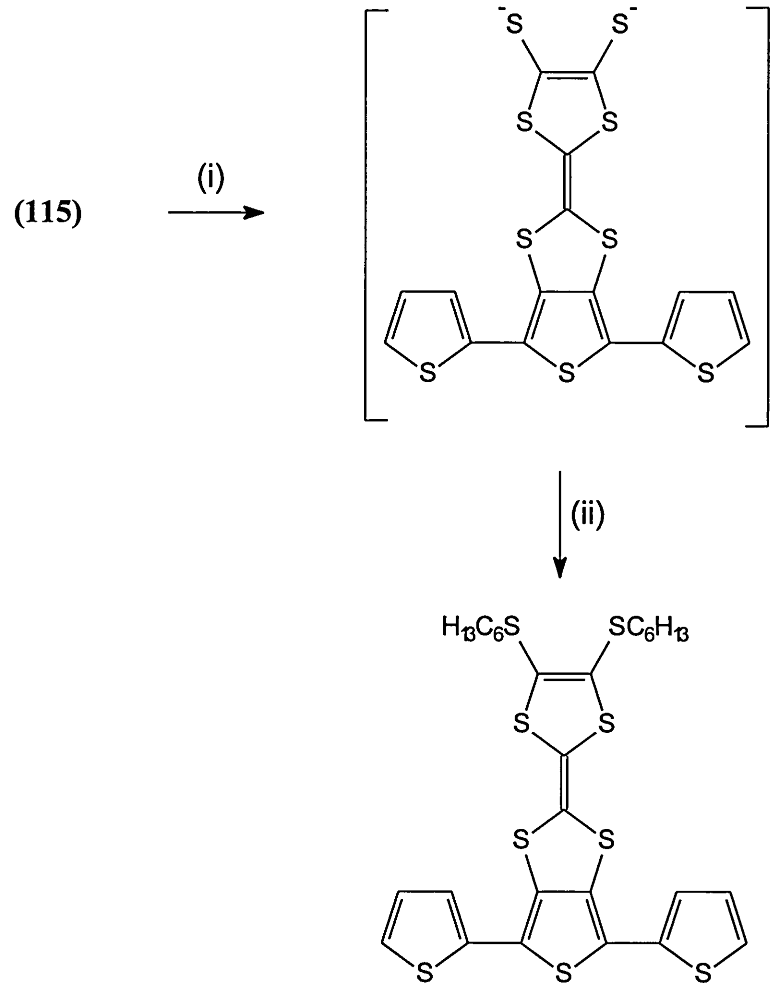
Tetrathiafulvalene derivative **(115)** was obtained in 61% yield by heating **(100)** with 4,5-bis(2-cyanoethylsulfanyl)-1,3-dithiole-2-thione **(114)** in triethyl phosphite at 120 °C for 6 h. Synthesis of the nitrile intermediate was favoured for purification purposes as, in this type of reaction, a number of side products are synthesised along with the desired product due to self-coupling between starting materials.



Scheme 17: Reagents and conditions (i) $POEt_3$, 110 °C, 6 h

Compound **(115)** was separated easily from the self coupled products by column chromatography (silica, dichloromethane). However, purification is difficult if 4,5-bis(hexylsulfanyl)-1,3-dithiole-2-thione **(79)** is used to couple with terthiophene **(100)**. Similar Rf values are observed for the desired tetrathiafulvalene derivative **(116)** and self-coupled 4,5-bis(hexylsulfanyl)-1,3-dithiole-2-thione, even in non polar solvents.

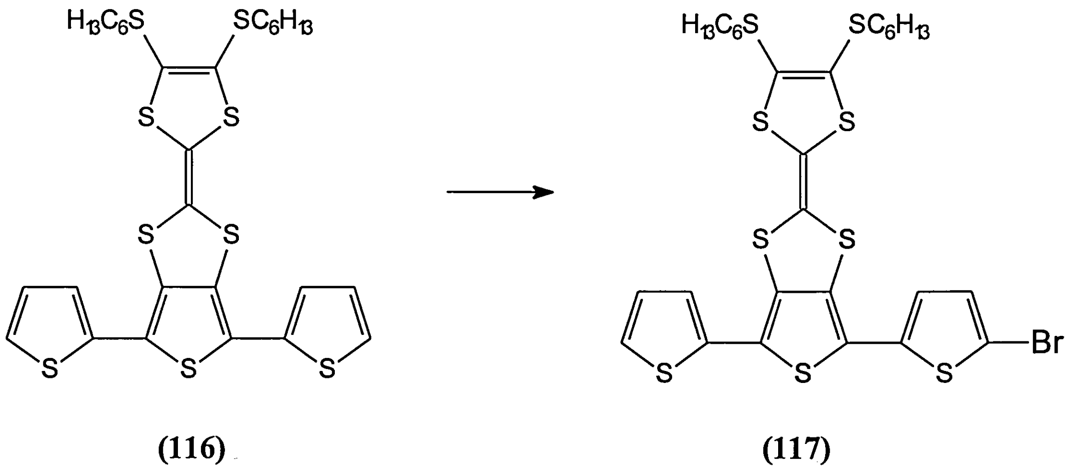
Conversion to tetrathiafulvalene **(116)** was achieved by allowing **(115)** to react with tetrabutylammonium hydroxide at 0 °C (scheme 18). The dithiolate intermediate formed in the reaction was then allowed to react with 1-bromohexane to afford **(116)** in 60% yield.



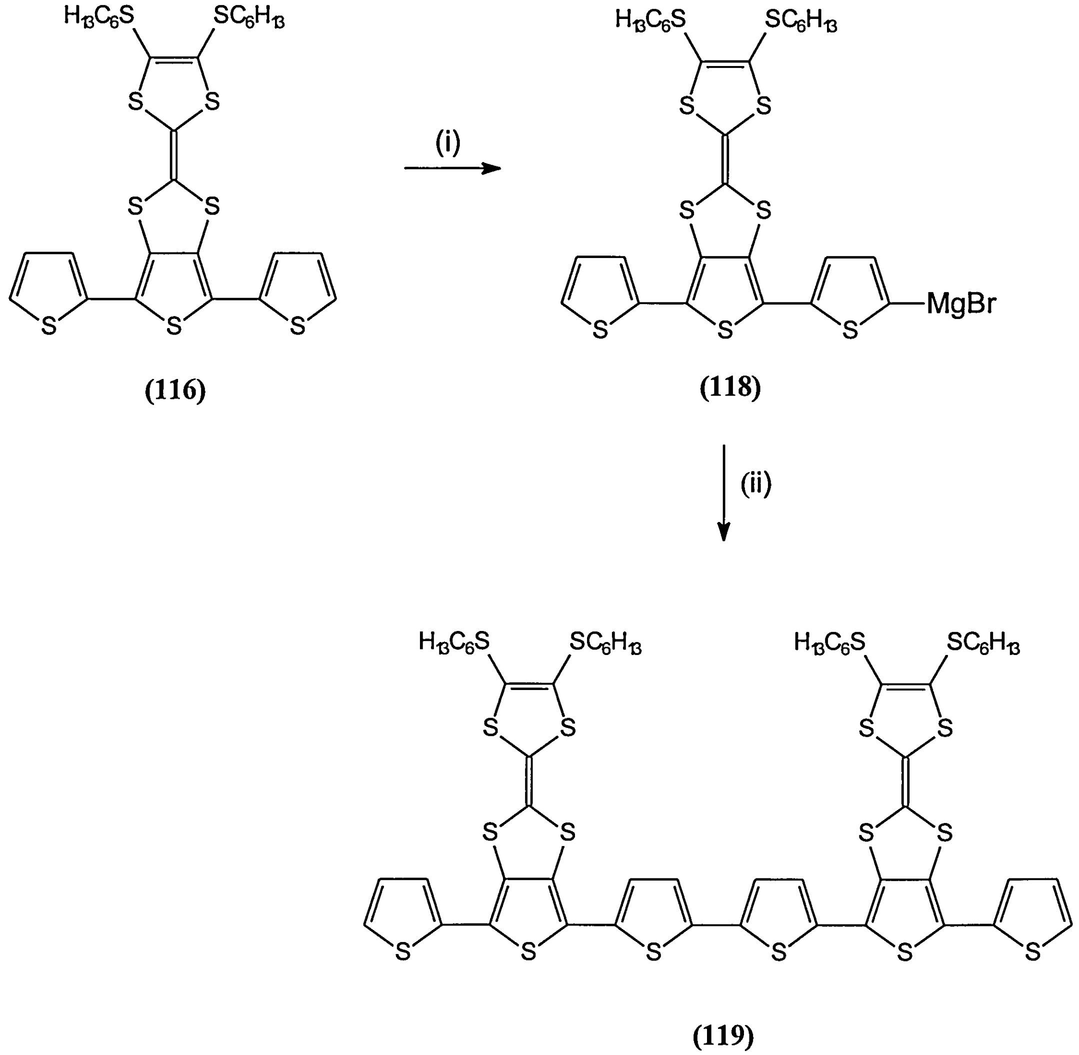
**(116)**

**Scheme 18:** Reagents and conditions (i) $nBu_4NOH$, 0 °C, THF, 1h (ii) 1-bromohexane

Bromination of tetrathiafulvalene derivative **(116)** was achieved via lithiation with LDA under mild conditions (-78 °C), followed by addition of 1,2-dibromotetrafluorethane. Column chromatography with petroleum ether isolated compound **(117)** successfully; however a low yield was obtained (22%). Synthesis towards the sexithiophene derivative **(119)**, via lithiation of **(116)** at -78 °C (LDA) with subsequent addition of magnesium bromide diethyl etherate to afford Grignard intermediate **(118)** followed by a Grignard coupling methodology with $NiCl_2$(dppp) and **(117)** was unsuccessful (scheme 20), and starting materials were re-claimed.



**Scheme 19:** Reagents and conditions (i) LDA, -78 °C, THF, 1h (ii) $BrCF_2CF_2Br$

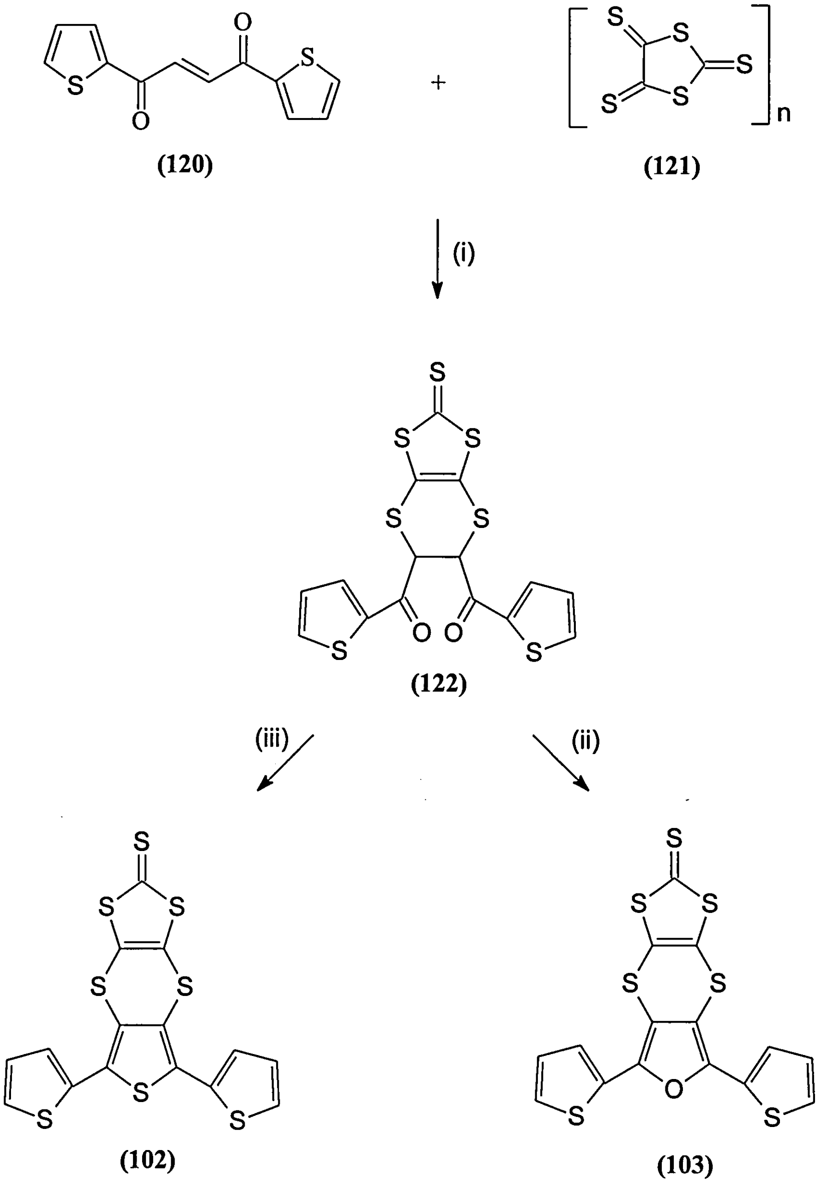


**Scheme 20:** Reagents and conditions (i) LDA, $MgBr(OEt)_2$ (ii) **(117)**, $NiCl_2$(dppp)

Chemical polymerisation of tetrathiafulvalene **(116)** was attempted via an oxidative coupling reaction with $FeCl_3$ in dichloromethane at room temperature.[166] The resulting solid product was extracted into a variety of organic solvents via Soxhlet extraction. Upon de-doping with hydrazine hydrate (10 ml for each fraction), each extraction was filtered and dried in vacuo. The major portion of the material was dissolved into dichloromethane and analysed by gel permeation chromatography. Results indicate that oligomers were formed in the reaction, with chain lengths up to 9 thiophene units. The average molecular weight of the system was 2047 with a polydispersity of 4.986 indicating that at best, the reaction gave a small amount of dimers and trimers.

Extended terthiophene monomer **(102)** was then developed to establish whether a reduction of unfavourable electronic effects caused by the 1,3-dithiole unit occurs by the fused dithiino spacer group, leading to a more stable radical cation upon electropolymerisation.

Diketone **(122)** was synthesised via a Diels-Alder coupling between 1,4-bis(2-thienyl)but-2-ene-1,4-dione[167] **(120)** and oligo(1,3-dithiole-2,4,5-trione)[168] **(121)** in refluxing toluene (scheme 21), and was obtained in 73% yield. An excess of oligomer **(121)** at this stage led to a decrease in the product yield due to side reactions between **(122)** and **(121)**.



**Scheme 21:** Reagents and conditions (i) toluene, reflux (ii) HBr, AcOH (iii) $P_2S_5$, $NaHCO_3$, 1,4-dioxane, 90 °C

Cyclisation of **(122)** to afford the corresponding thiophene derivative **(102)** proved difficult. This was thought to be due to the *trans* arrangement of the carbonyl groups with respect to the dithiin ring (confirmed by X-ray crystallography). The single crystal X-ray structure of compound **(122)** is shown in figure 12. The structure shows a central dithiin ring onto which is fused a 1,3-dithiole-2-thione moiety. The ring also has 2,3-diketone substituents which bear a thienyl ring connected at the 2-position. The arrangement of the carbonyl groups determines the orientation of the thienyl rings as a result of intramolecular interactions between O1 - S1 and O2 - S4 (2.958 + 2.951 Å, which are 0.36 and 0.37 Å less (respectively) than the sum of the contact radii. The angle of orientation between the mean plane of the dithiin ring and the thienyl substituents are 17.64 ° (axial) and 50.20 ° (bisectional substituents) for the C7 - C8 and C6 - C5 arms respectively. The rings have a planar conformation, analysed by a Cremer-Pople analysis,[169] with the sulfur atom lone pairs creating a puckering of the ring. An angle of 116.25(12)° is observed between the two least squares mean planes (S2 - C7 - C6 - S3) and (S2 - C13 - C14 - S3) of the dithiin ring, and subsequent puckering analysis gave $\theta = 94.2$ E and $\phi = 184.27$ E corresponding to a boat conformation.

Diketone **(122)** proved to be stable with respect to the normal conditions used in the preparation of such systems from 1,4-diketones (Lawesson's reagent in refluxing toluene or $P_2S_5$ and $NaHCO_3$ in ether at room temperature).[159] It was suspected that the low reactivity of **(122)** towards cyclisation is due to steric hindrance arising from the conformation of the 1,4-dithiin ring limiting the approach of sulfur reagents. However, the trans configuration of diketone **(122)** did not render the cyclisation impossible; under more vigorous reaction conditions ($P_2S_5$ and $NaHCO_3$, 1,4-dioxane, 90 °C), terthiophene **(102)** was synthesised successfully in 57% yield.

Furan derivative **(103)** was obtained by the acid catalysed cyclisation of diketone **(122)** However, in parallel to the reaction for the corresponding terthiophene **(102)** the yield of furan derivative **(103)** (35%) was substantially lower than expected for a non hindered system.[159,167]

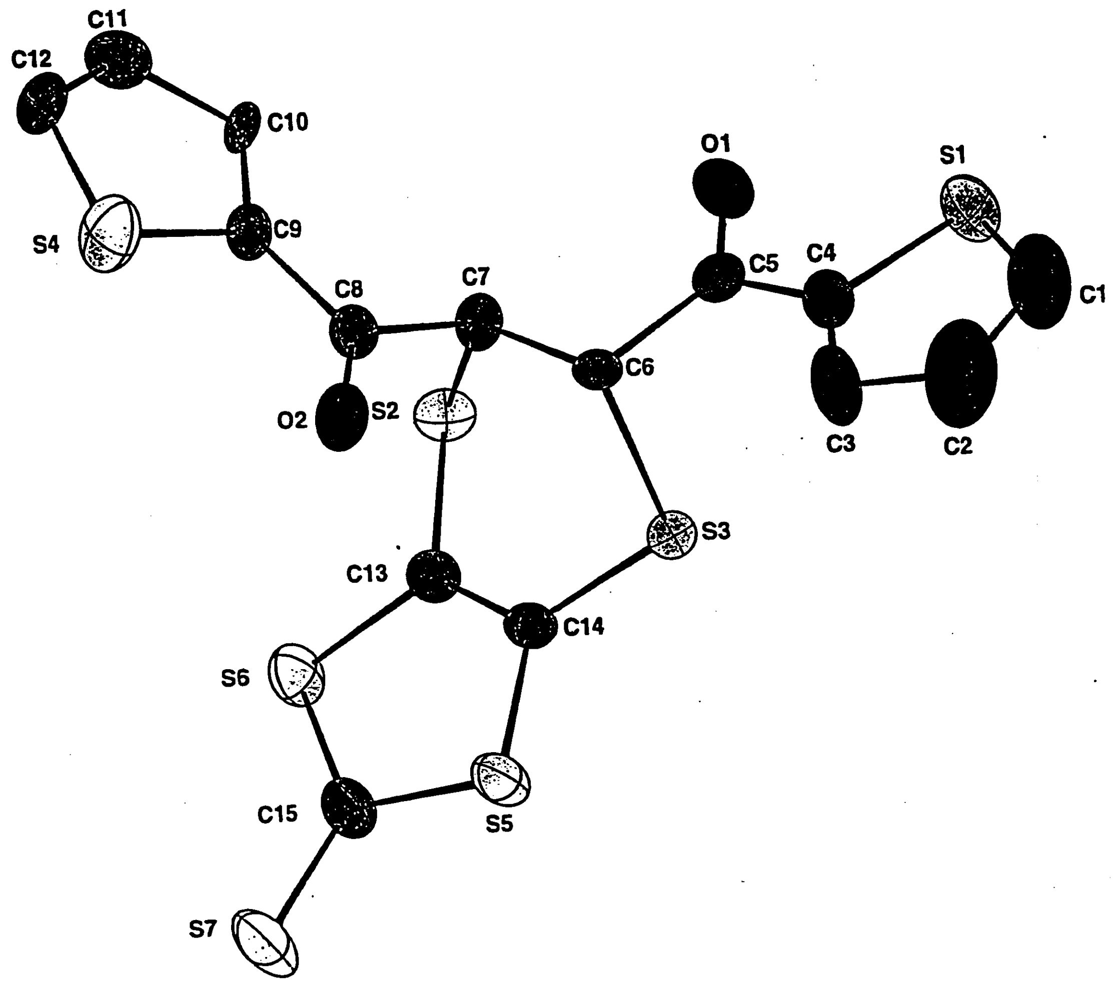


Figure 12: X-ray crystal structure of (122)

## 3.3 ELECTROCHEMISTRY

The cyclic voltammogram of terthiophene **(99)** reveals two oxidation processes. This corresponds to $E_1^{1/2}$ (+ 1.23 V) and $E_2^{1/2}$ (+ 1.73 V) with the latter being irreversible (figure 13).

Unusual redox behaviour has been observed for fused thiophene derivative **(86)**.[129e] A broad oxidation peak is observed between + 1.30 V and + 1.70 V, along with a distinct reduction wave at + 0.81 V (figure 14). The large difference between these two peaks does not correlate with the electrochemical behaviour observed for terthiophene **(99)**.

It can be assumed therefore, that the overall redox properties of this system are independent of the central thiophene ring, and that it is the oxidation of the terthiophene moiety that is responsible for the first redox process, with the second irreversible peak being due to the fused 1,3-dithiole ring.

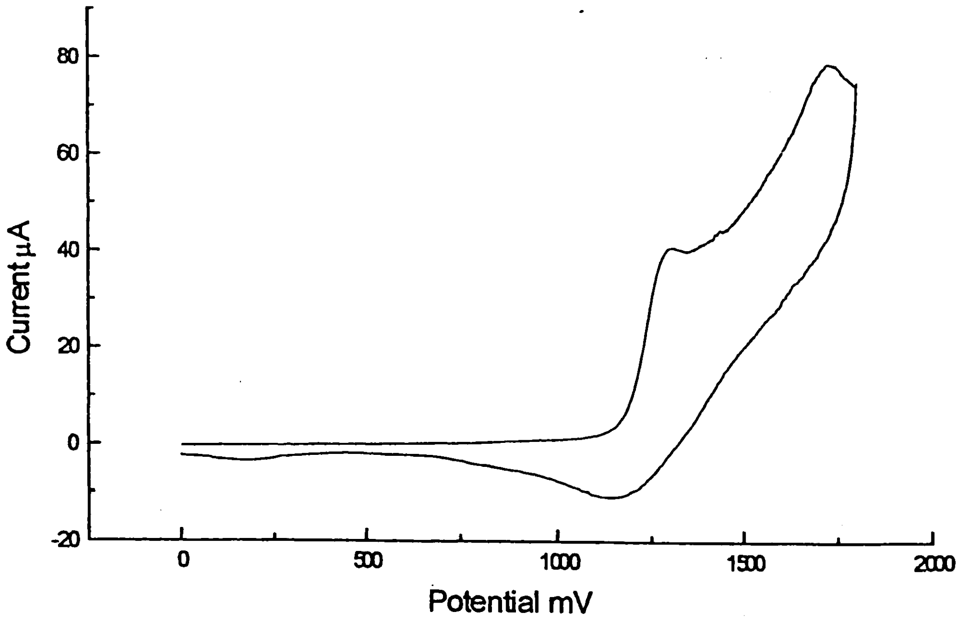


**Figure 13:** Cyclic voltammogram of **(99)** vs. Ag/AgCl; Au working electrode, platinum wire counter electrode, 0.1 M $Bu_4NPF_6$ in dry dichloromethane at 20 °C with *iR* compensation, scan rate 200 mV $s^{-1}$.

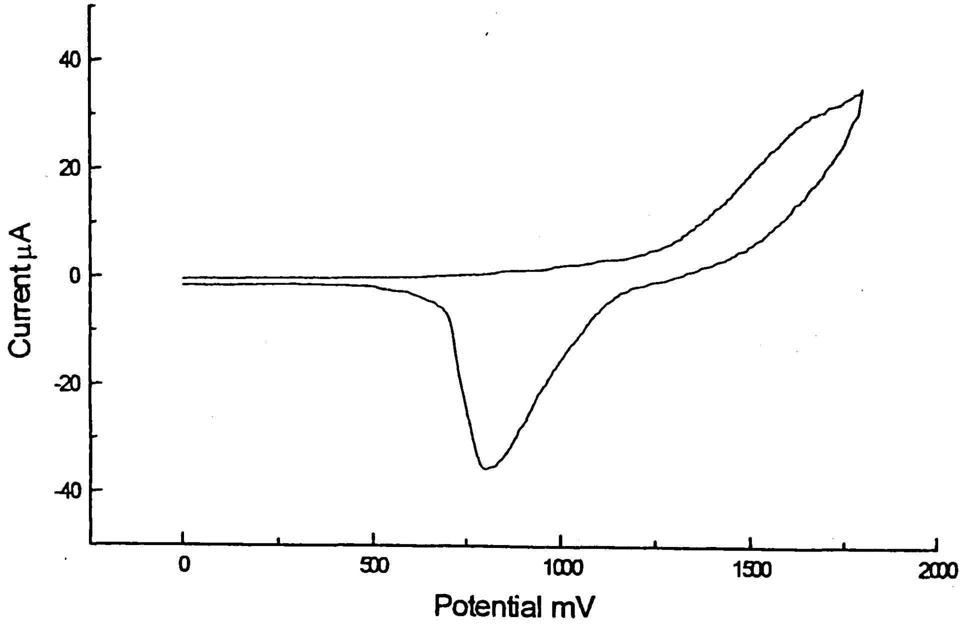


**Figure 14:** Cyclic voltammogram of **(86)** vs. Ag/AgCl; Au working electrode, platinum wire counter electrode, 0.1 M $Bu_4NPF_6$ in dry dichloromethane at 20 °C with *iR* compensation, scan rate 200 mV $s^{-1}$.

The voltammogram obtained for furan derivative **(101)** (figure 15) shows only one redox wave ($E^{1/2}$ + 1.13 V) which supports the assumption that the central ring is not involved in this process.

Analogous to the voltammogram obtained for **(99)**, the absence of a second irreversible peak is likely to be due to the enhanced electron withdrawing capacity of the furan ring of **(96)** than that of the corresponding thiophene **(99)** suppressing the electroactivity of the 1,3-dithiole unit.

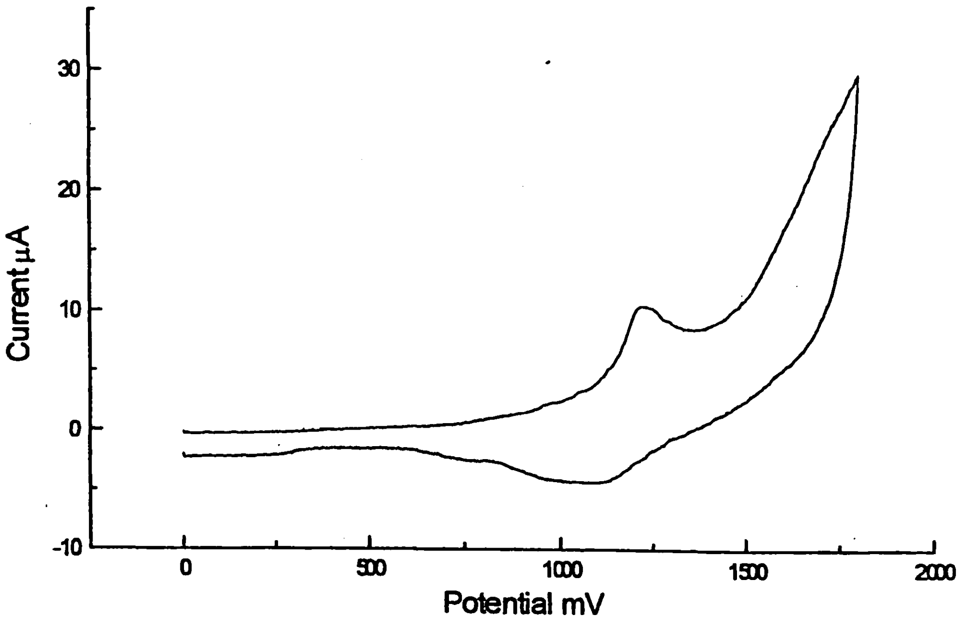


**Figure 15:** Cyclic voltammogram of **(101)** vs. Ag/AgCl; Au working electrode, platinum wire counter electrode, 0.1 M $Bu_4NPF_6$ in dry dichloromethane at 20 °C with *iR* compensation, scan rate 200 mV $s^{-1}$.

The voltammograms obtained for extended systems **(102)** and **(103)** (figure 16) are almost identical. An ill defined oxidation peak is observed between + 1.30 V and + 1.90 V, with corresponding reduction waves at + 0.85 V and + 0.88 V respectively.

The voltammogram obtained for the corresponding extended fused thiophene **(123)** (figure 17) is similar. A defined oxidation peak is observed at + 1.48 V with corresponding reduction wave at + 0.94 V.

Assignment of the redox processes in **(102)** and **(103)** becomes ambiguous as the potential activity of the 1,4-dithiino moiety cannot be discounted.

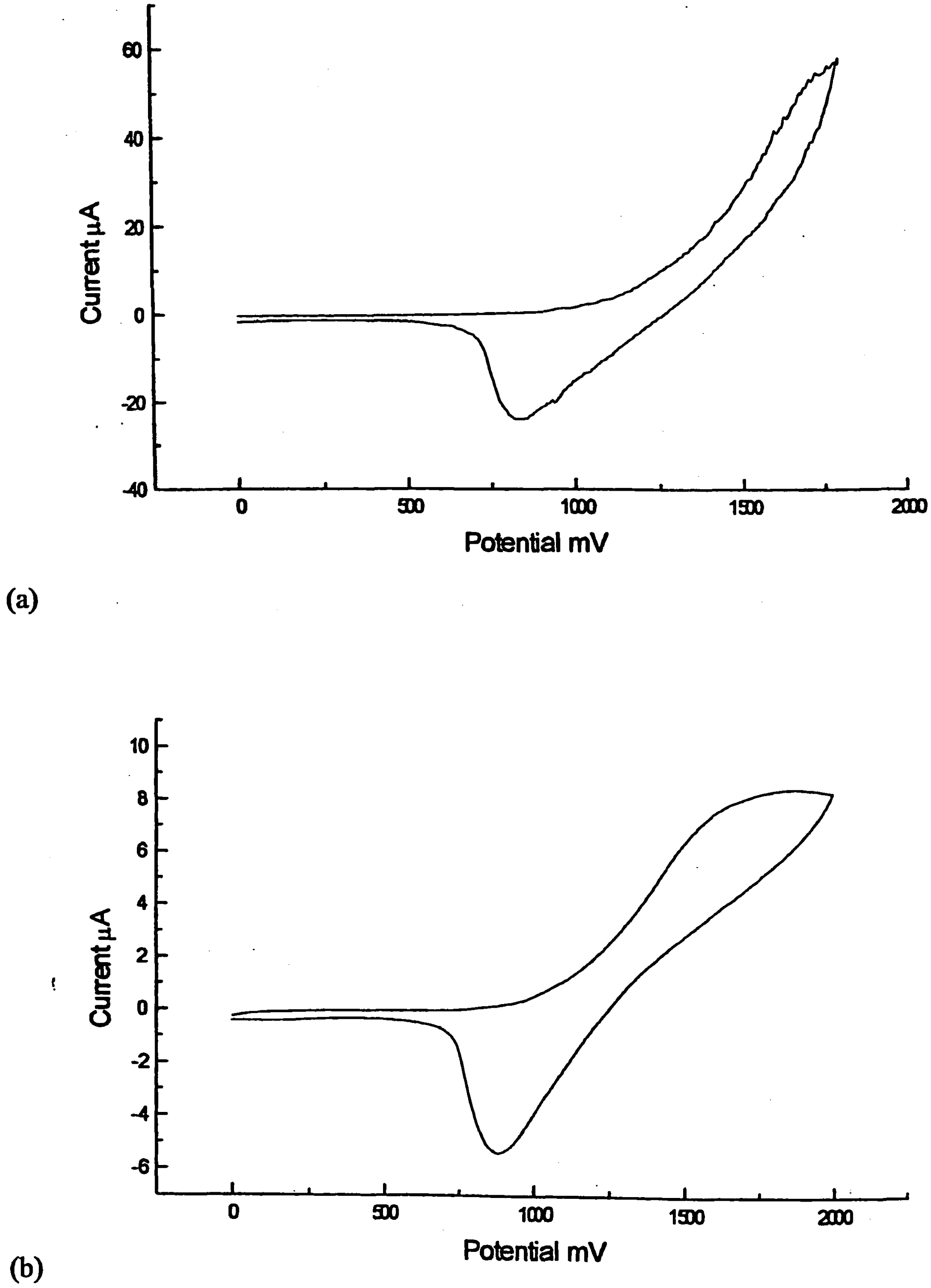
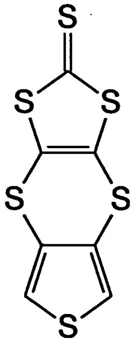


**Figure 16:** Cyclic voltammogram of (a) **(102)** and (b) **(103)** vs. Ag/AgCl; Au working electrode, platinum wire counter electrode, 0.1 M $Bu_4NPF_6$ in dry dichloromethane at 20 °C with *iR* compensation, scan rate 200 mV $s^{-1}$.

Polymerisation of compounds **(86)** and **(123)** by electrochemical procedures has been unsuccessful. However, initial studies on terthiophene derivatives **(99)-(103)** indicate that the monomers can be electrochemically polymerised successfully to form the corresponding polymers and copolymers, through repetitive scanning in the range from 0.00 V to + (1.60 - 2.00 V). Dark red films were deposited at the working (Au) electrode, which appear to be stable over several scans. However, the corresponding copolymer of furan derivative **(100)** loses its electroactivity upon cycling below - 0.5 V.



**(123)**

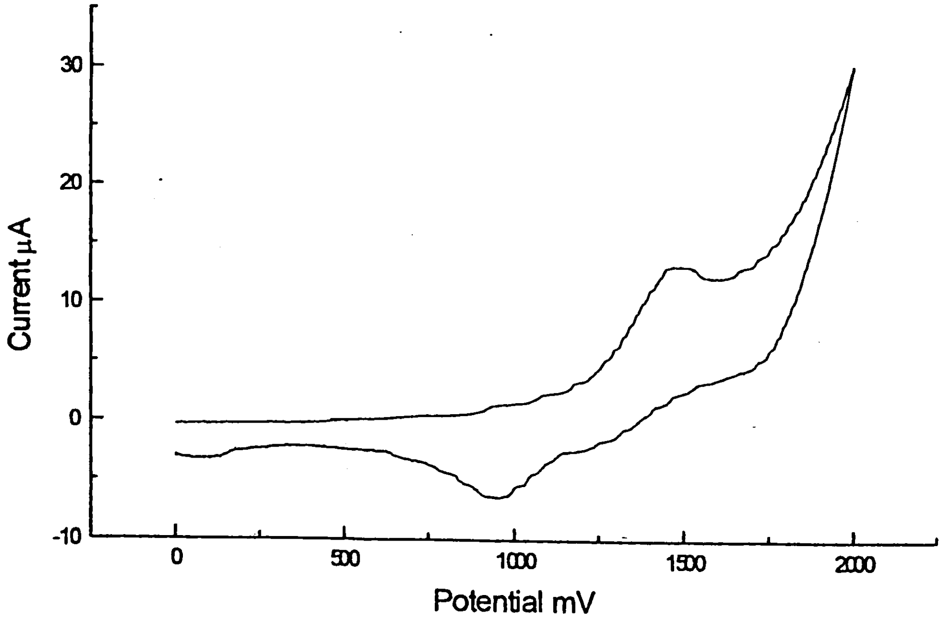


**Figure 17:** Cyclic voltammogram for extended system **(123)** vs. Ag/AgCl; Au working electrode, platinum wire counter electrode, 0.1 M $Bu_4NPF_6$ in dry dichloromethane at 20 °C with *iR* compensation, scan rate 200 mV $s^{-1}$.

An indistinguishable oxidation peak is observed for the corresponding polyterthiophene derived from **(101)**, however the reduction wave is very prominent, occurring in the region + 0.50 V to + 0.80 V depending on the anodic limit of the CV run. Successive voltammograms were taken from 0.00 V to maxima ranging from + 1.00 V to + 3.25 V (0.25 V intervals). A current of zero is observed for the reduction peak when run from 0.00 V to + 1.0 V which increases when the limit of the experiment reaches + 2.5 V up to a maximum of 167 μA.

A steady fall in the peak current for reduction occurs over the next two runs (+ 1.11 μA at E max = + 2.75 V and - 83 μA at E max = + 3.25 V).

Although the nature of the oxidation peak in **(99)** cannot be determined fully, the results obtained indicate that oxidation of the polymer occurs over a broad range.

The electroactivity of the corresponding copolymer resulting from furan derivative **(103)** is not clearly defined although the compound is stable to cathodic analysis up to - 2.00 V. The oxidation process is broad and takes place over a wide range (+ 1.00 V to + 2.00 V), whilst a more noticeable reduction wave is observed at + 0.44 V.

The corresponding polyterthiophene derived from compound **(102)** however, results in a more stable system and, unlike the rest of the series is the only system that shows cathodic redox activity. A defined, almost irreversible oxidation peak is observed at + 1.79 V, with a reduction of the polymer at - 0.25 V.

Estimation of the bandgap of system **(102)** from the onset potentials of the oxidation/reduction peaks results in a value of ~ 1.04 eV, and is amongst the lowest reported for polyterthiophene system.

Electrochemistry of tetrathiafulvalene derivative **(116)** reveals 3 oxidation processes. The oxidation peaks at + 0.57 and + 1.05 V correspond to the formation of the radical cation and dication of the TTF moiety. The oxidation wave at + 1.50 V corresponds to the terthiophene component of the molecule. All peaks are reversible with the reduction wave of the terthiophene moiety being similar to that observed for terthiophene **(99)** (figure 18). However, electropolymerisation of this system was unsuccessful: no appearance of any deposited material was observed on the electrodes. This may be due to unfavourable electronic effects exerted by the 1,3-dithiole moiety along with radical scavenging of electrons by the TTF functionality as previously observed in systems of this nature.

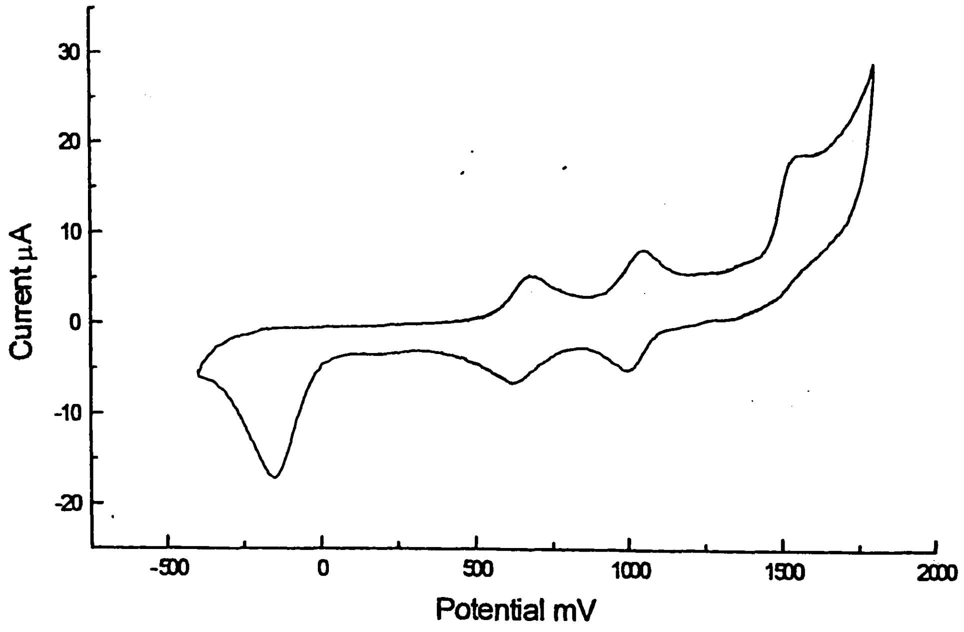


**Figure 18:** Cyclic voltammogram of **(116)** vs. Ag/AgCl; Au working electrode, platinum wire counter electrode, 0.1 M $Bu_4NPF_6$ in dry dichloromethane at 20 °C with *iR* compensation, scan rate 200 mV $s^{-1}$.

## 3.4 CONCLUSIONS AND FURTHER WORK

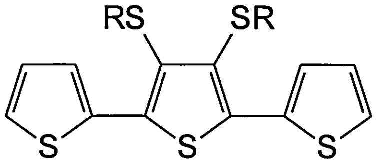
The development of terthiophene monomers **(99)**, **(100)** and **(102)** has led to novel systems incorporating the synthetically versatile 1,3-dithiole functionality which may lead to fascinating electroactive materials and conducting polymers.

The conversion of monomer **(100)** to the tetrathiafulvalene derivative has led to a novel system which can be chemically coupled to form oligomers in solution. Extension of the thiophene building block lowers the oxidation potential of the polymerisable moiety which should result in the electropolymerisation of the system. However, the unsuccessful electropolymerisation of **(116)** highlights the unfavourable interactions that arise between the two different redox units.

Further work in this area would involve the conversion of extended terthiophene monomer **(102)** to the corresponding tetrathiafulvalene derivative. The incorporation of a fused 1,4-dithiin bridging unit 'dilutes' the electronic effects of the 1,3-dithiole functionality, and may ensure a favourable spin density in the radical trication which could result in the successful electropolymerisation of the system.

# CHAPTER 4

## Synthesis of Terthiophene Derivatives and their Polymers



**(124) R = Me**

**(125) R = $C_6H_{13}$**

**(126) R = $-CH_2CH_2-$**

### 4.1 INTRODUCTION

The strategy of incorporating alkyl chains into polythiophene in order to increase the solubility of the system has been extensively studied over the last 20 years. Chemical modifications of polythiophenes by the introduction of various substituents has resulted in the synthesis of processable polymeric systems with a range of interesting properties.

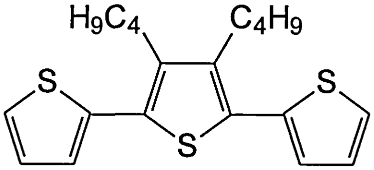
The study of polythiophenes originating from well-defined oligomers has generated interest over the last 10 years. Synthesis of conjugated polymers with both regio- and stereochemical control has been a major target in the hope that a reduction in the number of α,β and β,β thiophene ring linkages is achieved.[92]

The synthesis of mono-substituted thiophene polymers (i.e. poly(3-alkyl)thiophenes) has resulted in systems where reduced electrical conductivity compared to the unsubstituted polymer has been observed.[76] This is due to steric hindrance caused by the substituents of the thiophene rings disrupting the coplanarity of the polymer backbone. Another explanation for this structural irregularity arises from the fact that the 2- and 5- positions of the 3-alkylthiophenes are geometrically inequivalent, which may lead to two types of α-α couplings. Although head to tail couplings are preferred, up to 20% of the resulting polymer is coupled in a head to head manner.[92, 170]

The study of disubstituted polythiophenes has led to polymeric systems which, although soluble in common organic solvents experience steric effects which reduce the electronic properties of the resulting polymer. Poly (4,4′-dialkyl-2,2′-bithiophene)[171] and poly(3,3′-dialkyl-2,2′-bithiophene)[172] were synthesised in the early 1990's. The resulting polymers showed exclusive H-H couplings which resulted in a decreased conjugation length of the polymer compared to the unsubstituted material.

As a result of this, steric effects dominate through intrachain sulfur-alkyl repulsions which force the thiophene rings out of planarity, thus reducing $\pi$-conjugation. However, regiospecific polythiophenes have been prepared with 100% head to tail coupling, resulting in polymers with high conductivities.[93]

A strategy adopted in the synthesis of a soluble conjugated polythiophene absent of irregular couplings was achieved in the preparation of poly(3′,4′-dibutyl-2,2′:5,2″-terthiophene) (DBTT) **(127)**.[152c]



**(127)**

The solubility of the system is enhanced by the presence of two butyl groups and a polymer with reduced steric hindrance was achieved. The two opposite $\alpha$-positions of **(127)** are geometrically equivalent, which eliminates the problem of H-H coupling as observed in the polymerisation of 3-PATs.[173]

Steric hindrance with respect to planarity caused by the bulky alkyl substituents does not occur for DBTT. Within each repeating unit, the dibutyl functionalities are separated by a non-functionalised thiophene unit, thereby acting as steric diluents within the polymer chain. The reduced number of alkyl chains minimises steric hindrance within the polymer which results in a more coplanar backbone.

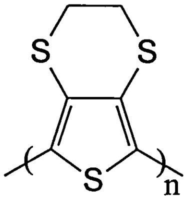
A reduced oxidation potential of the terthiophene monomer (+ 0.86 V vs. SCE) compared to a mono-thiophene monomer is observed which allows both chemical and electrochemical polymerisation under mild conditions.

Synthesis of alkylsulfanyl substituted polythiophenes has also been reported, however this area has not been well studied. The idea behind the incorporation of alkylsulfanyl substituents [e.g. PEMT **(44)** and PBEMT **(45)**] was that the loss of conjugation observed by poly(alkyl)thiophenes caused by steric effects of the β-substituents would be compensated by the mesomeric effect of the electron donating alkylsulfanyl groups.[84] Both polymers are soluble in common organic solvents and exhibit conductivities up to $10^{-3}$ $\Omega^{-1}$ $cm^{-1}$ in the oxidised state.

Electropolymerisation of these systems was unsuccessful which was thought to be due to the fact that neither have significant positive spin densities at both α-C atoms according to theoretical calculations. Calculations on terthiophene and bithiophene show that an increased spin density on the α- position results in facile electropolymerisation of the system.

Bridging the 3- and 4- positions of the thiophene ring system has resulted in a reduction of the bandgap. Poly(isothianaphthene)[105] **(55)** and poly(3,4-ethylenedioxythiophene)[119] **(64)** are two such systems that have produced systems with a reduced bandgap compared to poly(thiophene).

The sulfur analogue of poly (3,4-ethylenedioxythiophene) was reported in 1995.[174] Poly(3,4-ethylenedithio)thiophene **(128)** is more soluble than its oxygen analogue which has resulted in much simpler characterisation. A bandgap value of 2.19 eV is observed for this polymer which lies between that for mono and bis-substituted alkylsulfanyl polythiophenes. (PEMT- 2 eV, PBEMT- 2.24 eV).



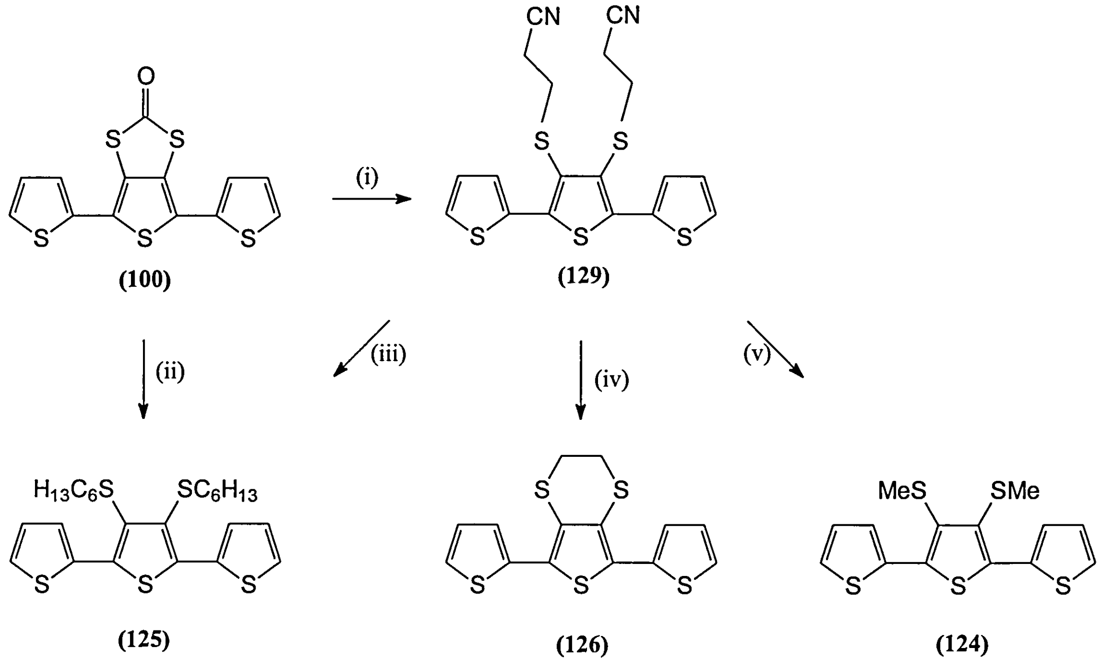
**(128)**

This system exhibits a conductivity in the neutral state of $10^{-10}$ $\Omega^{-1}$ $cm^{-1}$ and upon doping this increases to 0.1 $\Omega^{-1}$ $cm^{-1}$ and 0.4 $\Omega^{-1}$ $cm^{-1}$ when chemically and electrochemically polymerised respectively.

The development of monomer units **(124-126)** incorporate alkylsulfanyl groups [including an ethylene bridging moiety in the case of **(126)**], which will enhance the solubility of the system and incorporate a mesomeric effect to increase conjugation. An increased spin density of the terthiophene monomer along with a steric diluent effect may result in polymeric systems that will be both chemically and electrochemically polymerised to form a series of novel polythiophenes.

## 4.2 RESULTS AND DISCUSSION

Terthiophene derivatives **(124-126)** were obtained in 52%, 53% and 59% yields respectively, by the addition of varying alkyl halides to the dithiolate anion produced upon reaction of terthiophene **(129)** with tetrabutylammonium hydroxide, in dry tetrahydrofuran at 0 °C under dry nitrogen. The synthetic pathway initially investigated used sodium ethoxide as the basic source to deprotect terthiophene **(100)** to afford the corresponding dithiolate species, with subsequent addition of various alkyl halides to give the desired terthiophene derivative (scheme 22). However, low yields were obtained via this route (20 - 30%) and an alternative strategy had to be adopted. Synthesis of nitrile protected terthiophene derivative **(129)** as an intermediate proved to be a more efficient synthetic route to the desired product. A stronger basic source was also used in the deprotection of terthiophene **(100)** (KOBu$^t$), and intermediate **(129)** was isolated in 70% yield.



**Scheme 22** : Reagents and conditions (i) (a) KOBu$^t$, -10 °C (b) $BrCH_2CH_2CN$ (ii) (a) KOBu$^t$, -10 °C (b) $C_6H_{13}Br$ (iii) (a) $Bu_4NOH$, (b) $C_6H_{13}Br$ (iv) (a) $Bu_4NOH$, (b) $BrCH_2CH_2Br$ (v) (a) $Bu_4NOH$, (b) iodomethane.

Crystals of compound **(126)** were obtained by the slow evaporation of a dichloromethane solution of **(126)** at room temperature. The X-ray crystal structure obtained is shown in figure 19. The structure shows that the molecule adopts an all *syn* conformation with the six membered ring which is disordered over two puckered conformations, each with an occupancy of 50%. The angle between the two least squares mean plane for the dithiin ring are (C6 - S3 - C7A) = 101.55 (19 °) and (C6 - S3 - C7B) = 103.55 (19 °). To the best of our knowledge, there are no examples of **<u>all</u>** *syn* conformers of terthiophene derivatives. At most 10-20% of a particular terthiophene adopts this conformation, with the majority aligned in an *anti* arrangement. A torsion angle of 43 ° was observed for C6 - C5 - C4 - C3 which indicates a deviation from planarity in the terthiophene backbone.

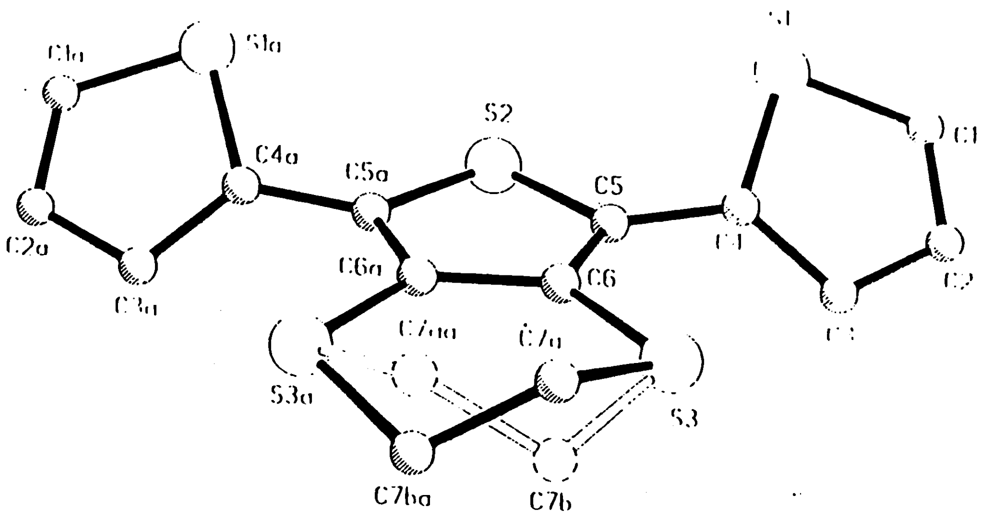
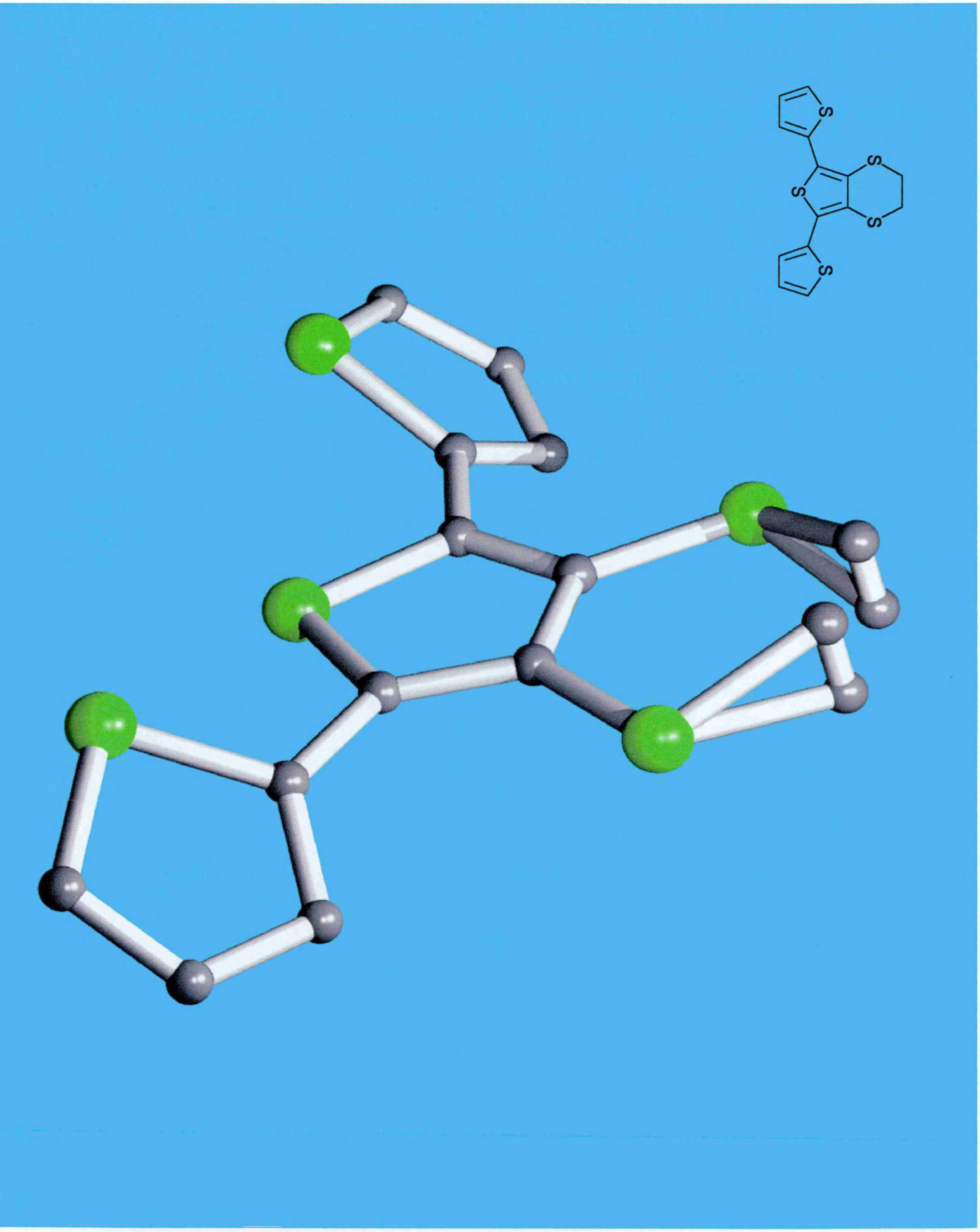


**Figure 19:** X-Ray crystal structure of compound **(126)**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Chemical polymerisation of compounds **(124-126)** was attempted employing an oxidative coupling methodology with $FeCl_3$. This method has been successful for a number of alkyl and alkylsulfanyl thiophene derivatives[175] and was chosen for the simplicity of the method. Each of the monomer units was dissolved into anhydrous dichloromethane and was added to a solution containing $FeCl_3$ in dichloromethane. The reactions were allowed to stir at room temperature for 24 h, filtered and soluble fractions were obtained via Soxhlet extraction. The samples were then subjected to hydrazine to afford the neutral polymer, filtered and dried. Analysis by Gel permeation chromatography indicated that a polymeric system was formed only for compound **(125)**. An average molecular weight of 6280 (polydispersity of 2.379) represents an average of approximately 40 thiophene units per polymer chain. $^1H$ NMR of the polymer showed broad peaks in the aliphatic region corresponding to the alkylsulfanyl chains and minor peaks in the aromatic region corresponding to the thiophene protons. An increase in conjugation upon the formation of the polymer resulted in a bathochromic shift of $\lambda_{max}$ in the UV spectra compared to the monomer unit (368 nm for monomer, 488 nm for polymer).

Although GPC analysis on compounds **(124)** and **(126)** treated with $FeCl_3$ indicated that the chemical polymerisation of these systems was unsuccessful, a shift in the wavelength value for $\lambda_{max}$ was observed for both compounds, indicating that oligomers/polymers had formed in the reaction. A bathochromic shift of 80 nm was observed for ethylene bridged terthiophene **(126)** (368 nm for monomer, 448 nm after treatment with $FeCl_3$), and a shift of 92 nm was observed for methylsulfanyl substituted terthiophene **(124)**. The optical bandgap for these systems was estimated at 2.3 eV for **(124)**, 1.91 eV for **(125)** and 2.26 eV for **(126)** from the band edges of the UV spectra.

Studies on 3,4-dialkyl substituted polythiophenes have shown a decrease in the wavelength of $\lambda_{max}$ compared to the mono-substituted polymer.[69] A wavelength of $\lambda_{max}$ 350 nm is observed for poly[3,4-bis(methyl)thiophene] compared to 520 nm for poly(3-methyl)thiophene. The introduction of alkylsulfanyl substituents onto the 3,4-positions of polythiophene has also resulted in a decrease of the wavelength of $\lambda_{max}$ from mono- to bis-substitution, which is due to steric effects arising from the presence of bulky substituents.

It should also be noted that the wavelength value of $\lambda_{\text{max}}$ for an unsubstituted terthiophene monomer is 355 nm. Introduction of alkyl substituents onto the central thiophene ring has led to a hypsochromic shift of the wavelength for $\lambda_{\text{max}}$, which is due to twisting of the thiophene rings when substituted by long alkyl chains.

Contrary to this, the introduction of alkylsulfanyl substituents in monomers **(124)** to **(126)** has resulted in a bathochromic shift in the wavelength of $\lambda_{\text{max}}$, which is likely to be due to the $\pi$ resonance effect of the alkylsulfanyl substituents along with reduced steric hindrance due to the presence of additional unsubstituted thiophene rings in these systems which results in increased conjugation and higher $\lambda_{\text{max}}$ values are obtained.

Cyclisation of the 3′,4′-substituents has resulted in a further decrease in steric hindrance by suppressing rotation about the C - S bond between the thiophene ring and the substituents resulting in increased $\lambda_{\text{max}}$ values. For example, cyclopenta[c]thiophene exhibits a wavelength $\lambda_{\text{max}}$ of 510 nm. This is identical to that obtained for electropolymerised ethylene bridged derivative **(126).** However, cyclopenta[c]thiophene is difficult to electropolymerise. The oxidation potential of this system is 0.76 V and is considerably larger than that obtained for terthiophene **(126)** [~ 0.5 V] which can be electropolymerised. This supports the idea that the presence of alkylsulfanyl substituents lowers the $E_{pa}$ of the system. Further electrochemical studies of terthiophenes **(124)** to **(126)** are discussed in section 4.3.

## 4.3 ELECTROCHEMISTRY

Electrochemistry of compound **(124)** in dichloromethane:hexane (2:1 v/v) revealed two reversible oxidation peaks. Repetitive scanning over the first oxidation potential did not result in polymerisation of the system. There was no appearance of any deposited polymer at the working electrode. However, upon switching the solvent to acetonitrile, two irreversible oxidation waves were observed at + 0.8 V and +1.5 V. The cyclic voltammograms obtained for monomers **(124)** to **(126)** are shown in figure 20. Compound **(124)** was successfully electropolymerised upon repetitive scanning over the first oxidation potential between 0.00 and + 1.4 V, which resulted in the appearance of a new redox couple at + 0.9 V, corresponding to polymer formation (figure 21). The peak current for the resulting polymer was proportional to the scan rate and is shown in figure 22. The linear relationship (R = 0.99892) indicates a surface reaction where an increase in the oxidation potential occurs upon an increase in the scan rate, indicating that the polymer is a stable system. Cyclic voltammetry of the polymer shows the appearance of a small shoulder at approximately 0.6 V, however this disappears after one scan and is probably due to stabilisation of the polymer. The cyclic voltammogram obtained for poly **(124)** is shown in figure 23. The bandgap of the system was estimated at approximately 1.6 eV from the onset of the peak potentials. The polymer appears to be stable up to 1.7/1.8 V but decomposes at 2.00 V.

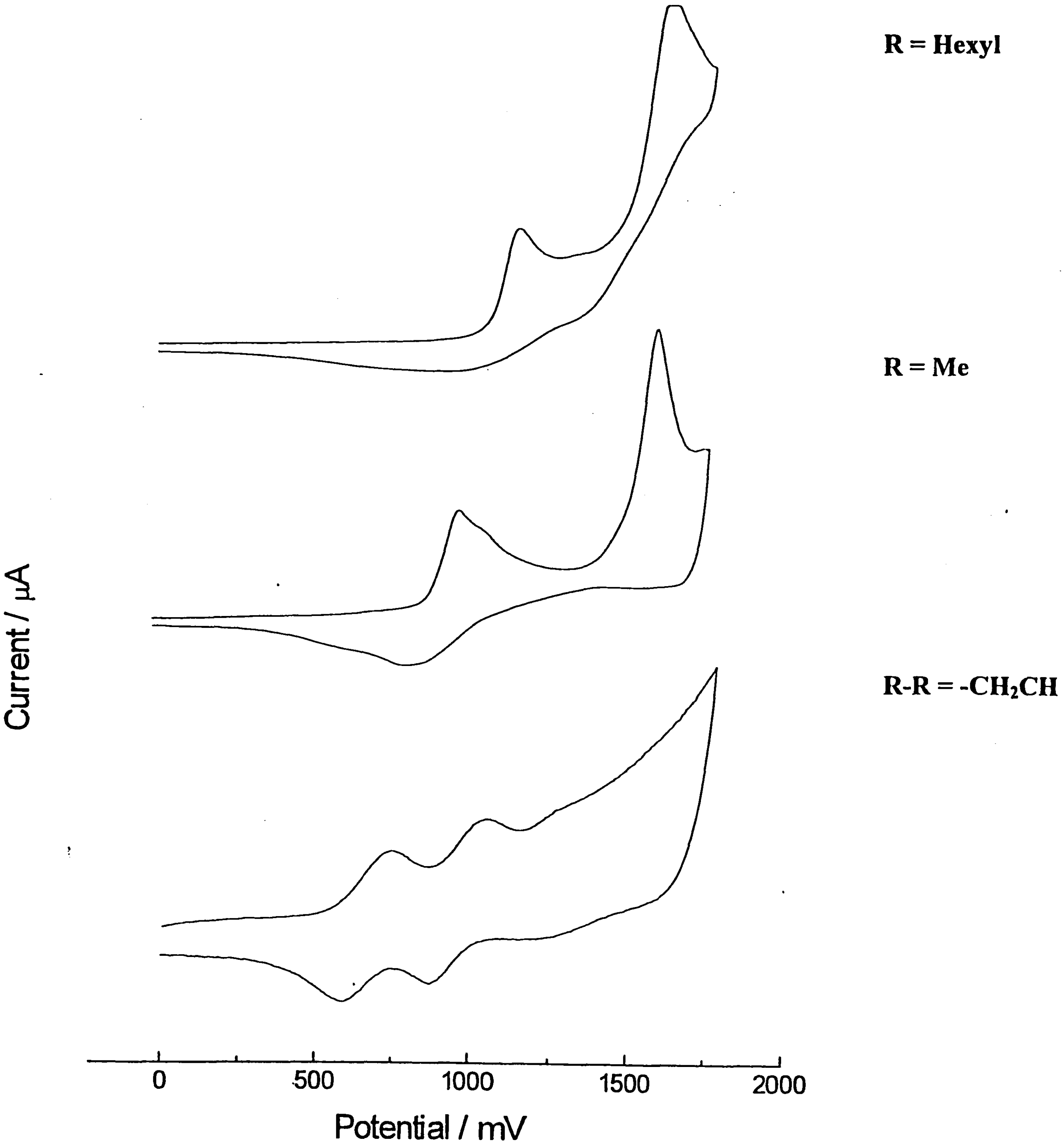


**Figure 20:** Cyclic voltammogram of **(124)** to **(126)** vs. Ag/AgCl. Scan rate 200 mV $s^{-1}$, Au disc in acetonitrile (0.10 M $Bu_4NPF_6$ as supporting electrolyte).

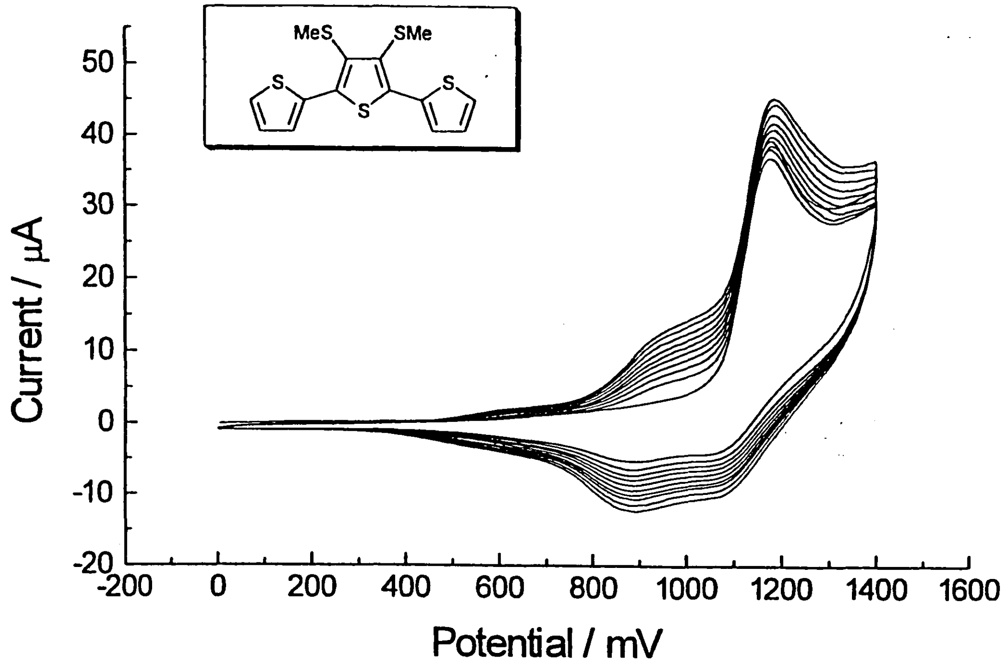


**Figure 21:** Electropolymerisation of **(124)** vs. Ag/AgCl. Scan rate 200 mV $s^{-1}$, Au disc in acetonitrile (0.10 M $Bu_4NPF_6$ as supporting electrolyte).

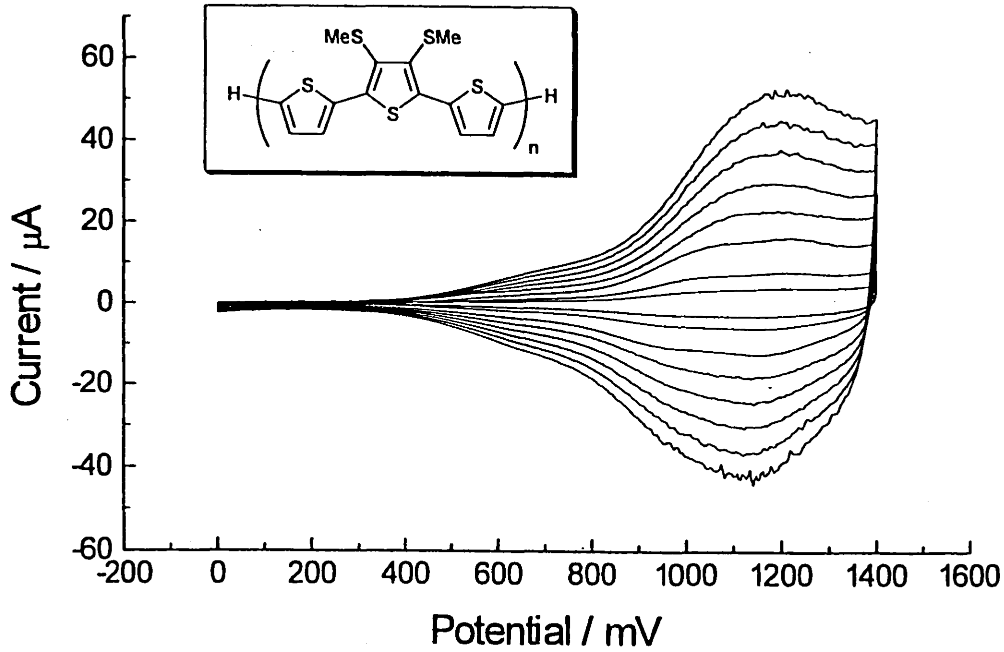
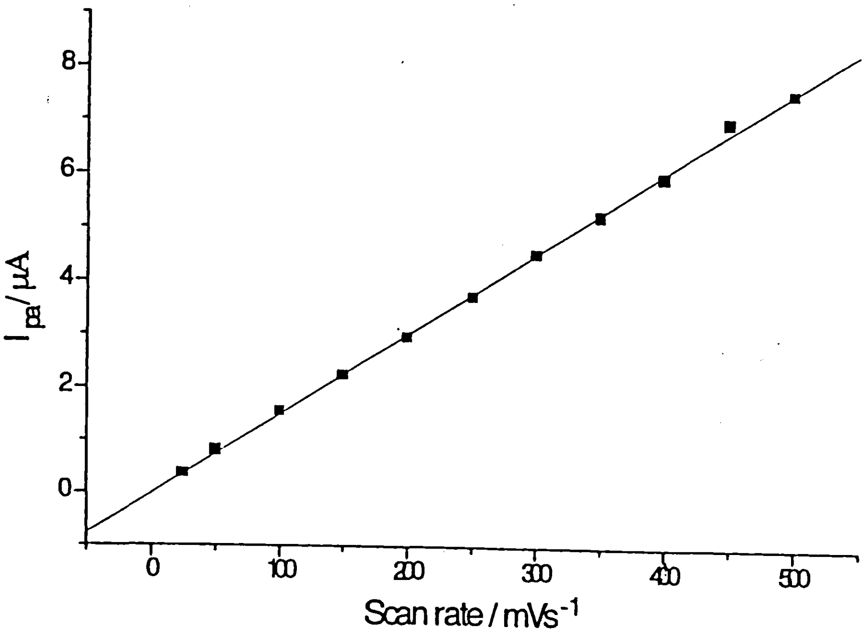


**Figure 22:** (a) Cyclic voltammogram of current against potential for poly **(124)** vs Ag/AgCl in acetonitrile. Au disc electrode ($Bu_4NPF_6$ as supporting electrolyte) for scan rate 25, 50, 100, 150, 200, 300, 350, 400, 450 and 500 mV $s^{-1}$.



**(b)** Linear plot of current against scan rate for poly **(124)** vs Ag/AgCl in acetonitrile. Au disc electrode ($Bu_4NPF_6$ as supporting electrolyte) for scan rate 25, 50, 100, 150, 200, 300, 350, 400, 450 and 500 mV s$^{-1}$.

A similar voltammogram was obtained for compound **(125)** (figure 20), with the appearance of a new redox peak at approximately + 0.9 V upon repetitive scanning between 0.00 and +1.4 V which is shown in figure 24. A linear plot of current against scan rate for the polymer was also observed (R = 0.99953) and is illustrated in figure 25. The cyclic voltammogram of the resulting polymer is shown in figure 23 and the estimated bandgap for this system was 1.3 V from the onset of the peak potentials.

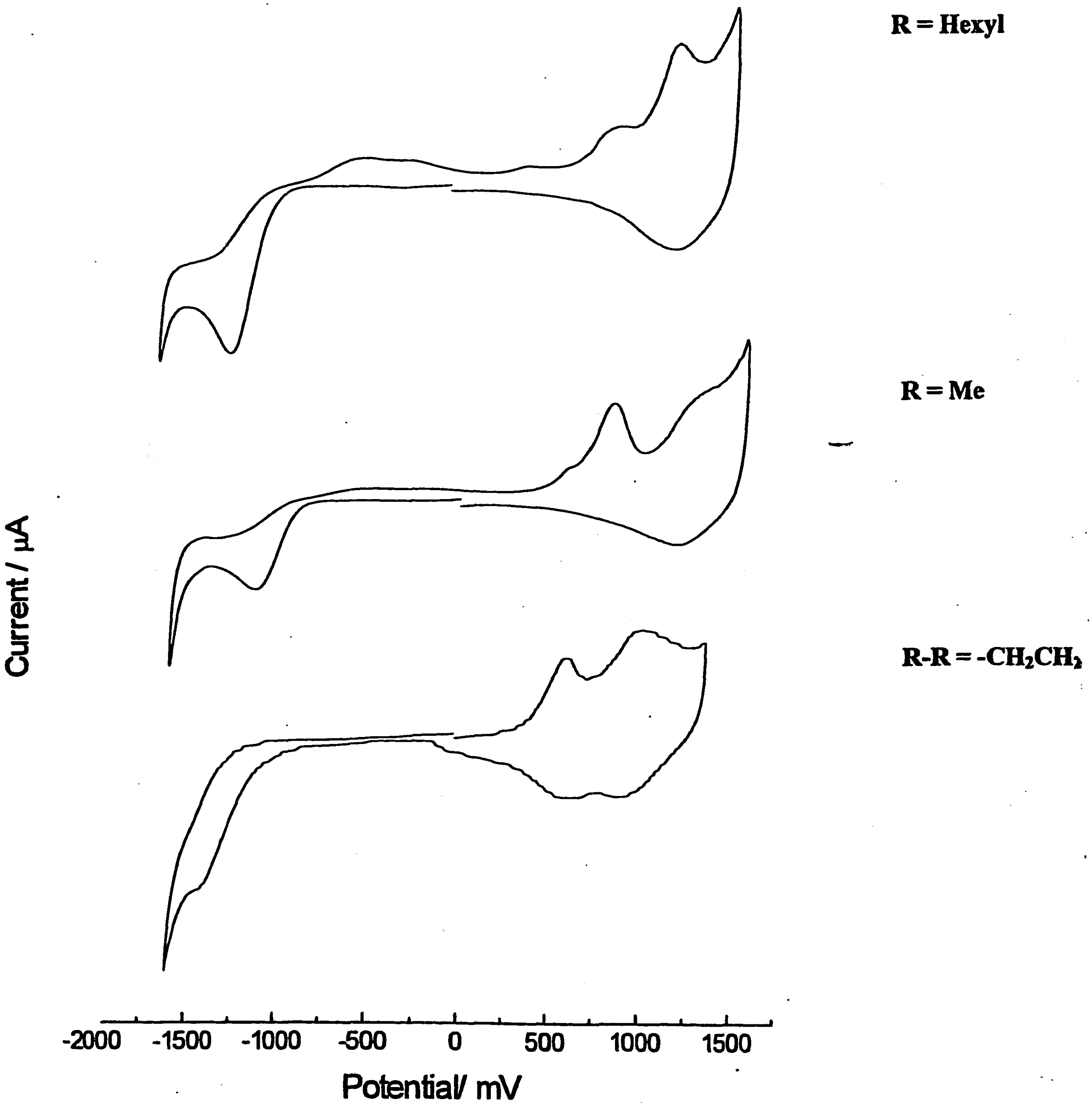


**Figure 23:** Cyclic voltammogram of poly **(124)** to **(126)** vs Ag/AgCl, Au disc electrode ($Bu_4NPF_6$ as supporting electrolyte), acetonitrile, monomer free solution.

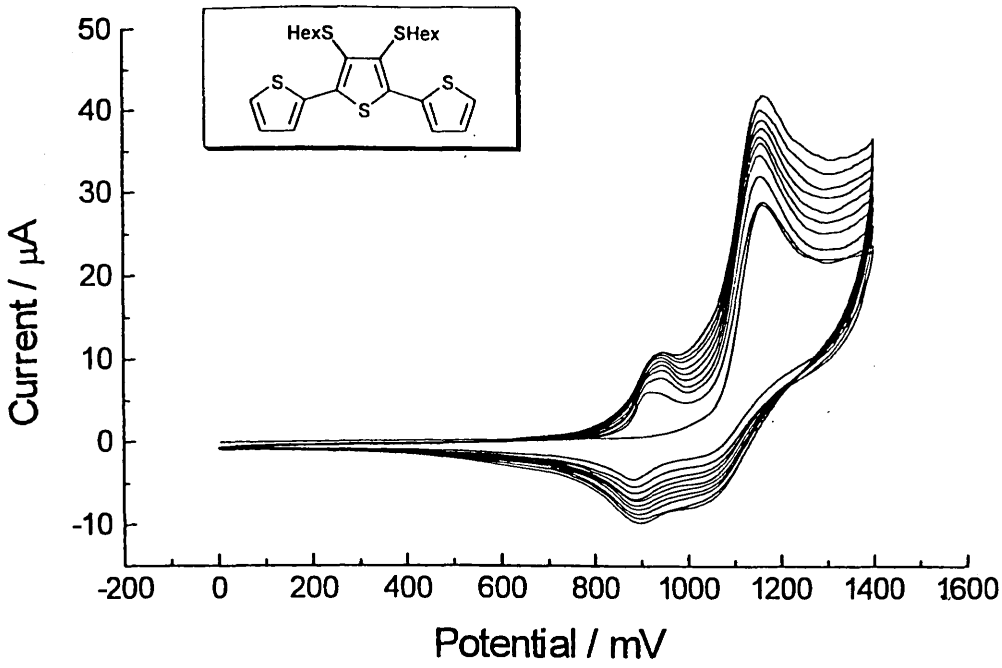


**Figure 24:** Electropolymerisation of compound **(125)** vs Ag/AgCl. Scan rate 200 mV $s^{-1}$, Au disc in acetonitrile (0.10 M $Bu_4NPF_6$ as supporting electrolyte).

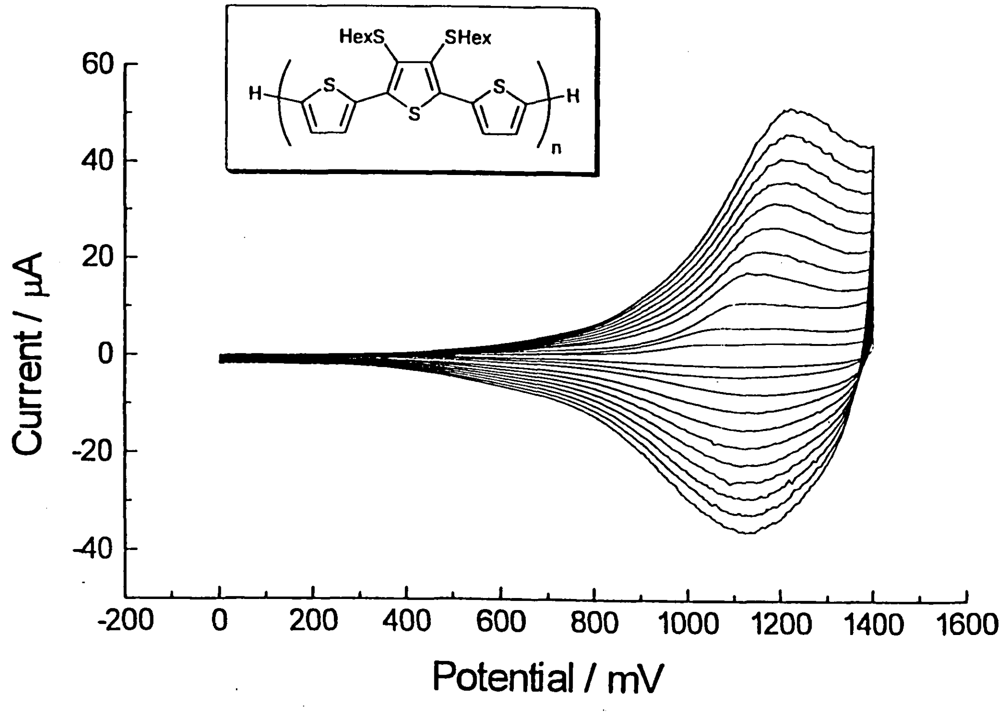
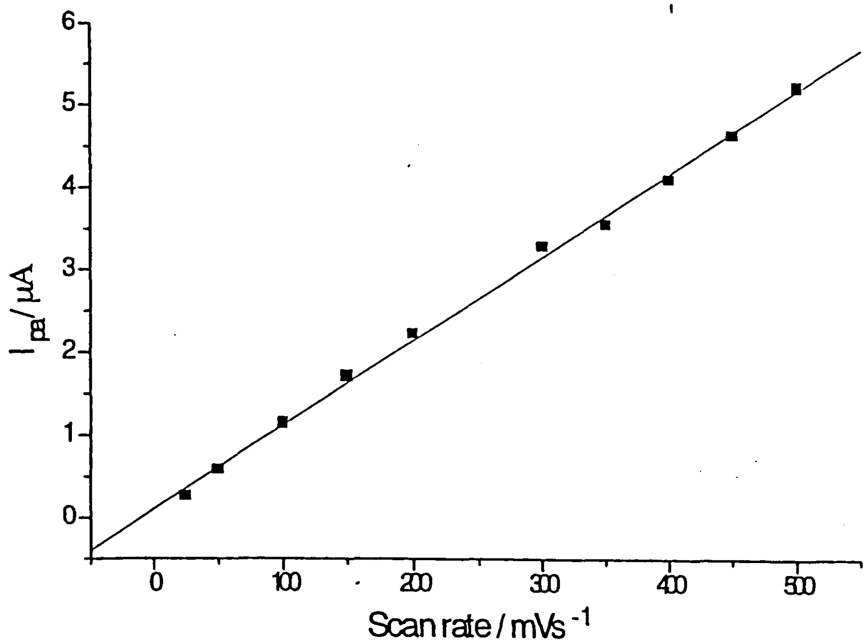


**Figure 25:** **(a)** Cyclic voltammogram of poly **(125)** vs Ag/AgCl in acetonitrile. Au disc electrode ($Bu_4NPF_6$ as supporting electrolyte) for scan rate 25, 50, 100, 150, 200, 250, 300, 350, 400, 450 and 500 mV $s^{-1}$.



**(b)** Linear plot of current against scan rate, vs Ag/AgCl in acetonitrile. Au disc electrode ($Bu_4NPF_6$ as supporting electrolyte) for scan rate 25, 50, 100, 150, 200, 250, 300, 350, 400, 450 and 500 mV s$^{-1}$.

Electropolymerisation studies of compound **(126)** indicate that this system will also polymerise under electrochemical conditions. An increase in polymer growth was observed at the working electrode upon repetitive scanning over the oxidation potential of the monomer (0 to +1.4 V) at a scan rate of 200 mV s$^{-1}$ in acetonitrile (figure 26). A plot of current vs. scan rate reveals regions of linearity (R = 0.99524) as shown in figure 27 and the cyclic voltammogram of the resulting polymer is shown in figure 23. Further voltammetric and infrared studies on this system are currently being conducted by N.S. Sariciftci at the Johannes-Kepler University, Linz, Austria. Photoinduced activated infrared vibration (IRAV) spectroscopy measurements have been made on electropolymerised samples of compound **(126)**. Figure 28 shows the spectra obtained for an electropolymerised film of **(126)** when excited at 488 nm. The spectra show three main bands at 1375, 1300 and 1150 cm$^{-1}$, which correspond to polythiophene and are typical of polythiophene peaks found in this region. The peak at 850 cm$^{-1}$ corresponds to the counter ion ($PF_6^-$) used in the experiment and the broad band spanning most of the spectrum represents the presence of radical cations. Figure 29a shows an in-situ IRAV spectrum during the electropolymerisation of compound **(126)** with repetitive scanning in the range from + 0.68 V to + 1.20 V. The appearance of the broad band indicates radical cation formation, and the characteristic polythiophene bands become apparent (figure 29b shows an expansion of the 1500 - 1000 cm$^{-1}$ region). The results show a photoinduced response by poly **(126)** when excited in this region of the infrared, which may exhibit interesting properties for application in photovoltaic devices.

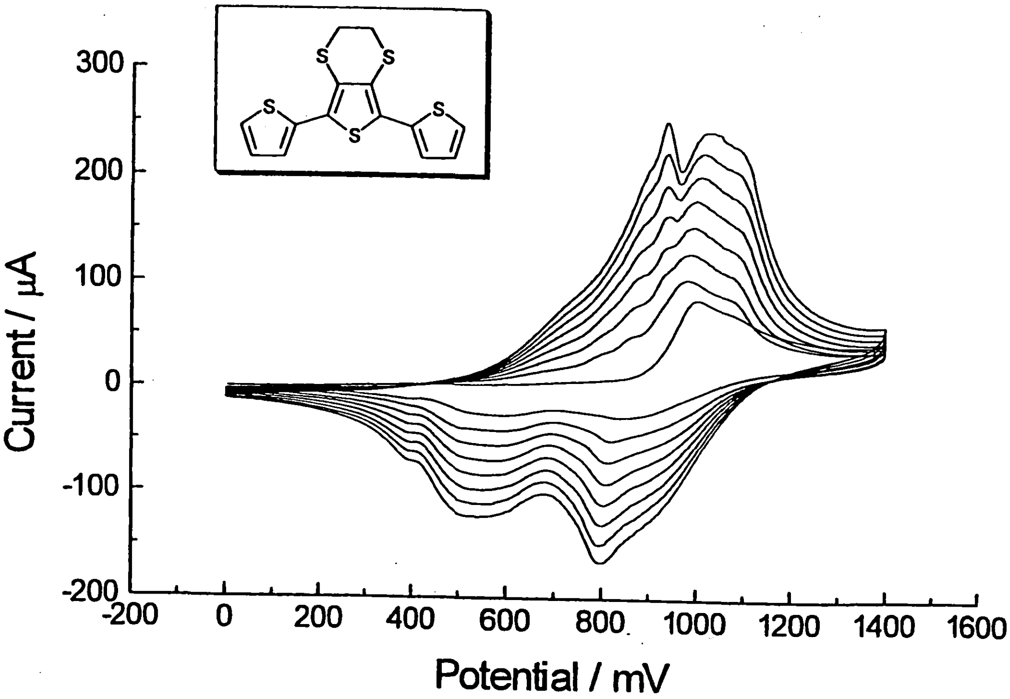


**Figure 26:** Electropolymerisation of compound **(126)** vs Ag/AgCl. Scan rate 200 mV s$^{-1}$, Au disc in acetonitrile (0.10 M $Bu_4NPF_6$ as supporting electrolyte).

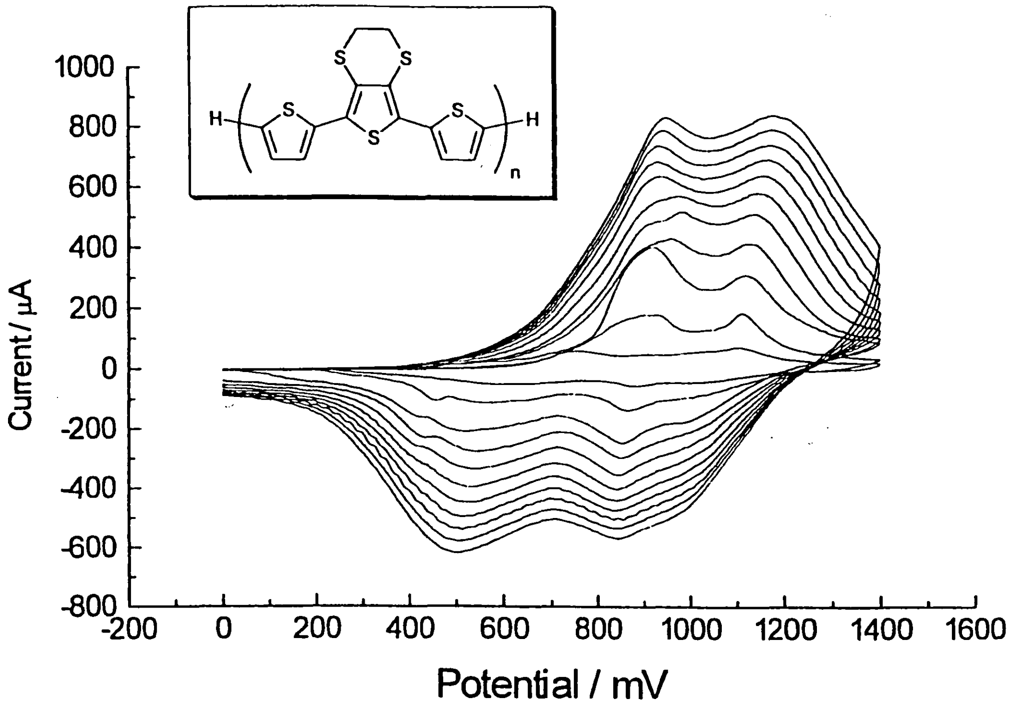
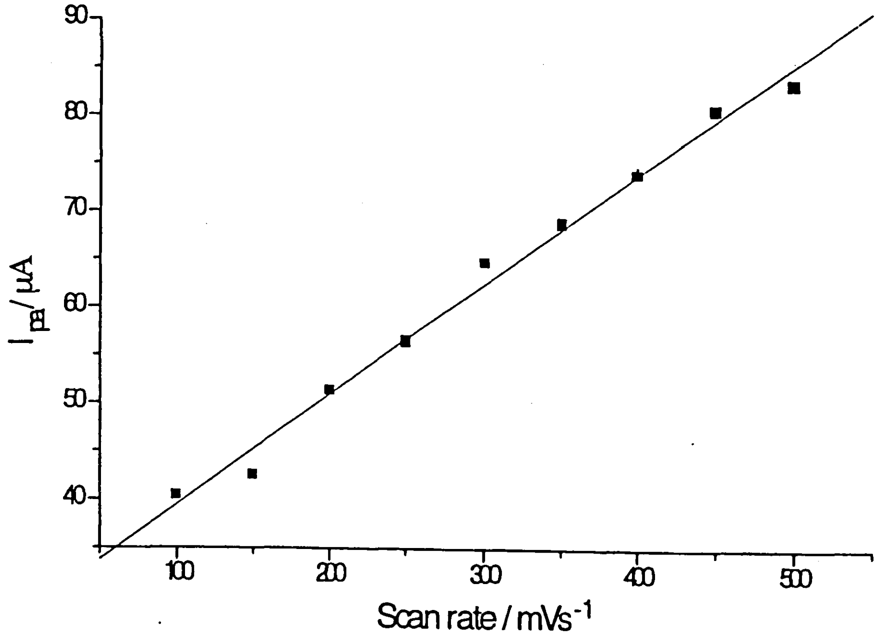


**Figure 27:** **(a)** Cyclic voltammogram of poly **(126)**, vs Ag/AgCl in acetonitrile. Au disc electrode ($Bu_4NPF_6$ as supporting electrolyte) for scan rate 100, 150, 200, 250, 300, 350, 400, 450 and 500 mV $s^{-1}$.



**(b)** Linear plot of current against scan rate for poly **(126)** vs Ag/AgCl in acetonitrile. Au disc electrode ($Bu_4NPF_6$ as supporting electrolyte) for scan rate 100, 150, 200, 250, 300, 350, 400, 450 and 500 mV $s^{-1}$.

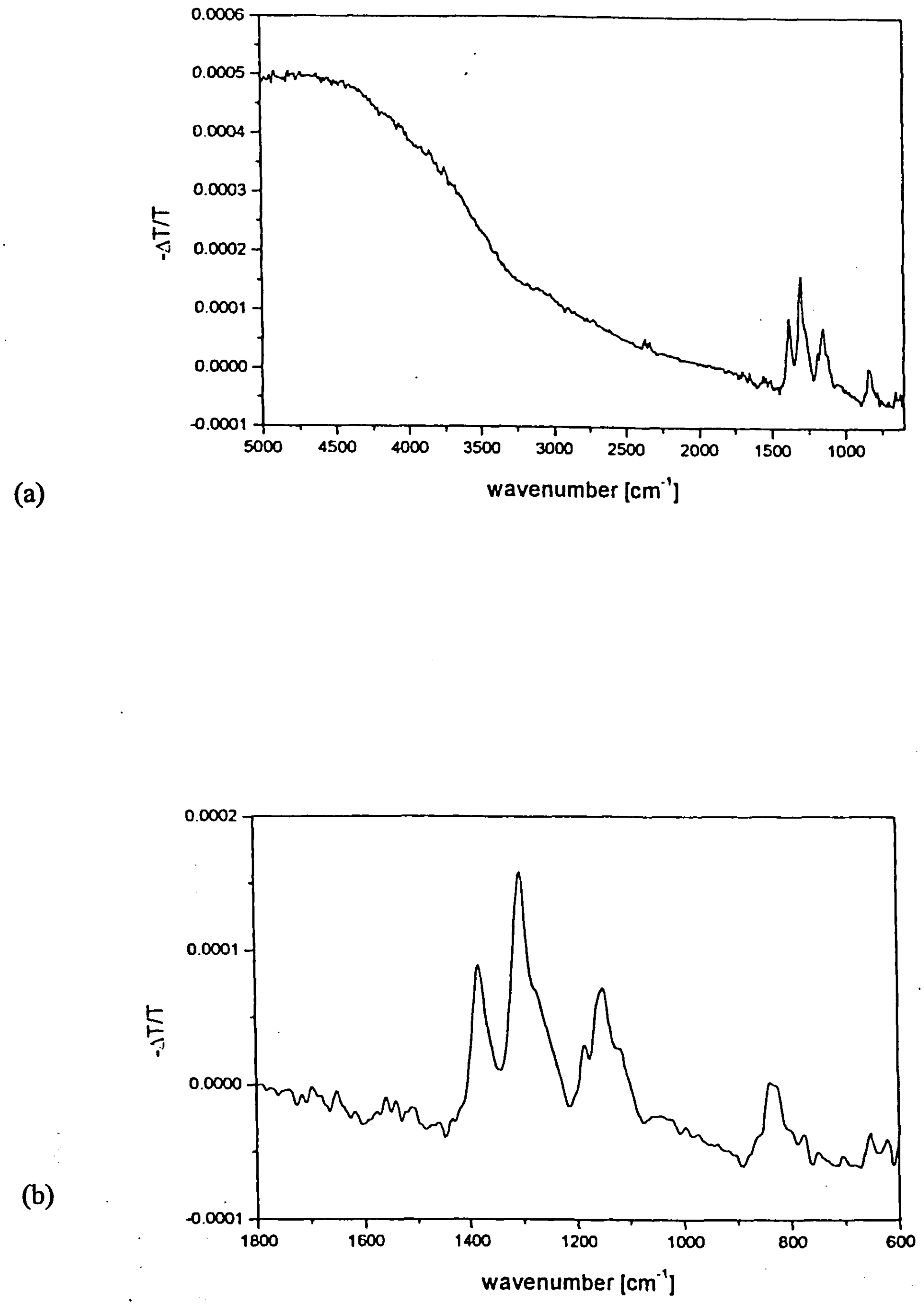


**Figure 28**: (a) IRAV spectra of electropolymerised **(126)** on Ge reflection element coated with ultrathin layer of Pt. Laser excitation at 488 nm. (b) Expansion of 1800 - 600 cm$^{-1}$ region.

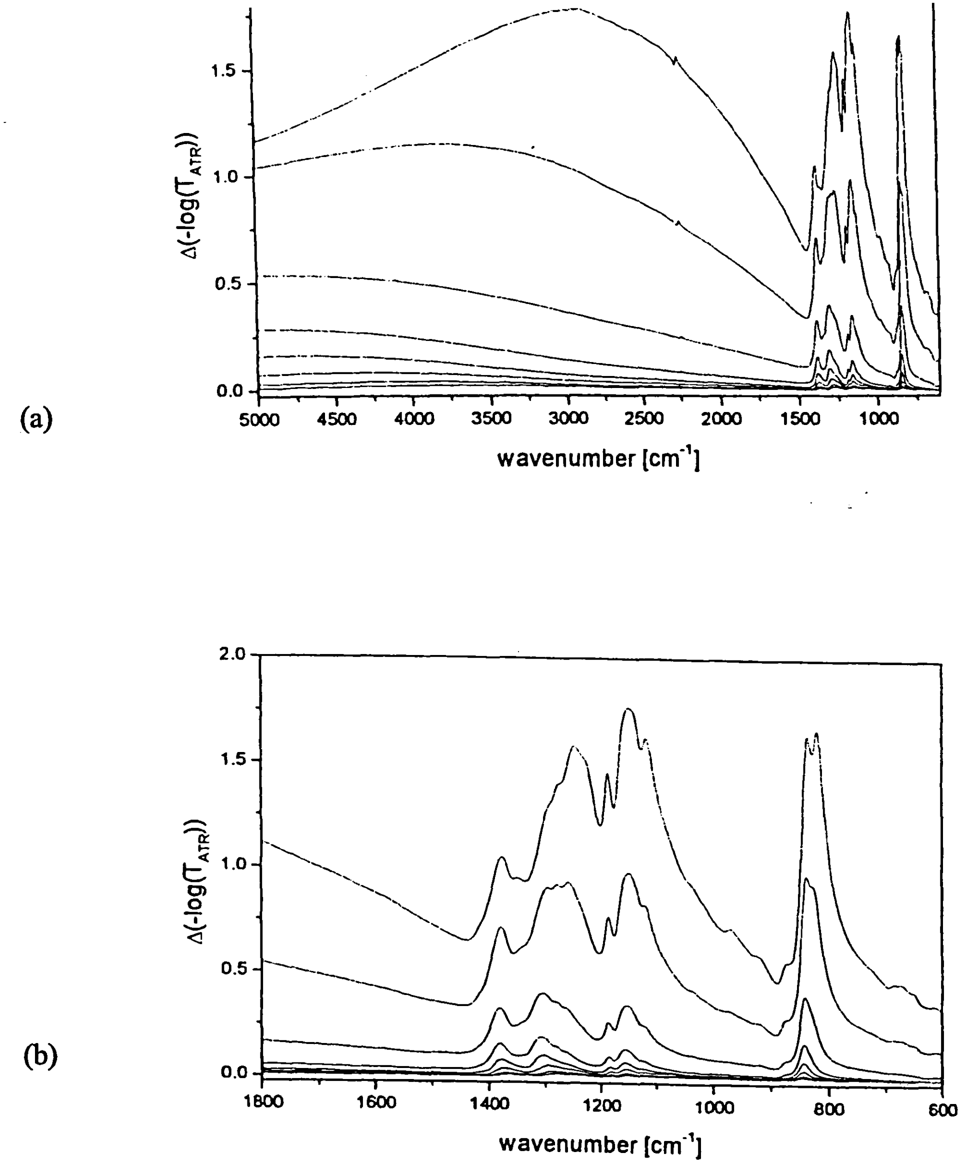


**Figure 29**: (a) In-situ IR difference spectra during electrochemical oxidation of compound **(126)**; $Bu_4NPF_6$ in $CH_3CN$, counter electrode: Pt foil; reference electrode: quasi Ag/AgCl wire; scan rate 5 mV/s$^{-1}$. Reference spectrum recorded at ca. 0 V. Sequence: from bottom (ca. 0.68) to top (1.20 V). (b) Expansion of the 1500 - 1000 cm$^{-1}$ region.

Samples of the polymer were then electrochemically grown onto ITO glass and the resulting UV spectra were recorded. A wavelength $\lambda_{max}$ of 484 nm was obtained for the electrochemically prepared polymer of **(125)** with an estimated optical bandgap of 1.97 eV which is comparable to that obtained for the chemically prepared polymer (1.91 eV). Notably, the $\lambda_{max}$ wavelength obtained for electropolymerised **(124)** is similar (490 nm), but a higher wavelength $\lambda_{max}$ was obtained for the electropolymerised ethylene bridged polymer (510 nm). This indicates that, upon polymerisation better conjugation is achieved for this system compared to alkylsulfanyl substituted derivatives of terthiophene, due to decreased steric hindrance, as $\lambda_{max}$ values for all three monomers are very similar (~ 360 nm). It appears that a more planar structure is obtained for poly**(126)** compared to the monomer, which deviates from planarity due to its adopted syn conformation (figure 19).

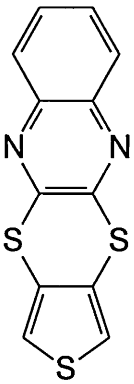
## 4.4 CONCLUSIONS AND FURTHER WORK

The development of terthiophene monomers **(124)** - **(126)** incorporating alkylsulfanyl functionalities has led to systems which can be electrochemically polymerised in acetonitrile to form novel polymers that are soluble in common organic solvents. The polymer of compound **(126)** has shown to exhibit photoinduced activity, which may find uses in voltaic applications.

Further work in this area would involve investigation into the chemical polymerisation of the monomer units, as oxidative polymerisation with $FeCl_3$ showed to be successful only for compound **(125)** by GPC analysis, although UV studies gave indication of oligomer/polymer formation. Studies into the properties of the polymer of **(126)** compared to analogous poly(ethylenedithio)thiophene **(128)** and oxygen analogue PEDOT **(64)** may also be considered in the search for soluble, polymerisable derivatives of terthiophene.

# CHAPTER 5

## Synthesis, Electropolymerisation and Molecular Recognition of Metal Cations by thieno[3′, 4′-*d*:5,6][1,4]dithiino[2,3-b]quinoxaline



**(130)**

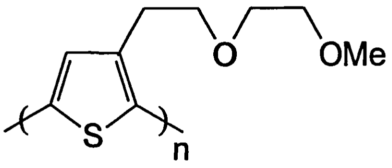
### 5.1 INTRODUCTION

Molecular recognition is an increasingly important area within the field of supramolecular chemistry.[176]

The ability of a particular species to act as a receptor 'host' molecule, where a change in the physicochemical properties of the system is observed upon the interaction with a specific guest molecule or ion, is becoming a fascinating area in the fabrication of chemosensor devices. This change in behaviour of the host system can be detected by spectroscopic, electrochemical or structural techniques, and while most of the research in this area has involved molecular recognition in solution, with signal transduction using electroluminescence[177] or electrochemical techniques[178], the application of systems of this nature to thin films are proving significant in the assembly of sensor devices.[178]

The use of conjugated polymers in this area has become an important feature[179] and, in particular, polythiophene derivatives[180] have attracted much attention, although electrochemical recognition of transition metal ions with conjugated polymer films has not been extensively reported.

The earliest example of molecular recognition by a conjugated polythiophene was reported by Roncali et al in 1989[181] where electrochemical recognition of lithium ions was observed by poly[3-(3,6-dioxaheptyl)thiophene] **(131)**.



**(131)**

The principle behind this observation was that the interaction of the ether chains with metal atoms results in an alteration of the conformation of the conjugated polymer chain, whereby a more planar and increasingly conjugated state results upon the complexation of $Li^+$. A change in the electrochemistry of the system was observed, where a negative shift in the anodic oxidation potential of the system occurred upon the addition of lithium cations. Figure 30 shows the voltammogram obtained in the investigation. Replacement of the electrolyte $Bu_4NClO_4$ by $LiClO_4$ resulted in an enhancement of intensity of the first redox system of the polymer, and a negative shift of the anodic wave occurs. Further examination of the system showed that the electrochemical response is independent of the concentration of $Bu_4NClO_4$ added, but is dependent on the concentration of lithium ions. A further decrease in the peak potential and a narrowing of the potential wave was observed with higher concentrations of $Li^+$.

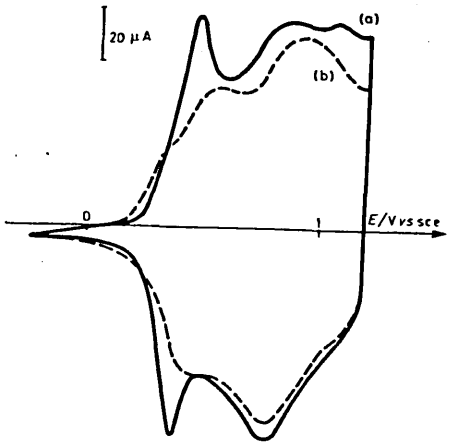
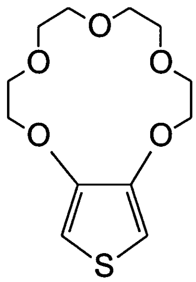


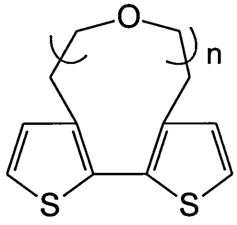
**Figure 30**: Cyclic voltammogram of **(131)** in MeCN, scan rate 30 mV $s^{-1}$, Pt electrode, electrolyte concentration 5 x 10 $^{-1}$ mol $^{-1}$ in (a) $LiClO_4$ (b) $Bu_4NClO_4$

In 1995, Bäuerle and Scheib described the electropolymerisation of crown-annelated thiophene system[182] **(132)**, where the resulting polymer displayed selective binding of sodium ions. The disadvantage of this system was that upon complexation of the metal ion, subsequent oxidation of the system became more difficult as a result of the electron withdrawing nature of the bound cation. Also, the CV response became stable after 30 cycles with a maximum shift in potential of 0.8 V. This suggests that the diffusion of sodium ions becomes hindered in polymer films of **(132)**, which lowers its potential for application into sensor devices.

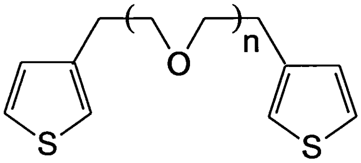


**(132)**

Crown annelated bithiophene derivative **(133)** was synthesised in 1990 by the electropolymerisation of open chain 3,3′-bithiophene derivative **(134)**[183].



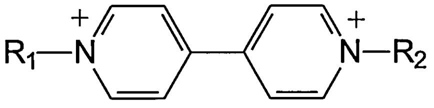
**(133)**



**(134)**

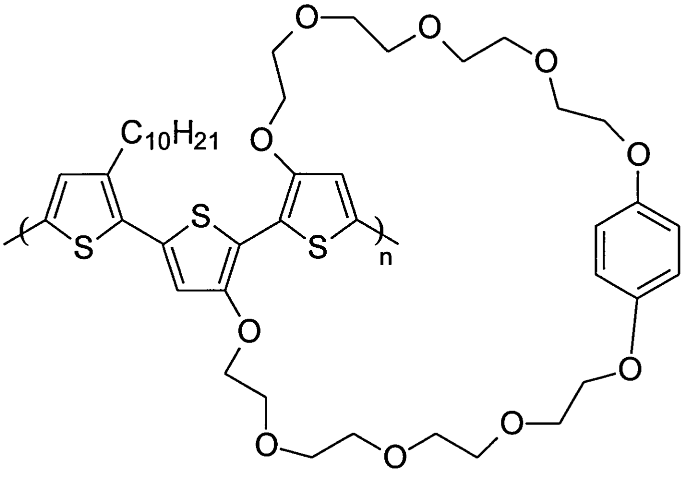
This occurred via a ‘template’ synthesis whilst in the presence of lithium cations. Only for the polymer formed where n = 5 did an electrochemical molecular response occur, where a 50 mV positive shift was observed compared to the response when using $Bu_4NClO_4$ as electrolyte.

A series of more complex polythiophenes was reported in the mid-1990's[184], where the complexation of the strong electron acceptor paraquat [and its derivatives **(135 a-c)**] resulted in a positive shift in oxidation potential of the polymer. The binding of a donor and acceptor molecule results in a higher potential required to oxidise the system. The driving force for complexation is a charge transfer process between the electron deficient guest molecule and polythiophenes **(136-138)**, causing a shift in the oxidation potential.



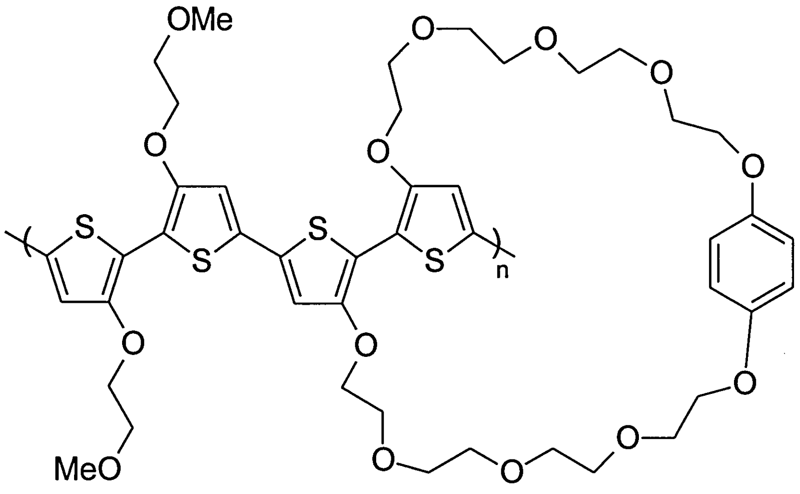
**(135)**

**(a) $R_1 = R_2 = Me$**
**(b) $R_1 = R_2 = 4\text{-F-}C_6H_4$**
**(c) $R_1 = Et; R_2 = C_{18}H_{37}$**

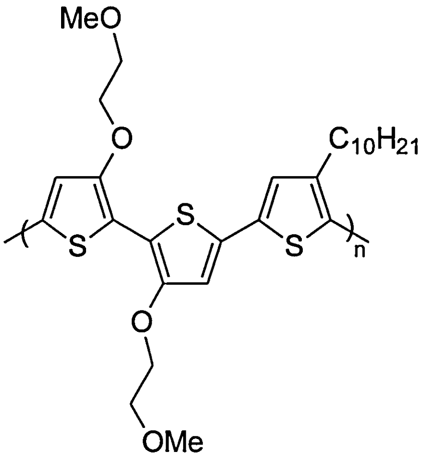


**(136)**

A positive shift of 100 mV was observed for polymeric system **(136)** with the strong acceptor **(135 b)**, the electron affinity of which is enhanced by the presence of *para*-fluorophenyl substituents.

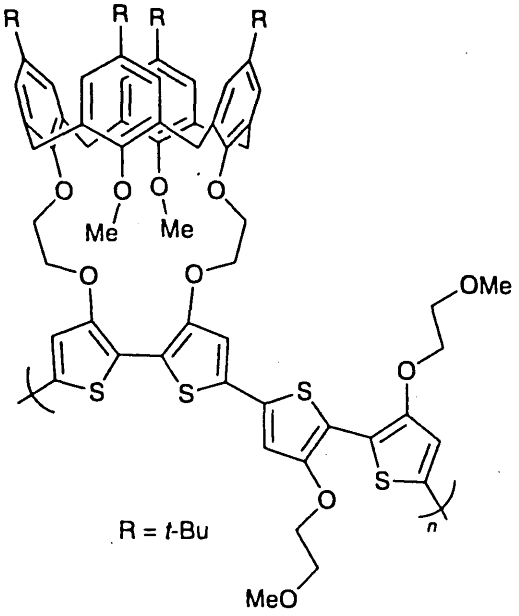


**(137)**



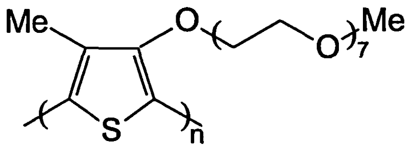
**(138)**

Polythiophene derivatised by calixarene receptors has also resulted in a notable positive shift in the CV response when in the presence of metal cations. Compound **(139)** was prepared in 1995 by Swager and co-workers[185] which exhibited remarkable selectivity towards $Na^+$ over $K^+$ and $Li^+$, where a positive shift in the peak potential of 100 mV was observed in the presence of 0.5 mmol $Na^+$.



**(139)**

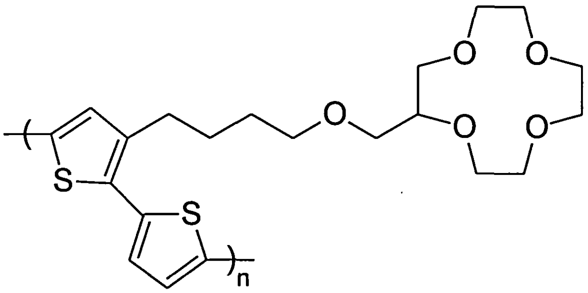
Synthesis of polythiophene derivative **(140)** was reported by Leclerc *et al* in 1995,[186] where electrochemical cation recognition was demonstrated in thin films of this polymeric system.



**(140)**

A change in conformation of the polymer backbone upon the introduction of alkali metal salts was observed where the polymer changed from a conjugated form to a more twisted form which resulted in a decrease of conjugation length, hence an increase in the redox potential. This polymeric system was able to recognise $K^+$, $Na^+$ and $Li^+$ ions and was capable of recognising $K^+$ at the sub mM level.[187]

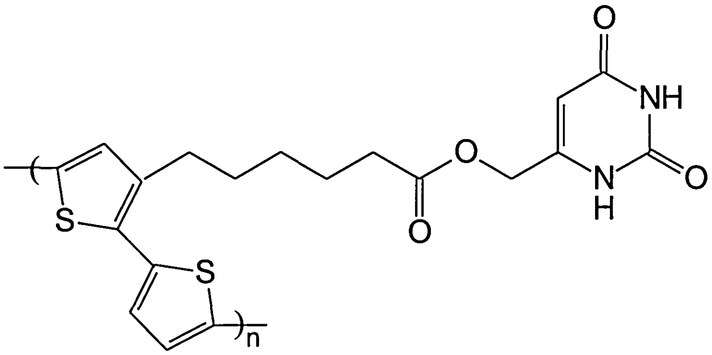
Systems of type **(141)** were synthesised by Bäuerle and Scheib in the early 1990s,[188] in which the receptor unit is attached to the conjugated polymer via a flexible spacer group. The idea behind this was that the receptor could remain close to the polymer backbone which alters the electronic state of the conjugated chain. The selectivity of metal cations of polymer **(141)** is a reversal to that observed for system **(140)**. This is due to the fact that the crown ether cavity in **(141)** is more applicable to $Li^+$ ions, and a CV response was observed at very low concentrations of metal ions ($5 \times 10^{-5}$ M).



**(141)**

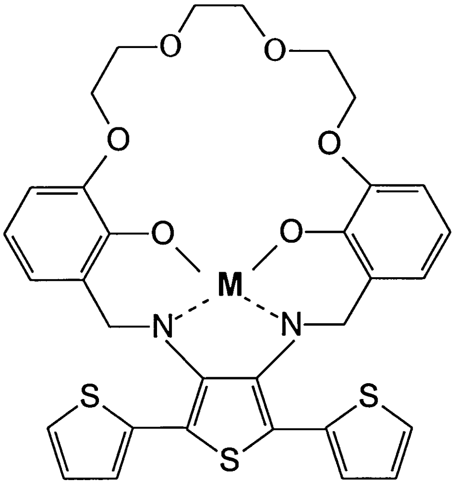
The molecular recognition of biological species is also an important area of sensor devices, and conjugated polymers containing receptor moieties specific to particular biological compounds are being developed. Polybithiophene derivative **(142)** containing a uracil functionality has been used for the recognition of the complementary base adenine.[189]

Electropolymerised films of **(142)** were prepared, however only a slight electrochemical response was observed when in the presence of acetyl-9-octyladenine.



**(142)**

In 1998, thiophene derivative **(143)** was synthesised.[190] The structure comprises a salophen group with a strongly chelated metal such as Ni and Cu, which is adjacent to a thiophene moiety, also adopting an oligo(oxyethylene) functionality which is present for metal binding. Template synthesis methodology was adopted in the presence of $Ba^{2+}$, with subsequent ion removal by addition of guanidine sulfate and electropolymerisation. A shift in the redox potential in the order of 25-145 mV was observed for the polymer in solution upon addition of various alkali and alkali earth metal ions, giving the trend $Li^+ < Na^+ < Mg^{2+} < Ba^{2+}$. This occurred via metal exchange which was reversible with group I metal ions but irreversible with group II metals, which had to be chemically removed (guanidine sulfate). A sharpening of the redox peaks was also observed upon the addition of monocations, indicating enhanced ion mobility.



**(143)**

The novel system thieno[3′,4′-*d*:5,6][1,4]dithiino[2,3-*b*]quinoxaline **(130)**[191] is potentially capable of coordinating to metal ions through the two $sp^2$ nitrogen atoms within the quinoxaline moiety. Numerous transition metal complexes incorporating this feature have been reported,[192] and the chelating ability of quinoxaline derivatives is well known. Through this, it is justifiable to say that, upon electropolymerisation, the resulting polymer of **(130)** will bind to transition metals, along with the possibility of interaction with the two sulfur atoms of the dithiin ring system leading to a complex polymeric arrangement. A diagrammatic representation of the proposed structure is shown in figure 31.

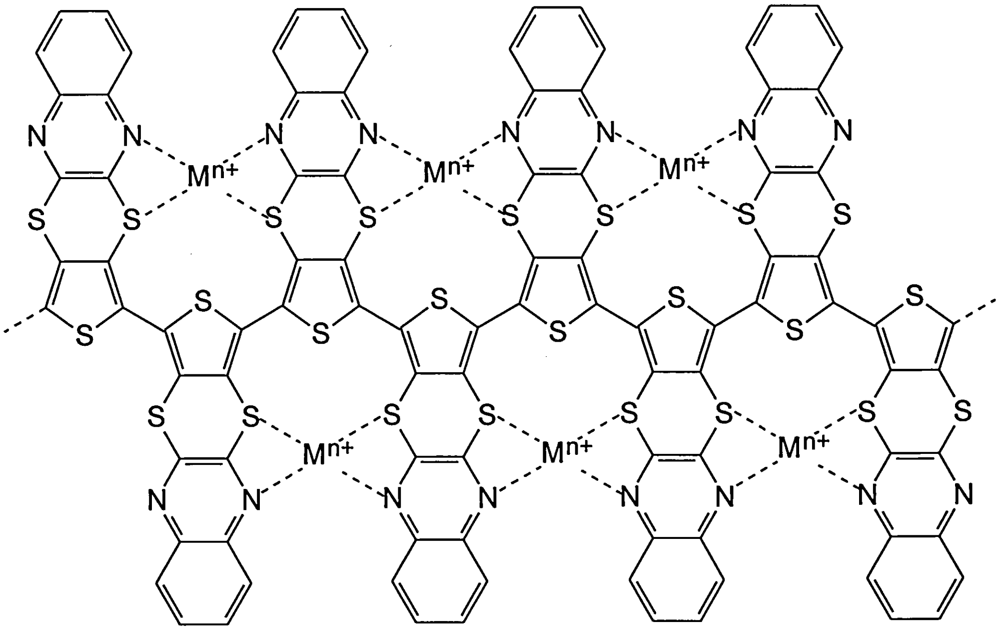
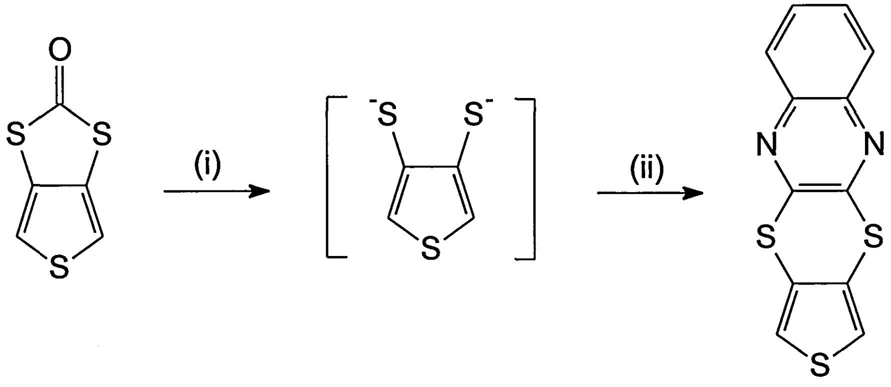


**Figure 31**

This chapter is concerned with the synthesis and electrochemistry of monomer unit **(130)**, along with its interaction and electrochemical recognition of silver and mercury cations, upon electropolymerisation.

## 5.2 RESULTS AND DISCUSSION

Thieno[3′,4′-*d*:5,6][1,4]dithiino[2,3-*d*]quinoxaline **(130)**[143] was synthesised by the reaction of thieno[3,4-*d*]-1,3-dithiole-2-thione **(78)** with sodium ethoxide. The resulting dithiolate intermediate was allowed to react with 2,3-dichloroquinoxaline to afford monomer **(130)** (42%) [scheme 23].



**(78)** **(130)**

**Scheme 23:** Reagents and conditions (i) NaOEt, THF, 1h (ii) 2,3-dichloroquinoxaline

Electrochemistry of **(130)** reveals the ability of the system to sustain both anodic oxidation and cathodic reduction processes. The presence of two oxidation peaks at + 1.60 V and + 1.93 V (at a scan rate of 200 mV $s^{-1}$) corresponds to the formation of the radical cation and dication species of **(130)** respectively (figure 32).

The irreversibility of these peaks suggests the existence of the dication as a stable aromatic 18 π system.

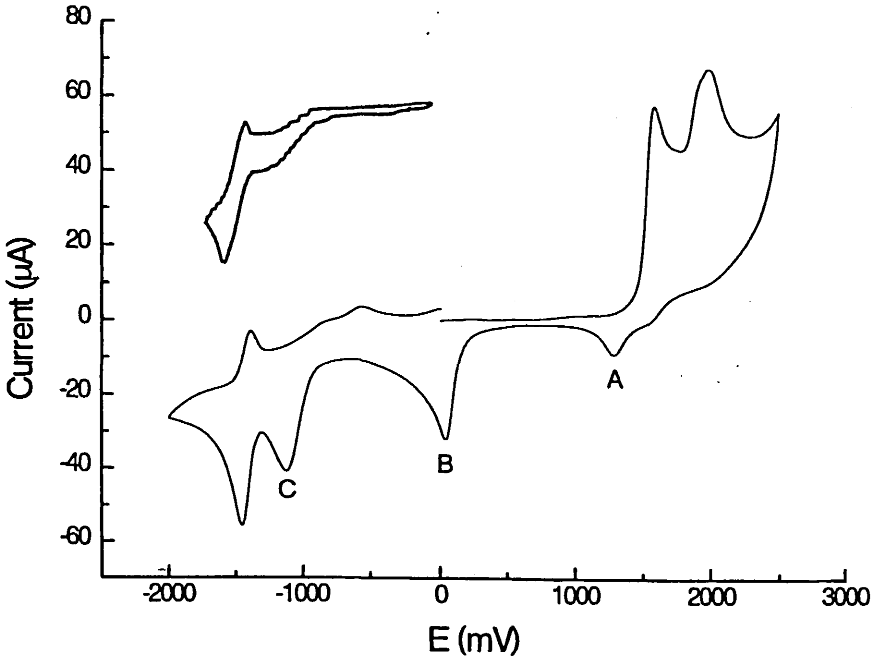


**Figure 32:** Cyclic voltammogram of monomer **(130)** vs. Ag/AgCl with *iR* compensation, Pt electrode, 20 °C under argon, 0.1 M $Bu_4NPF_6$ as supporting electrolyte in dry dichloromethane (inset - negative scan from 0.00 V to -1.8 V to 0.00 V).

A single electron reduction peak occurs at lower potentials, which may be due to the reduction of the dication back to the radical cation. However, no further reduction back to the neutral species is observed at this scan rate. If the scan rate is increased to 600 mV $s^{-1}$, this peak can be observed at -1.07 V. The quinoxaline moiety of the system can be assigned by the observed reversible single electron reduction wave at $E^{red}$ = -1.45 V, comparable to quinoxaline itself which is reduced at - 1.80 V vs. Ag/AgCl in DMF.[193] This confirms that the redox process involved is not simply the reduction of a positively charged species, as an identical trace and value for $E^{red}$ was observed upon switching of electrical parameters from an initial positive sweep to negative rather than the usual negative to positive direction.

Electropolymerisation of quinoxaline **(130)** was achieved by repetitive scanning over the first oxidation potential of the system from 0.00 to 1.7 V, vs Ag / AgCl using Pt, Au or GC electrodes in anhydrous dichloromethane. The voltammogram for the electropolymerisation process is shown in figure 33, which shows the appearance of a new redox couple at + 0.85 V vs Ag / AgCl.

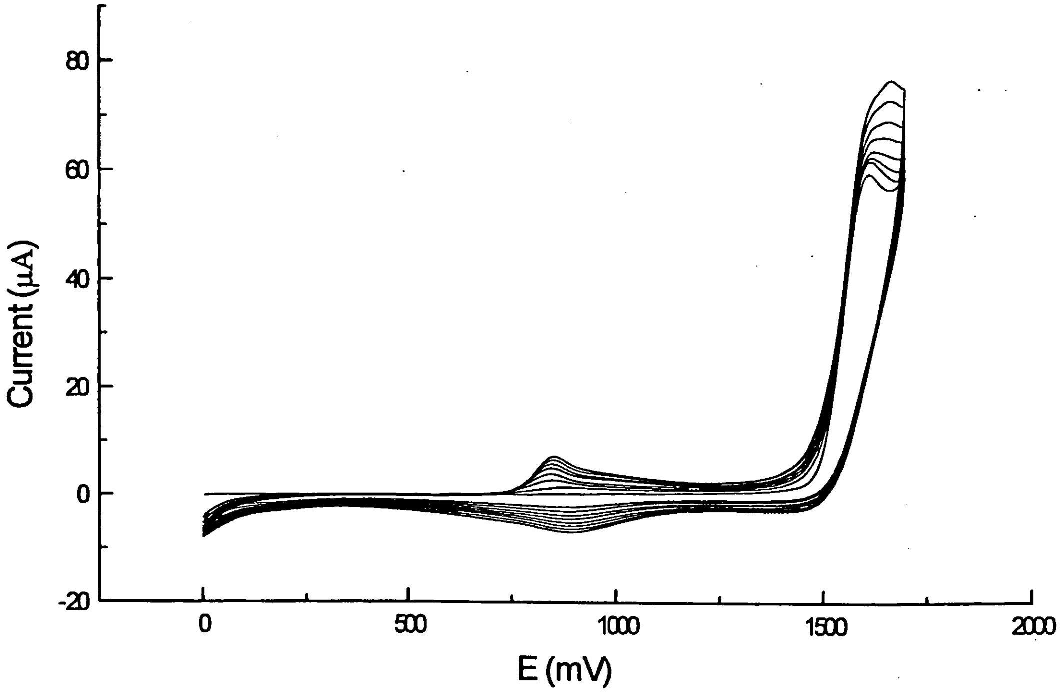
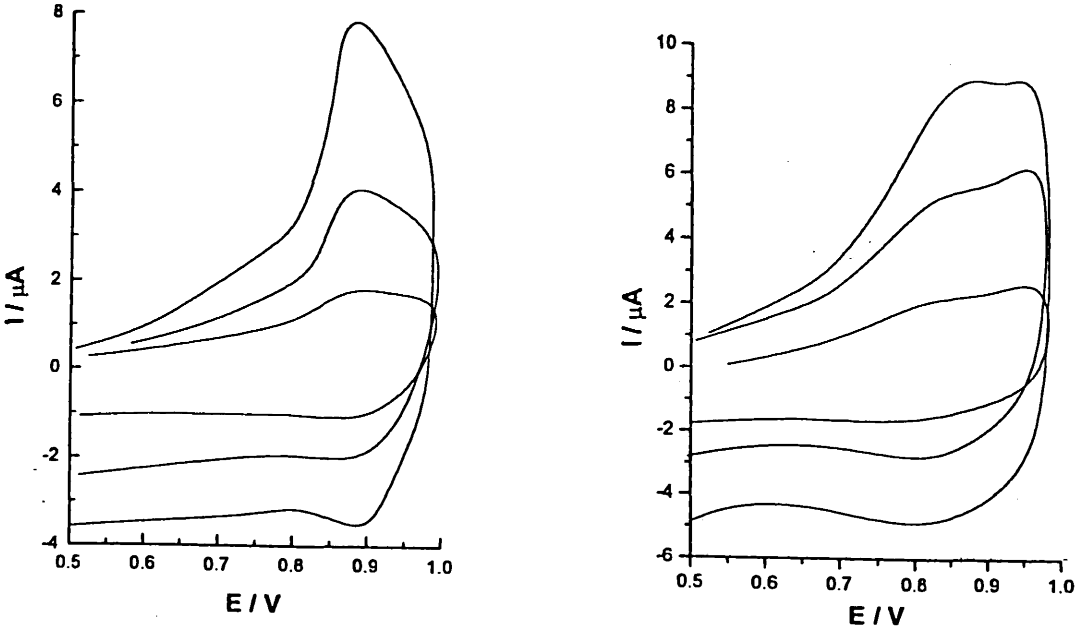


**Figure 33:** Electropolymerisation of **(130)** vs Ag/AgCl. Scan rate 200 mV $s^{-1}$, Au disc in $CH_2Cl_2$ (0.10 M $Bu_4NClO_4$ as supporting electrolyte)

Polymer growth on the electrode reaches a saturation point at a value of charge, which is consumed under the first oxidation peak [determined by graphical integration] (Γ) of approximately 4-5 nM $cm^{-2}$.

The nature of the electrode and thickness of film obtained had an effect on the shape of the redox couple and it was also observed that the time at which the monomer solutions were prepared before electropolymerisation also had an effect on the polymerisation of the monomer. A freshly prepared solution required a higher first oxidation potential and polymerisation occurred at a reduced rate. As a result of this, the ratio of currents for the first and second redox couple for this system fluctuates.

The polymer films obtained at the electrode appeared to be electroactive in both aqueous and non-aqueous electrolyte solutions and the results obtained are shown in figure 34. The response of the polymer in acetonitrile is represented in (a) and appears to be relatively stable. A 5 -10% decrease in the peak current is observed over 10 cycles of the system at a scan rate of 0.02, 0.05, and 0.1 V $s^{-1}$.



(a) (b)

**Figure 34**: CV response of polymer, GC electrode vs. Ag/AgCl (a) 0.2 M $Bu_4NClO_4$ (MeCN). Scan rate 0.02, 0.05, 0.1 V $s^{-1 \cdot}$ (b) 0.1 M $H_2SO_4$. Scan rate 0.05, 0.01, 0.2 $Vs^{-1}$.

A similar result was obtained for the same system in aqueous solution (b) at a scan rate of 0.05, 0.1 and 0.2 V $s^{-1}$.

In both aqueous and non-aqueous solution, the peak current was proportional to the scan rate, as shown in figure 35, indicating a surface electrochemical reaction, with a slight increase in the oxidation potential upon an increase in the scan rate.

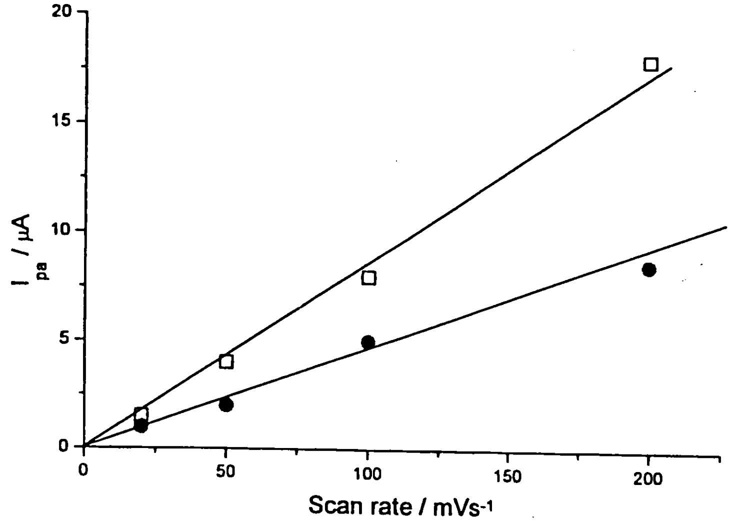


**Figure 35:** Plot of oxidation peak rate vs. current, □ experiment (a), figure 34, ● experiment (b), figure 34.

The electrochemical recognition of a number of transition metal cations by the polymer was investigated. In particular, the interaction of $Ag^+$ displayed pronounced effects on the resulting CVs of thin polymer films.

It was observed that the presence of $Ag^+$ ions in solution may affect the potential of the Ag/AgCl electrode in non aqueous media. In order to counteract this effect, two approaches were adopted before any investigations were undertaken. Based on a method described by Bartlett et al[194], an internal reference was initially introduced whereby the potential of the system was referred to an internal $Fc/Fc^+$ couple which was measured on a blank electrode in the same solution. However, a disadvantage of this is the electrochemical activity of Fc on the resulting polymer film, which was observed at regular Fc potentials as a decrease in signal. This can be avoided by the use of a more suitable starting potential. However, the appearance of small shoulders at the onset of the oxidation peak potential were observed (similar to polybithiophene)[195] which are possibly due to the Fc/Fc$^+$ peak on the compact polymer film, which caused complications in the determination of the oxidation peak potential.

The second approach was to adopt the use of a reference electrode compartment filled with an aqueous electrolyte, employing a graphite junction between the non-aqueous solution in the cell and the Ag/AgCl reference electrode. This method proved more suitable for the molecular recognition of Ag$^+$ ions, by the shift in oxidation potential upon the addition of silver cations. The only disadvantage in this is that the position of the reference electrode could not be checked independently.

The addition of Ag$^+$ ions to electropolymerised quinoxaline system **(130)** resulted in a measurable shift in the CV response. Different electrodes and polymer film thickness were used in the process and a negative shift was observed for both oxidation ($E_{pa}$) and reduction ($E_{pc}$) potentials. Figure 36 shows the CV response for a polymer film upon the addition of Ag$^+$ ions to the electrolyte solution. The results show a negative shift in the oxidation potential upon the introduction of varying concentrations of Ag$^+$ ions.

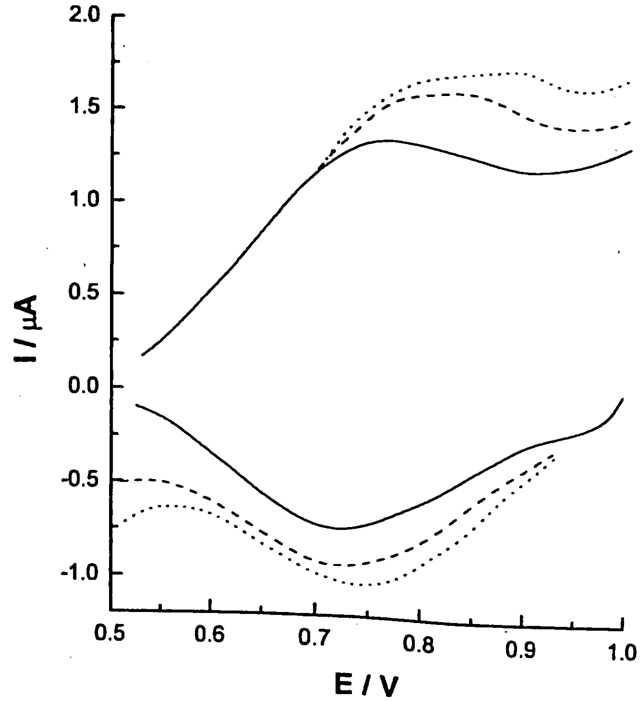


**Figure 36:** CV response of polymer in 0.2 M $LiClO_4$ (MeCN). Au electrode, scan rate 0.05 V s$^{-1}$ vs Ag/AgCl — (No Ag$^+$), ----- (Ag$^+$) ($1.7 \times 10^{-3}$ M) ······· (Ag$^+$) ($1.3 \times 10^{-2}$ M).

It was observed that the concentration of $Ag^+$ ions in solution had an effect on the oxidation peak potential of the system. Figure 37 shows that the response of the polymer to $Ag^+$ ions is initiated at a concentration of $10^{-4}$ M. This becomes saturated at approximately $10^{-2}$ M and a maximum shift in potential of ca. 150 mV was observed.

The reproducibility of this process, and establishing various ways of determining the shift in oxidation potential was demonstrated by points obtained by a number of different electrodes and counterions.

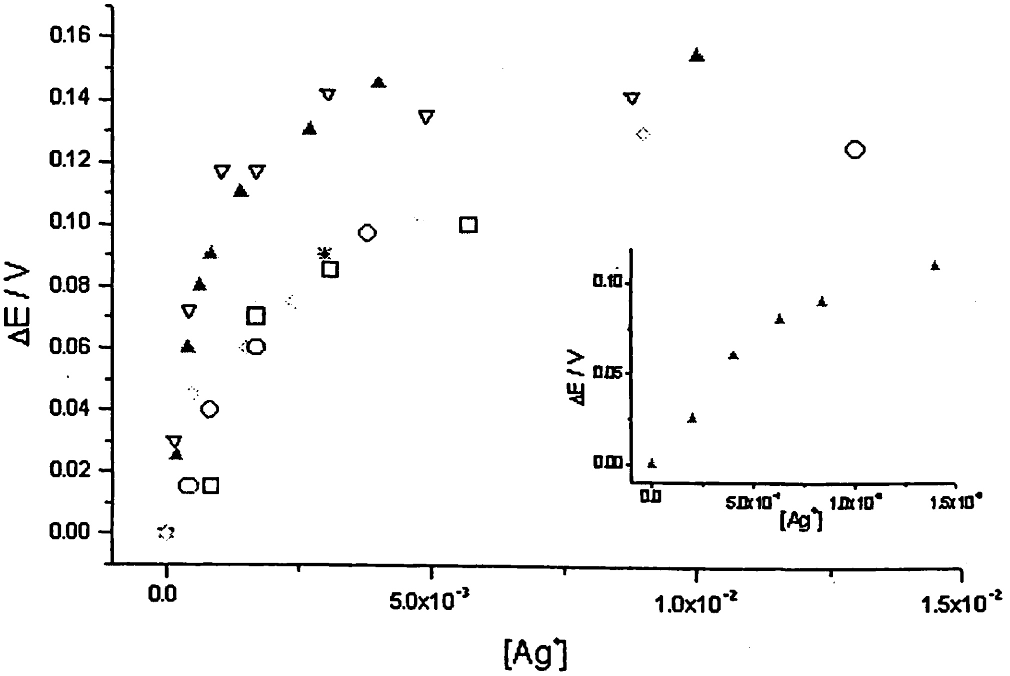


**Figure 37:** Shift of redox potential of polymer in 0.2 M $LiClO_4$/ acetonitrile vs $[Ag]^+$; solid sign ($E_{pa}$+$E_{pc}$/2), open sign ($E_{pa}$), Δ and * ($AgClO_4$), ∇ and ◊ ($AgBF_4$), □ and O ($AgNO_3$); triangles refer to $Fc/Fc^+$, others refer to Ag/AgCl | $LiClO_4$ aqueous/ graphite; Δ, ◊, □ , O - **Au** electrodes; - ∇ **GC** electrode. Insert shows extended scale up for triangle.

A linear dependence in the plot of current at a fixed potential vs. alkali metal concentration in crown substituted PT was found by Bäuerle and Scheib.[188] A similar plot was observed for the polymer of **(130)** using a GC electrode at a fixed potential vs. $Fc/Fc^+$. Although the plot is not completely linear, there are two linear regions in the log $[Ag^+]$ plot (figure 38).

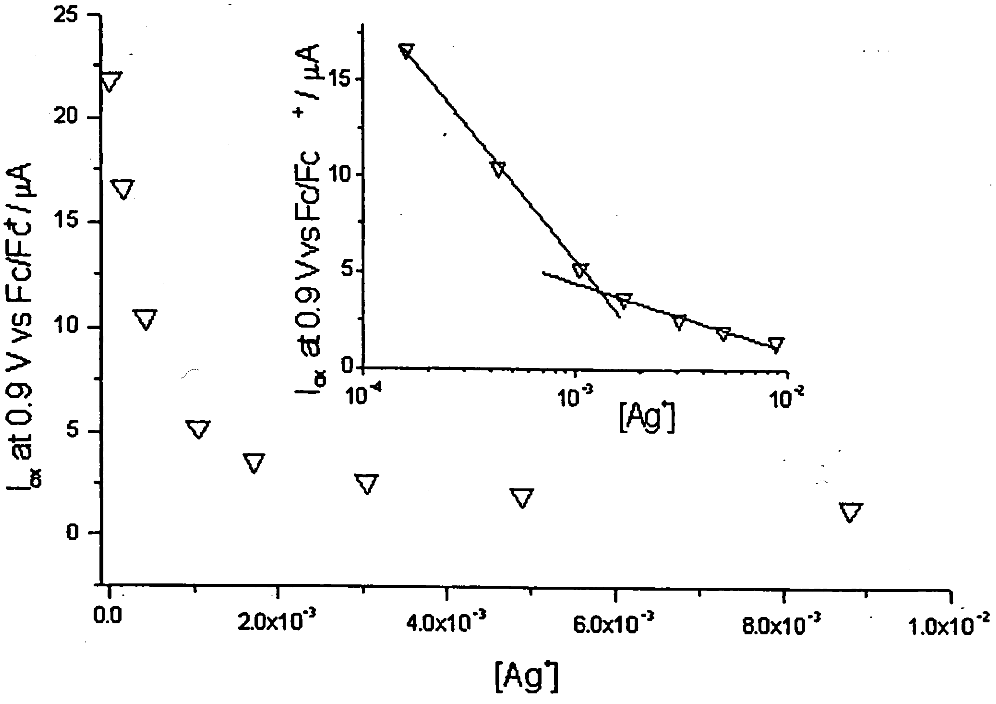


**Figure 38:** Oxidation current at 0.9 V vs. Fc/Fc$^+$ versus [Ag]$^+$. Data from experiment recorded in conditions of figure 37, down triangles. Insert shows log [Ag]$^+$ scale.

The CV response to Ag$^+$ ions in acidic solution (HBF$_4$) was also investigated. However, the observed shift in potential was either very small (ca 20 mV) or was not observed at all. This may be due to protonation of the quinoxaline moiety by the acidic medium used in the process, as it is known that 5,6-disubstituted-1,4-dithiino[2,3-*b*]-quinoxaline derivatives may be protonated or alkylated at the sp$^2$ nitrogen atoms to afford their corresponding quinoxaline salts.[196]

For this reason, the use of a neutral aqueous electrolyte was employed, although a lower electroactivity of the system results.

Figure 39 shows the results obtained for the response of Ag$^+$ in solution using a GC electrode in a 0.5 M aqueous electrolyte solution (LiClO$_4$), at a scan rate of 0.02 V s$^{-1.}$ A relatively well defined CV response was obtained with a maximum response to Ag$^+$ cation, shown by a shift in the E$_{pc}$ of the polymer to 400 mV.

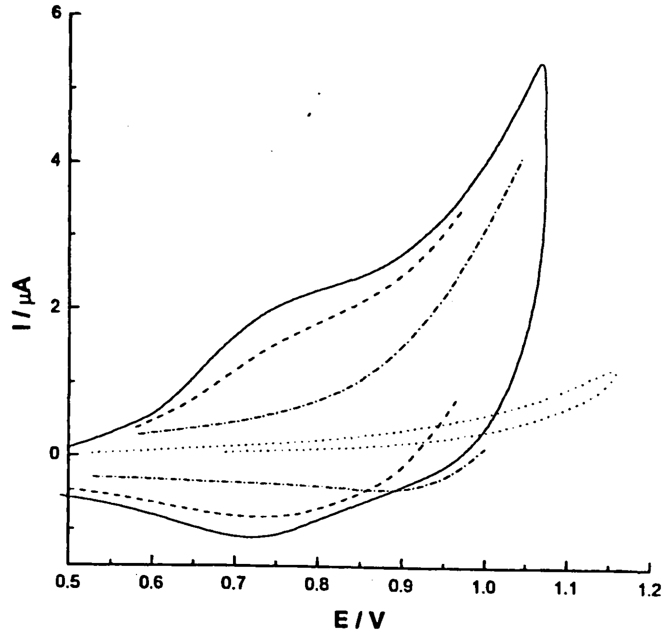


**Figure 39:** CV response of polymer using a GC electrode. 0.5 M aqueous $LiClO_4$, scan rate 0.02 V $s^{-1}$ $AgClO_4$ and $H_2O$ used ·········· blank electrode, ------- Polymer with 1.8 x $10^{-5}$ M $Ag^+$ -·-·-· Polymer with 1 x $10^{-4}$ M $Ag^+$, —— No $Ag^+$

Different concentration levels of $Ag^+$ ions were also introduced to the system and the corresponding electrochemical response was recorded. Figure 40 shows the results obtained in determining the dependence of the shift in the redox peak versus the concentration of ions added. This shows that detection of $Ag^+$ ions is possible at concentrations as low as $10^{-5}$ M levels.

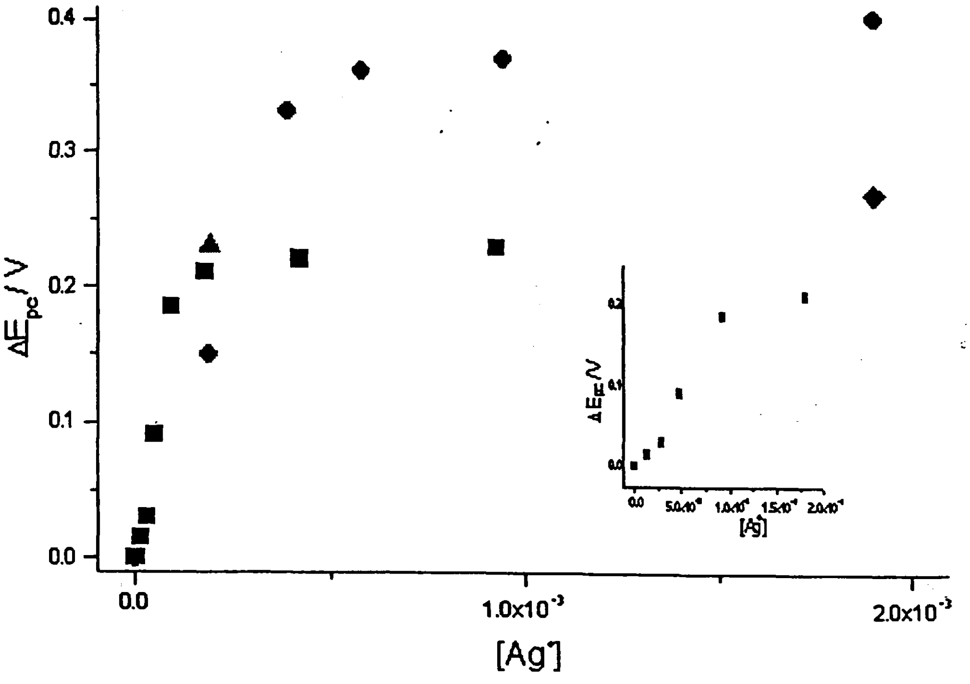


**Figure 40:** Shift of potential GC electrode. Epc in 0.5 M $LiClO_4$ vs [$Ag^+$], □, O, Δ, ◊ - Γ = 2.5, 2.1, 1.5, and 2.3 nM $cm^{-1}$ respectively; insert - extended scale for □.

From our investigations, it was also found that the binding of silver cations by polymer films of **(130)** is reversible. The soaking of the electrode in a solution of KCl for approximately 0.5 h results in the predominant restoration of the original peak position, with the expulsion of the bound silver cations as insoluble AgCl. Contradictory to this, soaking of the electrode in water for 20 h results in only a slight restoration of $E_{pc}$, which may indicate that the binding of $Ag^+$ ions in a harder solvent ($H_2O$) results in a stronger binding of the metal. This phenomenon has also been observed with the binding of $Ag^+$ ions in a crown annelated TTF.[197]

A further investigation into molecular recognition of $Ag^+$ ions by this polymeric system involved amperometric detection. A series of short pulses were applied to the system from the area where the polymer is in its neutral state up to the potential of $E_{pa}$ (0.6 - 0.8 V), as shown in figure 41. A decrease in the intensity of the pulse upon the introduction of $Ag^+$ indicates a response to the metal ions.

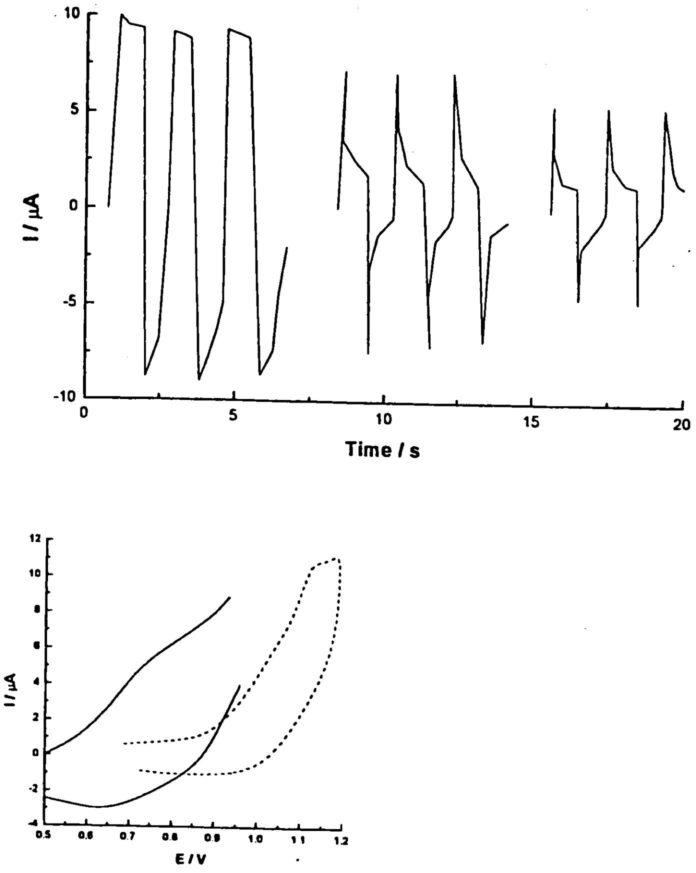


**Figure 41:** **(a)** Change in current with addition of $Ag^+$, first plot (no $Ag^+$), second plot ($[Ag^+] = 1.7 \times 10^{-3}$ M), third plot ($[Ag^+] = 5 \times 10^{-3}$ M) **(b)** —— initial CV of polymer, ------ CV of polymer after experiment (i.e. containing $Ag^+$)

The electrochemical recognition of the soft dication $Hg^{2+}$ by polymer films of quinoxaline derivative **(130)** was also observed, although this was not as well defined as for $Ag^+$ ions. A shift of 130 mV in the $E_{pc}$ of the polymer was observed whilst in the presence of $Hg^{2+}$ ions in a neutral aqueous electrolyte solution ($LiClO_4$). In non-aqueous electrolyte solution only a small shift in potential is observed (table 5).

| **Cation, conditions** | **$\Delta E$/ mV** |
|---|---|
| $Ag^+$, acetonitrile | 150 |
| $Ag^+$, $HBF_4$ | 0 |
| $Ag^+$, (aq), $LiClO_4$ | 400[a] |
| $Hg^{2+}$, acetonitrile | 30[b] |
| $Hg^{2+}$ (aq), $LiClO_4$ | 130[a] |

[a] $\Delta E_{pc}$; [b] a small shift was observed with $Hg(NO_3)_2.xH_2O$, but not with $HgCl_2$. $Hg(NO_3)_2.xH_2O$ is only slightly soluble in acetonitrile and maximum concentration was estimated to be ca. $5 \times 10^{-4}$ - $1 \times 10^{-3}$ M. The issue is also complicated by the reduction of $Hg^{2+}$ occurring at the beginning of polymer wave.

**Table 5:** Voltammetric recognition parameters for different cations

## 5.3 CONCLUSIONS

The synthesis and electropolymerisation of thieno[3′,4′-d:5,6][1,4]dithiino[2,3-b]quinoxaline **(130)** has resulted in a novel polymeric material which is electroactive in both aqueous and non-aqueous solution. This conjugated system has the ability to detect low levels of transition metal ions in solution, which is observed by a shift in the redox potential of the polymer whilst in the presence of various metal cations. $Ag^+$ ions show an increase in the redox potential of the polymer of 150 mV in non-aqueous solution. Upon similar investigations in an aqueous electrolyte solution, shifts in the potential have been observed of 400 mV, indicating stronger binding of the metal ions to the host substrate. The softer $Hg^{2+}$ dication is also recognised by this system, with a shift in the $E_{pa}$ of the polymer of 130 mV in neutral aqueous solution.

# CHAPTER 6

## Experimental

**General.** All melting points were taken using electrothermal melting point apparatus and are uncorrected. Solvents were dried and purified by standard methods. Chemical reagents were purchased from the Aldrich chemical company unless referenced and were used as supplied unless stated. All $^1$H and $^{13}$C nmr spectra were recorded using a Brüker AC 250 instrument; chemical shifts are given in ppm; all *J* values are in Hz. Mass spectrometry data was recorded on a VG Micromass 7070E analytical mass spectrometer.

Infrared spectra were obtained using a Mattson Genesis series FTIR spectrometer and UV data were obtained using a Unicam UV2 instrument.

Gel permeation chromatography analysis was obtained using a Polymer Laboratories PL LogiCal GPC instrument employing a UV detector at 254 nm. Samples were analysed at 40 °C in chloroform using a 2 x PL Gel micron mixed bed and guard column, and were run against a polystyrene standard and a toluene flow marker.

Elemental analyses were obtained by MEDAC Ltd.

**Cyclic Voltammetry.** CV measurements and electropolymerisations were carried out using a BAS CV 50W voltammetric analyser with iR compensation. Anhydrous dichloromethane and acetonitrile were used as solvents along with a Ag/AgCl reference electrode, platinum wire and gold disk/glassy carbon as the counter and working electrodes respectively.

All solutions were degassed prior to determination ($N_2$) and contained the substrate in concentrations of $\sim 10^{-2}$ - $10^{-4}$ M together with $Bu_4NPF_6$ (0.1 M) as the supporting electrolyte. Voltammograms of polymer films were obtained in monomer free solutions (anhydrous acetonitrile) containing $Bu_4NPF_6$ (0.1 M) as the supporting electrolyte.

**Single Crystal X-Ray Structure determination.** Crystal data for **(98)** $C_{20}H_{26}Br_2S_7$. M = 650.65, triclinic, space group P-1, a = 7.7910(16)Å, b = 11.819(2) Å, c = 15.064(3) Å, $\alpha$ = 96.69(3)°, U = 1311.9(5) Å$^3$, T = 150(2)K, Z = 2,

$\mu$ (Mo - K$\alpha$) = 3.654 mm$^{-1}$, F(000) = 656, 14353 reflections collected, $\theta$ range 2.09 - 27.4 ° (index ranges h = -10 to 8, k = -15 to 15 and l = -19 to 19) which merged to give 5919 unique reflections (R $_{int}$ = 0.0720) to refine against 275 parameters. Final R indices were wR$_2$ = 0.1149 and R$_1$ = 0.0430 [F$_2$ >2$\sigma$ (F$_2$] and 0.1308 and 0.0595 respectively for all data. Residual electron densities were 1.024 and -0.880 e Å$^3$.

Data were collected for a crystal of size 0.55 x 0.075 x 0.025 mm$^3$ on an Enraft Nonius Kappa CCD area detector diffractometer (∅ scans and $\omega$ scans to fill an Ewald sphere) using a molybdenum target $\lambda$ (Mo - K$\alpha$ = 7.1073 Å). The structure was solved by direct methods SHELX-97 and then subjected to full matrix least squares refinement on F$_o^2$ SHELXL-97. Absorption correction was achieved using SORTAV software.[198]

**Single-crystal X-ray Structure determination.** Crystal data for **(122)**: $C_{15}H_8O_2S_7$, *M* = 444.63, monoclinic, space group P2$_{1/n}$ (alternative setting of P2$_{1/c}$, No. 14), a = 8.773(20, b = 20.104(4), c = 10.983(2) A, $\alpha$ = 111.08(3)°, U = 1807.5(4) Å$^3$, T = 293(2) K, Z = 4, $\mu$(Mo-K$\alpha$) = 0.878 mm$^{-1}$, F(000) = 904, 7039 reflections collected, $\theta$ range 2.03-25.07° (index ranges; h = -8 to 9, k = -22 to 22 and l = -12 to 11), which merged to give 2657 unique reflections (R$_{int}$ = 0.0620) to refine against 217 parameters. Final R indices were w R$_2$ = 0.1037 and R$_1$ = 0.0482 [I > 2$\sigma$(I)] and 0.1112 and 0.0802 respectively for all data. Residual electron densities were 0.406 and -0.492 e Å$^3$.

Data were collected for a crystal of size 0.45 x 0.2 x 0.2 mm on a Delft instruments FAST TV area detector diffractometer at the window of a rotating anode FR591 generator (50 kV, 55 mA), using a molybdenum target ($\lambda$ (Mo-K$\alpha$) = 0.71069 Å], controlled by a MicroVax 3200 and driven by MADNES[199] software.

The structure was solved by direct methods (SHELXS-97) and then subjected to full matrix least squares refinement based on F$_o^2$ (SHELXL-97)[200]. Non-hydrogen atoms were refined anisotropically with hydrogens included in idealised positions (C - H distance = 0.97 Å) with isotropic parameters free to refine. The weighting scheme used was w = 1/[$\sigma^2$(F$_o^2$)]. An absorption correction was deemed unnecessary, as the structure had been fully refined to a satisfactory standard.

**Single Crystal X-Ray Structure determination.** Crystal data for **(126)** $C_{14}H_{10}S_5$, *M* = 338.52, orthorhombic, space group C*mc*$2_1$, a = 20.6948(7) Å, b = 8.7890(3) Å, c = 7.7472(3) Å, *U* = 1409.11(9) Å$^3$, T = 150(2)K, *Z* = 4, μ(Mo-Kα) = 0.803 mm$^{-1}$, *F* (000) = 696, 6285 reflections collected, θ range 3.64 to 25.01 ° (index ranges; h = -24 to 24, k = -10 to 10, l = -9 to 9), which merged to give 1246 unique reflections ($R_{int}$ = 0.0276) to refine against 98 parameters. Final R indices were *w*$R_2$ = 0.0579 and $R_1$ = 0.0224 [$I > 2\sigma(I)$] and 0.0583 and 0.0231 respectively for all data. Residual electron densities were 0.237 and -0.492 e Å$^{-3}$.

Data were collected upon a crystal size 0.22 x 0.18 x 0.10 mm$^3$ on an Enraft Nonius Kappa CCD area detector diffractometer (∅ scans and ω scans to fill an Ewald sphere) using a molybdenum target λ (Mo - Kα = 7.1073 Å). The structure was solved by direct methods SHELX-97 and then subjected to full matrix least squares refinement on $F_o^2$ SHELXL-97. Absorption correction was achieved using SORTAV software.[198]

# EXPERIMENTAL FOR CHAPTER 2

## Thieno[3,4-*d*]-1,3-dithiole-2-ylidine-4,5-bis(hexylsulfanyl)-1,3-dithiole (77)[129e]

Compounds **(78)** (1.9 g, 11 mmol) and **(79)** (10 g, 27 mmol) were allowed to stir under dry nitrogen with freshly distilled triethyl phosphite (5 ml) at 110 °C for 4 h. Upon cooling, the product was isolated from the reaction mixture by column chromatography (silica, petroleum ether with gradual change to petroleum ether: ethyl acetate 1:1 v/v) to afford **(77)** as a dark yellow solid. (18%,1 g, 2.03 mmol).

mp 71 - 73 °C (Lit 73 - 74 °C)

$^1$ H NMR ($CDCl_3$) δ 6.87 (2 H, s), 2.83 (4 H, t), 1.65 (4 H, m), 1.32 (12 H, m), 0.90 (6 H, t).

## Thieno-[3,4-*d*]-1,3-dithiole-2-one (78)[143]

To a solution of **(86)** (2.96 g, 1.56 mmol) in dichloromethane:glacial acetic acid (3:1 v/v), was added mercury (II) acetate (7.93 g, 2.49 mmol). The reaction was stirred at room temperature for 2 h, filtered, the solid precipitate washed with dichloromethane (150 ml) and water was added (50 ml). The organic phase was washed with copious amounts of water and saturated sodium bicarbonate solution. The organic extracts were dried ($MgSO_4$) and the solvent was removed in vacuo to afford **(75)** as an off-white solid (87%, 2.36 g, 1.36 mmol).

mp 105 - 107 °C (lit 107 - 108 °C).

## 4,5-Bis(hexylsulfanyl)-1,3-dithiole-2-thione (79)[201]

Compound **(80)**[137] (10 g, 1.39 mmol) and 1-bromohexane (5.74 g, 3.48 mmol) were allowed to react in refluxing acetonitrile (100 ml) for 2-3 h. The solvent was removed in vacuo and the product was extracted into dichloromethane (150 ml). The organic phase was washed with water (3 x 100 ml) and dried ($MgSO_4$). The solution was stirred with charcoal for 1 h, filtered and the solvent removed to afford **(79)** as an orange oil (71%, 5.7 g, 0.0155 mmol)

m/z (EI) ($M^+$, 100) 366.0

$^1$H NMR (CDCl$_3$) δ 2.7 (4 H, t, *J* = 7.33 Hz), 1.7 (4 H, m), 1.4 (12 H, m), 0.7 (6 H, t, *J* = 6.75 Hz).

### Bis(tetraethylammonium)bis(1,3-dithiole-4,5-dithiol)zincate (80)[137]

To dry, degassed dimethylformamide (240 ml) was added carbon disulfide (120 ml) and this was cooled to 0 °C. Finely cut sodium (7.3 g) was added in one portion and the mixture was stirred for approximately 8 h with cooling, until all of the sodium was consumed in the reaction (if any sodium remained at this stage, methanol was slowly added). To this was added separate solutions of (i) ZnCl$_2$ (10.8 g) dissolved in 33% ammonia solution (175 ml) and water (50 ml), and (ii) Et$_4$NBr (33 g) dissolved in water (250 ml), in equivolume portions over 0.5 h. The reaction was stirred for 16 h at room temperature, at which time the solution was filtered and washed with iso-propanol (500 ml) and diethyl ether (300 ml) to afford **(80)** as analytically pure red crystals.
mp 204 - 206 °C (Lit 206 - 208 °C).

### Ethylene Trithiocarbonate (81)[138]

To a mixture of carbon disulfide (500 ml) and sodium hydroxide (33% solution (w/v), 500 ml) was added tetrabutylammonium hydrogen sulphate (19.7 g, 0.058 mol). The solution was stirred for 0.5 h whilst cooling to 0 °C, at which time was added 1,2-dibromoethane (50 ml, 0.58 mol). This was stirred for 16 h at room temperature, and the product was extracted into diethyl ether (3 x 250 ml). The combined organic extracts were washed with water (3 x 200 ml), saturated sodium chloride solution (2 x 200 ml) and dried (MgSO$_4$). The solvent was removed in vacuo to afford **(81)** as a yellow crystalline solid (46.96 g, 0.34 mol, 59% ).
mp 32 -34 °C (Lit 34 - 36 °C)
$^1$H NMR (CDCl$_3$) δ 3.97 (4 H, s)

### Dimethyl-1,3-dithiole-2-thione-4,5-dicarboxylate (82)[139]

Compound **(81)** (23.97 g, 0.176 mol) and dimethylacetylene dicarboxylate (DMAD, 25 g, 0.176 mol) were allowed to react in refluxing toluene for 24 h. The solvent was removed in vacuo and the product was isolated by column chromatography (silica, petroleum spirit 40-60 °C: ethyl acetate 10:1 v/v). Recrystallisation from petroleum ether:ethyl acetate (4:1 v/v) afforded **(82)** as light orange crystals (75%, 33.11 g, 0.132 mol).

mp 74 - 76 °C (Lit 72 - 72.5 °C)

m/z (EI) ($M^+$, 100) 250.0

$^1$H NMR ($CDCl_3$) δ 3.97 (6 H, s)

## 4,5-Bis(hydroxymethyl)1,3-dithiole-2-thione (83)[140]

To a suspension of lithium chloride (1.4 g, 33 mmol) in tetrahydrofuran (130 ml) at -10 °C with stirring, was added sodium borohydride (13.8 g) and methanol (130 ml). A solution of **(82)** (13.8 g, 55 mmol) in tetrahydrofuran (50 ml) was added to the mixture portionwise over approximately 0.5 h, ensuring that the temperature remained at approximately -10 °C at all times. Further additions of sodium borohydride (1 g) were made at various intervals until the addition of **(82)** was complete. The reaction mixture was allowed to stir for 3 h at 0 - 10 °C, at which time iced water (200 ml) was added. The product was extracted into chilled ethyl acetate (3 x 150 ml) and the combined organic extracts were washed with water (3 x 100 ml) and saturated sodium chloride solution (2 x 50 ml). The organic extracts were dried ($MgSO_4$) and the solvent removed in vacuo. The product was isolated by column chromatography (silica, petroleum ether (40-60 °C):ethyl acetate 10:1 v/v) to afford **(83)** as a yellow/orange solid (65%, 6.99 g, 36 mmol).

mp 83-85 °C (Lit 86-87 °C)

## 4,5-Bis(bromomethyl)-1,3-dithiole-2-thione (84)[129c]

To a suspension of **(83)** (6 g, 0.03 mol) in dry dichloromethane (200 ml) under dry nitrogen with stirring, was added carbon tetrabromide (20.49 g, 0.061 mol). A solution containing triphenylphosphine (17.67 g, 0.061 mol) in dry dichloromethane (50 ml) was added dropwise over a period of 1h. The reaction mixture was allowed to stir for a further 2 h, at which time water was added (50 ml). The organic phase was washed with water (3 x 100 ml), saturated sodium chloride solution (2 x 100 ml) and dried ($MgSO_4$).

The solvent was removed in vacuo and the product was isolated by column chromatography (silica, petroleum ether (40-60 °C):ethyl acetate 5:1 v/v) to afford **(84)** as fine yellow crystals (66%, 6.5 g, 0.02 mol).

mp 121-123 °C (Lit 124-126 °C)

m/z (EI) ($M^+$, 100) 320

$^1$H NMR ($CDCl_3$) δ 4.3 (4 H, s)

### 4,6-Dihydro-[3,4-*d*]-thieno-1,3-dithiole-2-thione (85)[141]

To ethanol (200 ml) with stirring, was added simultaneously solutions of **(84)** (1 g, 3.12 mmol) in tetrahydrofuran (25 ml) and ethanol (175 ml), and $Na_2S.9H_2O$ (0.82 g, 3.44 mmol) in ethanol (150 ml) and water (50 ml), over a period of 1-2 h. Upon complete addition, the solvent was removed in vacuo to dryness. The product was extracted into dichloromethane (200 ml) and the organic phase was washed with water (5 x 50 ml). The organic extracts were dried ($MgSO_4$) and the solvent was removed in vacuo to afford **(85)** as a dark yellow solid (83%, 0.5 g, 2.6 mmol).

mp 129-131 °C (Lit 131-133 °C)

m/z (EI) ($M^+$, 100) 192

$^1$H NMR ($CDCl_3$) δ 4.0 (4 H, s).

### Thieno-[3,4-*d*]-1,3-dithiole-2-thione (86)[142]

Compound **(85)** (1.85 g, 9.62 mmol) was allowed to react with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (2.18 g, 9.62 mmol) in refluxing toluene (150 ml) for 4 h. The solvent was removed in vacuo and the product was extracted into dichloromethane (100 ml). The organic phase was washed with a copious amount of water and dried ($MgSO_4$). The solvent was removed under reduced pressure and the product was isolated by column chromatography (silica, petroleum ether (40-60 °C): ethyl acetate 3:1 v/v) to afford **(86)** as a yellow solid (78%, 1.42 g, 7.46 mmol).

mp 139 - 141 °C (Lit 142 °C)

### 4-Methylene t-butyldiphenylsilylether-5-(methylcarboxylate)-1,3-dithiol-2-ylidine-4,5-bis(hexylsulfanyl)-1,3-dithiole (91)

Compounds **(79)** (1.99 g, 5.43 mmol) and **(93)** (1 g, 2.17 mmol) were allowed to stir under dry nitrogen with freshly distilled triethyl phosphite (5 ml) at 110 °C for 6 h. Upon cooling, the product was isolated by column chromatography (silica, petroleum ether 40-60 °C) to afford **(91)** as a dark brown oil (24 %, 0.4 g).

m/z (EI) 763

### 1,3-dithiole-2-thione-4-hydroxymethyl-5-methylcarboxylate (92)

To a suspension of lithium chloride (0.8 g) in tetrahydrofuran (130 ml) at -10 °C with stirring, was added sodium borohydride (3.97 g) and methanol (130 ml). A solution of **(82)** (13.26 g, 53 mmol) in tetrahydrofuran (50 ml) was added and the reaction mixture was allowed to stir for 5 min at -10 °C, at which time iced water was added. The product was extracted into chilled ethyl acetate (3 x 150 ml) and the combined organic extracts were washed with water (3 x 100 ml) and saturated sodium chloride solution (2 x 50 ml). The organic extracts were dried ($MgSO_4$) and the solvent removed in vacuo. The product was isolated by column chromatography (silica, petroleum ether (40-60 °C):ethyl acetate 10:1 v/v to afford **(92)** as a yellow/orange solid (56%, 6.61 g, 29.7 mmol).

mp 62 - 64 °C

HRMS (EI) calcd for C6H6O3S3 221.94791, found 221.94744

$^1$H NMR ($CDCl_3$) $\delta$ 4.9 (2 H, s), 3.9 (3 H, s), 3.8 (1 H, s)

$\nu_{max}$ /cm$^{-1}$ (KBr) 3325, 1711, 1549, 1276, 1066, 1024 and 758.

### 4-Methylene t-butyldiphenylsilyl-5-(methylcarboxylate)-1,3-dithiole-2-thione (93)

To a solution of **(92)** (5.5 g, 24.7 mmol) in dimethylformamide (60 ml) was added *tert*-butyldichlorodiphenylsilane (8.16 g, 29.7 mmol) and imidazole (3.33g, 4.95 mmol). The reagents were allowed to react at room temperature for 24 h, at which time water was added (100 ml). The product was extracted into diethyl ether (2 x 150 ml), washed with water (3 x 50 ml) and dried ($MgSO_4$). The solvent was removed in vacuo and the product was isolated by column chromatography (silica, petroleum ether:ethyl acetate 5:1 v/v) to afford **(93)** as an off white solid (71%, 8.09 g, 17.6 mmol).

mp 72 – 74 °C

$\nu_{max}$ /cm$^{-1}$ (KBr) 3061, 2954, 2932, 2856, 1730, 1679, 1650, 1428, 1140, 1070 and 863.

### **1,3-Dithiole-2-thione-4-hydroxymethyl-5-carboxylic acid (94)**

Compound **(92)** (0.86 g, 3.87 mmol) was allowed to reflux with concentrated hydrochloric acid (2.5 ml), water (3.4 ml) and glacial acetic acid (1.1 ml) for 2 h. The reaction mixture was cooled to afford a dark brown solid in 48% yield (0.38 g, 1.82 mmol).

m/z (EI) 208

$\nu_{max}$/cm$^{-1}$ 3397, 2952, 1682, 1539, 1400, 1252, 1071 and 485.

### **1,3-Dithiole-2-thione-4,5-dicarboxylic acid (95)**[143]

Diester **(82)** (2 g, 7.99 mmol) was allowed to reflux with concentrated hydrochloric acid (8.6 ml), water (12 ml) and glacial acetic acid (4 ml) for 2 h. The reaction mixture was cooled to afford a bright orange solid which was filtered and dried under reduced pressure (80%, 1.42 g, 6.39 mmol).

mp 162 - 164 °C (lit ca. 160 °C)

m/z (EI) 222

### **2,5-Diiodothieno[3,4-*d*]-1,3-dithiole-2-ylidine[4,5-bis(hexylsulfanyl)-1,3-dithiole(96)**

To a solution of compound **(77)** (1.0 g, 2.02 mmol) in anhydrous THF (50 ml) at -78 °C under dry nitrogen was added LDA (2.84 ml, 4.26 mmol). The mixture was allowed to stir at this temperature for 1 h, at which time perfluorohexyl iodide (0.92 ml, 4.24 mmol) was added. The reaction was stirred for 12 h whilst warming to room temperature, and dichloromethane was added (100 ml). The organic phase was washed with water and dried ($MgSO_4$). The product was isolated by column chromatography (silica, dichloromethane:hexane 3:1 v/v) to afford **(96)** as an orange red solid in 88% yield (1.32 g, 1.77 mmol).

mp 64 - 66 °C

m/z (EI) 744.1

$^1$H NMR ($CDCl_3$) δ 2.82 (4 H, t, *J* = 7.28 Hz), 1.63 (4 H, m), 1.38 (12 H, m), 0.90 (6 H, t, *J* = 6.74 Hz)

$\nu_{max}/cm^{-1}$ (KBr) 3413, 2952, 2923, 2851, 2348, 1636 and 1288.

## 2,5-Dibromothieno[3,4-*d*]-1,3-dithiole-2-one (97)

To a suspension of **(78)** (0.65 g, 3.73 mmol) in carbon tetrachloride (50 ml) was added an excess of bromine (1 ml). The reaction was allowed to reflux for 1 h and upon cooling, dichloromethane was added (50 ml). The organic extracts were washed several times with water and dried ($MgSO_4$). The solvent was removed in vacuo to yield a beige solid which was re-dissolved in dichloromethane (50 ml) and stirred with charcoal for 0.5 h. Upon filtration, the solvent was removed in vacuo to yield **(97)** as a white solid (61%, 0.75 g, 2.26 mmol).

mp 126 - 128 °C

$^{13}$C NMR ($CDCl_3$) - 189.5, 130.4, 101.4 ppm

$\nu_{max}/cm^{-1}$ 1700, 1648, 1277, 898 and 838

HRMS (EI) calcd for $C_5S_3OBr_2$ 331.74576, found 331.74585.

## 2,5-Dibromothieno[3,4-*d*]-1,3-dithiole-2-ylidine-4,5-bis(hexylsulfanyl)-1,3-dithiole (98)

Compounds **(78)** and **(97)** were stirred under dry nitrogen with freshly distilled triethyl phosphite (5 ml) at 120 °C for 6 h. Upon cooling, the product was purified directly by column chromatography (silica, petroleum spirit 40 - 60 °C) to yield **(98)** as an orange crystalline solid.

mp 62 - 64 °C

$^1$H NMR ($CDCl_3$) δ 2.81 (4 H, t, *J* = 7.3 Hz), 1.65 (4 H, m), 1.35 (12 H, m), 0.89 (6 H, t, *J* = 7.3 Hz)

$^{13}C$ NMR ($CDCl_3$) 137.8, 128.0, 117.6, 111.9, 97.6, 36.7, 35.6, 31.6, 30.0, 28.5, 22.9, 14.4 ppm

$\nu_{max}/cm^{-1}$ 2921, 2850, 1462, 1287, 1037 and 890

m/z (EI) $M^+$ 650

## Polymerisation of (98)

Compound **(98)** (560 mg, 0.86 mmol) was allowed to dissolve in anhydrous dimethylformamide (5 ml) and this was added dropwise to a solution containing $Ni(COD)_2$ (320 mg, 1.16 mmol), COD (100µl) and 2,2'bipyridyl (180 mg, 1.15 mmol) in DMF (10 ml). The mixture was allowed to stir in the absence of light at 60 °C for 48 h. Upon cooling, the reaction was poured into an excess of methanol (100 ml). The solvent was removed in vacuo and dichloromethane was added (150 ml). The organic extract was washed with (a) dil. HCl (2 x 75 ml), (b) $Na_2EDTA$ (aq) (2 x 75 ml), (c) $Na_2EDTA$ (2 x 75 ml in aqueous $NH_3$), (d) $NH_3$ (aq) (2 x 75 ml), (e) $H_2O$ (100 ml), (f) dil HCl (2 x 75 ml), (g) $H_2O$ (100 ml). The solvent was evaporated in vacuo to yield a dark purple solid in 92% yield.

# EXPERIMENTAL FOR CHAPTER 3

## 4,6-Bis(2-thienyl)thieno[3,4-*d*]-1,3-dithiole-2-thione (99)

A mixture of **(107)** (1.0 g, 2.80 mmol), $P_2S_5$ (3 g, 13 mmol) and $NaHCO_3$ (1 g) in 1,4-dioxane (20 ml), was stirred under dry nitrogen whilst the temperature was increased from 60 to 100 °C over 1h. The mixture was cooled, water was added (150 ml) (CAUTION! $H_2S$ and $CO_2$ evolution) and the suspension was allowed to reflux for 15-20 min. The crude product was filtered, dried under vacuum and purified by column chromatography (silica, toluene). The volume of the eluent was reduced in vacuo to 15-20 ml, petroleum ether (40-60 °C) was added (50 ml) and upon filtration and drying afforded **(99)** as an orange powder (0.7g, 70%).

mp 195-196 °C

$^1$H NMR ($CDCl_3$, 55°C) $\delta$ 7.38 (2 H, dd, *J* = 5.1 and 1.0 Hz), 7.21 (2 H, dd, *J* = 3.7 and 1.2 Hz), 7.11 (2 H, dd, *J* = 5.1 and 3.7 Hz)

$\nu_{max}$/ cm$^{-1}$ (KBr) 3072, 1487, 1415, 1068, 838 and 687

m/z (EI) 354 ($M^+$, 100)

Anal calcd for $C_{13}H_6S_6$: C, 44.0; H, 1.7. Found: C, 43.6; H, 1.8.

## 4,6-Bis(2-thienyl)thieno[3,4-*d*]-1,3-dithiole-2-one (100)

A mixture of **(113)** (1 g, 2.95 mmol), $P_2S_5$ (3.2 g, 13.7 mmol) and $NaHCO_3$ (1 g) in 1,4-dioxane (20 ml) was stirred under dry nitrogen whilst the temperature was raised from 60 - 90 °C over 1h. The mixture was cooled, water was added (150 ml) (CAUTION! $H_2S$ and $CO_2$ evolution) and the suspension was allowed to reflux for 0.5 h. Upon cooling, the crude product was filtered, washed with water (50 ml) and dried in vacuo. The product was isolated by column chromatography (silica, petroleum spirit 40 - 60 °C with gradual change to dichloromethane) to afford **(100)** as a light orange solid (63%, 0.63 g, 1.86 mmol).

mp 170-172°C

$^1$H NMR ($CDCl_3$) $\delta$ 7.39, (2 H, dd, *J* = 0.96 and 4.52 Hz), 7.24 (2 H, dd, *J* = 0.95 and 3.61 Hz), 7.12 (2 H, m,)

$\nu_{max}$/cm$^{-1}$ 2361, 1653, 840 and 700

HRMS (EI) calcd for $C_{13}H_6OS_5$ 337.90222, found 337.90107.

## 4,6-Bis(2-thienyl)furo[3,4-*d*]-1,3-dithiole-2-thione (101)

### Method A

A mixture of **(112)** (25 mg, 0.073 mmol), DDQ (23 mg, 0.10 mmol), and toluene (10 ml) was allowed to reflux for 3 h. The volume of solvent was reduced to 2 - 3 ml and the product was isolated by column chromatography (silica, toluene) to afford crude **(101)** (9 mg, 35%)
mp 178 - 186 °C.

### Method B

A solution of **(111)** (20 mg) and 3 drops of concentrated HBr in acetone (1 ml) was allowed to stand at room temperature for 24 h. Water (0.5 ml) was added and the precipitate was filtered and washed with a small amount of cold acetone: petroleum ether (1:3 v/v) mixture to afford **(101)** as scarlet thin needles (17 mg, 89%).
mp 193 -195 °C
$^1$H NMR ($CDCl_3$, 55 °C) δ 7.39 (2 H, dd, $J$ = 5.1 and 1.0 Hz), 7.22 (2 H, dd, $J$ = 3.8 and 1.1 Hz), 7.14 (2 H, dd, $J$ = 5.0 and 3.8 Hz)
HRMS (EI) calcd for $C_{13}H_6OS_5$ 337.90222, found 337.90424.

## 5,7-Bis(2-thienyl)thieno[3'4':5,6]-1,4-dithiino[2,3-*d*]-1,3-dithiole-2-thione (102)

A suspension of **(122)** (1.0 g, 0.90 mmol), $P_2S_5$ (4.5 g, 20 mmol), and $NaHCO_3$ (1.5 g) in dry 1,4-dioxane (50 ml) was stirred at 90 °C for 1.5 h on vigorous stirring. After cooling, the mixture was diluted with water (100 ml) (CAUTION! $H_2S$ and $CO_2$ evolution), heated to 50 °C and filtered. Water was added and the mixture was allowed to reflux for 10 min. The precipitate was filtered, dried and the solid was treated with boiling toluene (150 ml). The hot toluene solution was eluted through a layer of silica (∅ 5 x 5 cm) and the silica was washed with hot toluene (150 ml). The volume of the filtrate was reduced to ca. 40 ml in vacuo, affording **(102)** as yellow-orange needles (567 mg, 57%)

mp 230 - 232 °C

$^1$H NMR (acetone $d_{6,}$ 50 °C) δ 7.67 (2 H, dd, *J* = 5.2 and 1.0 Hz), 7.43 (2 H, dd, *J* = 3.6 and 1.0 Hz), 7.21 (2 H, dd, *J* = 5.2 and 3.6 Hz)

HRMS (EI) calcd for $C_{15}H_6S_8$ 441.82352, found 441.82323.

### 5,7-Bis(2-thienyl)furo[3'4':5,6]-1,4-dithiino[2,3-*d*]-1,3-dithiole-2-thione (103)

To a solution of **(122)** (20 mg) in boiling acetic acid (7 ml) was added concentrated HBr (0.5 ml), and the mixture was allowed to reflux for 3 h. Water was added (3 ml), and the precipitate was filtered, dried, and purified by column chromatography (silica, toluene) to afford **(103)** as a yellow powder (7 mg, 35%).

mp 180 - 210 °C (dec)

$^1$H NMR ($CDCl_3$, 50 °C), δ 7.42 (4 H, m,), 7.14 (2 H, dd, *J* = 5.1 and 3.7 Hz)

m/z (EI) found 426 required for 425.84637

Anal calcd for $C_{15}H_6S_7O$: C, 42.2; H, 1.4. Found: C, 42.3; H, 1.7.

### 1,4-Bis(2-thienyl)but-2-yne-1,4-diol (105)

A solution of ethylmagnesium bromide was prepared from Mg (1.42 g, 59 mg-atom) and ethyl bromide (4.92 ml, 64 mmol) in tetrahydofuran (50 ml), under standard Grignard conditions. Acetylene gas was purified by passing the reagent through a trap cooled to -70 °C, and a second trap with concentrated sulfuric acid; the gas was immediately transferred into the Grignard solution over 2 h at 50 °C, at a rate of 2-3 L/min on vigorous stirring. After this time, the flow of acetylene was interrupted and a fraction of the solvent (10 - 15 ml) was removed by distillation at ambient pressure, to ensure the complete decomposition of acetylene monomagnesium bromide. 2-Thiophenecarboxaldehyde (5 ml, 54 mmol) was added at room temperature and the mixture was allowed to stir overnight. The reaction was poured into 20% aqueous $NH_4Cl$ (200 ml) and the product was extracted into ethyl acetate (2 x 30 ml). The organic phase was dried over $MgSO_4$, the solvent was removed in vacuo, and the residue was purified by column chromatography (silica, $CH_2Cl_2$ with gradual change to $CH_2Cl_2$:ethyl acetate = 2:1 v/v) to afford **(105)** (3.30 g, 50%).

mp 110 - 113 °C (Lit mp 116 °C)[164]

### 1,4-Bis(2-thienyl)but-2-yne-1,4-dione (106)

To a solution of **(105)** (50 mg, 0.20 mmol) in $CH_2Cl_2$ (5 ml) was added $MnO_2$ (600 mg). The mixture was stirred for 2 min at room temperature, slowly filtered through a layer of silica (∅ 2 x 5 cm), then the silica was washed with dichloromethane (30 ml). Evaporation of the solvent under reduced pressure afforded **(106)** (28 mg, 55%).

mp 133-135 °C

$^1H$ NMR (acetone-$d_6$) $\delta$ 8.21 (2 H, dd, $J$ = 3.9 and 1.1 Hz), 8.17 (2 H, dd, $J$ = 4.9 and 1.3 Hz), 7.36 (2 H, dd, $J$ = 4.9 and 3.9 Hz)

$\nu_{max}$ /cm $^{-1}$ (KBr) 1628 (C=O)

HRMS (EI) calcd for $C_{12}H_6O_2S_2$ 245.98093, found 245.98165.

### 4,5-Bis(2-thenoyl)-1,3-dithiol-2-thione (107)

#### Method A

A solution of **(106)** (33 mg, 0.13 mmol) and **(81)** (20 mg, 0.15 mmol) in toluene (1 ml) was heated in a sealed tube under nitrogen at 100 °C for 16 h. The solvent was removed in vacuo and the product was isolated by column chromatography (silica, $CH_2Cl_2$: petroleum ether = 1:1 v/v), affording **(107)** (4 mg, 8%).

#### Method B

To a solution of **(109)** (300 mg, 0.85 mmol) in dichloromethane (50 ml) was added $MnO_2$ (3 g). The mixture was stirred for 2 minutes at room temperature and was immediately filtered through a layer of silica (∅ 2 x 3 cm), whilst eluting with dichloromethane (100 ml). Evaporation of the solvent under reduced pressure afforded **(107)** as a yellow tar which gradually solidified upon standing (99%, 298 mg, 0.84 mmol).

mp 91-93 °C

$^1$H NMR ($CDCl_3$) δ 7.72 (4 H, m), 7.11 (2 H, dd, *J* = 5.0 and 3.9 Hz)

$\nu_{max}$/cm$^{-1}$ (KBr) 3102, 1636, 1407, 1271, 1066 and 732

m/z (EI) 354 ($M^+$, 100)

Anal calcd for $C_{13}H_6O_2S_5$: C 44.1; H 1.7. Found: C 44.1; H 1.6

### ***dl*- and *meso*-4,5 bis(2-thienylhydroxymethyl)-1,3-dithiole-2-thione (109a & 109b), and 4-(2-thienylhydroxymethyl)-1,3-dithiole-2-thione (110)**

To a solution of vinylene trithiocarbonate **(108)** (Fluka) (1g, 7.5 mmol) in dry tetrahydrofuran (30 ml) at -55 °C, was added lithium diisopropylamide monotetrahydrofuran (5.8 ml, 8.6 mmol, 1.5 M solution in cyclohexane). The mixture was stirred under dry nitrogen for 15 min, cooled to -70 °C and 2-thiophenecarboxaldeyde (0.7 ml, 7.5 mmol) was added over 1-2 min. This was allowed to stir for a further 3 min, then a second portion of LDA was added (5.4 ml, 8.1 mmol). The mixture was stirred at -55 °C for 10 min, and a further portion of 2-thiophenecarboxaldehyde (0.7 ml, 7.5 mmol) was added over 1-2 min. The reaction was warmed to -30 °C and poured into saturated sodium bicarbonate solution (100 ml), to which potassium bromide was added (10 g). The product was extracted into ethyl acetate (3 x 75 ml) and the combined organic extracts were dried ($MgSO_4$). The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica, dichloromethane with gradual change to dichloromethane:ethyl acetate [10:1 v/v]) to afford essentially pure (mono) and (diol) respectively, in order of elution.

Analytical samples were obtained by treating methanolic solutions with charcoal, removal of solvent under reduced pressure and reprecipitation of solids with petroleum ether (40 - 60 °C) from dichloromethane.

**(109 a)**: Pale yellow-green crystals (1.8 g, 67%)

mp 109-110 °C

$^1$H NMR (acetone-$d_6$) δ 7.50 (2 H, dd, *J* = 5.2 and 1.0 Hz), 7.20 (2 H, m), 7.03 (2 H, dd, *J* = 5.2 and 3.6 Hz), 6.35 (2 H, d, *J* = 3.4 Hz) and 6.11 (2 H, d, *J* = 3.8 Hz)

$\nu_{max}$/cm$^{-1}$ (KBr) 3330, (br) 3105, 1431, 1380, 1279, 1029, and 720

m/z (EI) 358 ($M^+$, 100)

Anal calcd for $C_{13}H_{10}O_2S_5$: C, 43.6; H, 2.8. Found: C, 43.3; H, 2.6.

**(109 b)** : Yellow-brown tar (0.4 g, 15%)

$^1$H NMR (acetone - $d_6$) δ 7.50 (2 H, dd, $J$ = 5.2 and 1.0 Hz), 7.20 (2 H, m), 7.03 (2 H, dd, $J$ = 5.2 and 3.6 Hz), 6.35 (2 H, d, $J$ = 3.4 Hz) and 6.11 (2 H, d, $J$ = 3.8 Hz)

$\nu_{max}$/cm$^{-1}$ (neat on KBr) 3330 (br), 3104, 1434, 1381, 1230, 1153, 1060, 1036, 838, and 704

HRMS (EI) calcd for $C_{13}H_{10}O_2S_5$ 357.92844, found 357.92605.

**(110)** Pale green-yellow crystals (0.20 g, 12%)

mp 67-69 °C

$^1$H NMR (acetone-$d_6$) δ 7.47 (1 H, dd, $J$ = 5.1 and 1.2 Hz), 7.33 (1 H, d, $J$ = 1.2 Hz), 7.14 (1 H, m), 6.21 (1 H, dd, $J$ = 4.4 and 0.9 Hz) and 6.03 (1 H, dd, $J$ = 4.4 and 0.9 Hz)

$\nu_{max}$/cm$^{-1}$ (KBr) 3363 (br), 3097, 1058, and 707

HRMS (EI) calcd for $C_8H_6S_4O$ 245.93015, found 245.93090.

### 4-(2-Thenoyl)-5-(2-thienylhydroxymethyl)-1,3-dithiole-2-thione (111)

To a solution of **(109)** (50 mg) in dichloromethane (2 ml) was added $MnO_2$ (150 mg), and the mixture was stirred at room temperature for 2 min. The product was purified directly from the reaction mixture by column chromatography (silica, $CH_2Cl_2$). The solvent was removed in vacuo to afford **(111)** as a yellow tar (25 mg, 50%).

$^1$H NMR ($CDCl_3$) δ 7.91 (1 H, dd, $J$ = 3.9 and 1.0 Hz), 7.81 (1 H, dd, $J$ = 5.0 and 1.0 Hz), 7.31 (1 H, dd, $J$ = 5.1 and 3.6 Hz), 7.19 (1 H, dd, $J$ = 3.9 and 5.0 Hz), 7.14 (1 H, m), 6.98 (1 H, dd, $J$ = 5.1 and 3.6 Hz), 6.41 (1 H, d, $J$ = 0.8 Hz), 3.6 (1 H, br)

$\nu_{max}$ / cm$^{-1}$ (neat on KBr) 3420 (O-H, br), and 1623 (C=O)

HRMS (EI) calcd for $C_{13}H_8O_2S_5$ 355.91278, found 355.91103.

### 4,6-Bis(2-thienyl)-4,6-dihydrofuro[3,4-*d*]-1,3-dithiole-2-thione (112)

Two drops of concentrated HBr was added to a suspension of **(109)** (400 mg, 1.13 mmol) in dichloromethane (10 ml). The mixture was stirred at room temperature for 20 min, and the product was isolated by column chromatography (silica, $CH_2Cl_2$: petroleum ether 1:1 v/v). The major fraction was treated with cold acetone-water

(10:1 v/v, 15 ml) and an insoluble yellow precipitate formed which was filtered and washed with a small amount of cold acetone to afford **(112)** (55 mg, 14%).

mp 134 °C (dec).

$^1$H NMR ($CDCl_3$) δ 7.40 (2 H, dd, *J* = 5.1 and 1.0 Hz), 7.17 (2 H, dd, *J* = 3.6 and 1.0 Hz), 7.02 (2 H, dd, *J* = 5.1 and 3.6 Hz), 6.38 (2 H, s)

HRMS (EI) calcd for $C_{13}H_8S_5O$ 339.91788, found 339.91634.

### 4,5-Bis(2-thenoyl)-1,3-dithiol-2-one (113)

To a solution of **(107)** (3.36 g, 9.49 mmol) in dichloromethane:glacial acetic acid (3:1 v/v) was added mercuric acetate (4.84 g, 0.152 mol). The mixture was stirred at room temperature for 16 h, filtered and washed with dichloromethane (50 ml). The organic extracts were washed with copious amounts of water and saturated sodium bicarbonate solution, then dried ($MgSO_4$). The solvent was removed under reduced pressure to afford **(113)** as a pale yellow solid (76%, 2.45 g, 7.25 mmol).

mp 130-132°C

$^1$H NMR ($CDCl_3$) δ 7.71 (2 H, dd, *J* = 0.8 and 5.46 Hz), 7.69, (2 H, dd, *J* = 0.88 and 4.04 Hz), 7.09 (2 H, m)

$\nu_{max}/cm^{-1}$ 2173, 1623, 1506, 1405, 1268, 1110 and 1045

HRMS (EI) calcd for $C_{13}H_6O_3S_4$ 337.91998, found 337.91693.

### 4,5-Bis(2-cyanoethylsulfanyl)-1,3-dithiole-2-thione (114)

Compound **(80)** (10 g, 22 mmol) was allowed to react with 3-bromopropionitrile (5.5 ml) in refluxing acetonitrile (150 ml) for approximately 1 h. The solvent was removed in vacuo and dichloromethane was added. (100 ml). The solution was filtered and stirred with charcoal for 0.5 h, filtered and dried ($MgSO_4$). The solvent was removed in vacuo to afford **(114)** as a light orange solid which was recrystallised from dichloromethane/petroleum ether to afford light yellow/orange crystals (90%, 6 g, 19.7 mmol).

m/z (EI) 304

### 4,6-Bis(2-thienyl)thieno[3,4-*d*]-1,3-dithiole-2-ylidine-4,5-bis(2-cyanoethylsulfanyl)-1,3-dithiole (115)

Compounds **(100)** (0.5 g, 1.48 mmol) and **(114)** (1.12 g, 3.68 mmol) were stirred under dry nitrogen with freshly distilled triethyl phosphite (10 ml) at 120 °C for 6 h. Upon cooling, petroleum ether (40 - 60 °C) was added (50 ml) and the product was filtered and washed with petroleum ether (100 ml). The product was isolated by column chromatography (silica, dichloromethane) to afford **(115)** as a dark orange solid (61%, 0.54 g, 0.91 mmol).

mp 160-162 °C

$^1$H NMR ($CDCl_3$) $\delta$ 7.35 (2 H, d, $J = 4.41$ Hz), 7.17 (2 H, d, $J = 2.77$ Hz), 7.10 (2 H, m, $J = 0.94$ Hz), 3.1 (4 H, t, $J = 6.98$ Hz), 2.7 (4 H, t, $J = 6.98$ Hz)

$\nu_{max}/cm^{-1}$ 2922, 2361, 2338, 1410, 1288 and 685

m/z (EI) 594

### 4,6-Bis(2-thienyl)thieno[3,4-*d*]-1,3-dithiole-2-ylidine-4,5-bis(2-hexylsulfanyl)-1,3-dithiole (116)

To a solution of **(115)** (0.31 g, 0.52 mmol) in dry tetrahydrofuran (50 ml) under dry nitrogen at 0 °C was added tetrabutylammonium hydroxide (1.15 ml, 1.15 mmol, 1 M solution in methanol). The reaction was allowed to stir at this temperature for 1h, after which time 1-bromohexane was added (0.16 ml, 1.15 mmol). The mixture was allowed to warm to room temperature and was stirred for a further 3 h. Water was added (100 ml) and the product was extracted into ethyl acetate (3 x 75 ml). The combined organic extracts were washed with water (2 x 100 ml) and dried ($MgSO_4$). The solvent was removed in vacuo and the product was isolated by column chromatography (silica, petroleum ether 40 - 60 °C) to afford **(116)** as an orange solid (60%, 0.207 g, 0.32 mmol).

mp 62-64 °C

$^1$H NMR ($CDCl_3$) δ 7.33 (2 H, dd, *J* = 0.81 and 4.66 Hz), 7.17 (2 H, dd, *J* = 0.8 and 3.17 Hz), 7.08 (2 H, m), 2.9 (4 H, t, *J* = 7.15 Hz), 1.7 (4 H, m), 1.4 (12 H, m), 0.9 (6 H, t, *J* = 6.00 Hz)

$\nu_{max}/cm^{-1}$ 2915 (br), 1417, 838, 765 and 684

HRMS (EI) calcd for $C_{28}H_{32}S_9$ 655.99902, found 655.99942

Anal calcd for $C_{28}H_{32}S_9$ : C 51.18, H 4.91; Found C 51.06, H 4.91.

## 4,6-Bis(2-thienyl-5-bromo)thieno[3,4-*d*]-1,3-dithiole-2-ylidine-4,5-bis(2-hexylsulfanyl )-1,3-dithiole (117)

To a solution of **(116)** (0.1 g, 0.15 mmol) in dry tetrahydrofuran (50 ml) under dry nitrogen at -78 °C was added lithium diisopropylamide monotetrahydrofuran (0.11 ml, 1.5 M solution in cyclohexane). The mixture was allowed to stir at this temperature for 1 h at which time 1,2-dibromotetrafluoroethane was added (0.02 ml, 0.165 mmol). The reaction was allowed to warm to room temperature and was then stirred for a further 12 h. Water was added (50 ml) and the product was extracted into ethyl acetate (3 x 75 ml). The combined organic extracts were washed with water (2 x 100 ml) and dried ($MgSO_4$). The solvent was removed in vacuo and the product was isolated by column chromatography (silica, petroleum ether 40-60 °C) to afford **(117)** as an orange/red solid (0.025 g, 0.03 mmol, 22%).

mp 83-85 °C

$^1$H NMR ($CDCl_3$) δ 7.33 (1 H, dd, *J* = 0.96 and 4.94 Hz), 7.14 (1 H, dd, *J* = 0.96 and 3.58 Hz), 7.06 (1 H, t, *J* = 1.19 Hz), 7.01 (1 H, d, *J* = 3.89 Hz) 6.88 (1 H, d, *J* = 3.89 Hz), 2.83 (4 H, t, *J* = 7.29 Hz), 1.67 (4 H, m), 1.35, (12 H, m), 0.9 (6 H, t, *J* = 6.74 Hz)

Anal calcd for $C_{28}H_{31}S_9Br$ : C 45.69, H 4.25; Found C 45.75, H 4.37.

## *trans*-5,6-Bis(2-thenoyl)-5,6-dihydro-1,4-dithiino[2,3-*d*]-1,3-dithiole-2-thione (122)

A mixture of **(120)** (1.0 g, 4.0 mmol), **(121)** (860 mg, 2.2 mmol) and toluene (100 ml) was stirred at 90 - 100 °C for 20 - 30 min. The product was purified from the hot toluene solution by column chromatography (silica, toluene). The volume of eluate from the second fraction was reduced in vacuo to 30 - 40 ml, and left to crystallize affording **(122)** as red-brown crystals (960 mg, 53%): mp 174 -179 °C (with fast decomposition at 182 °C). The remainder of **(120)** together with some amount of the product was eluted from the column with toluene:ethyl acetate (10:1 v/v) and was used in an analogous synthesis affording additionally 360 mg (20%) of **(122)** (overall yield 73%).

$^1$H NMR ($CDCl_3$, 50 °C) δ 7.92 (2 H, dd, $J = 4.6$ and 0.8 Hz), 7.75 (2 H, dd, $J = 3.8$ and 0.8 Hz), 7.21 (2 H, dd, $J = 4.6$ and 3.8 Hz), 5.51 (2 H, s)

$\nu_{max}$ / cm$^{-1}$ (KBr) 1641 (C=O)

m/z (EI) 444 ($M^+$, 100)

Anal calcd for $C_{13}H_8O_2S_7$: C, 40.5; H, 1.8. Found: C, 40.8, H, 1.9.

# EXPERIMENTAL FOR CHAPTER 4

## 2,5-Bis(2-thienyl)-3,4-bis(methylsulfanyl)thiophene (124)

To a solution of **(129)** (200 mg, 0.48 mmol) in dry tetrahydrofuran (50 ml) at 0 °C under dry nitrogen was added tetrabutylammonium hydroxide (1M solution in methanol, 1.05 ml, 1.05 mmol). The reaction was allowed to stir at this temperature for 1 h at which time iodomethane was added (0.065 ml, 1.05 mmol). The reaction was allowed to warm to room temperature and was stirred for a further 3 h. Water was added (100 ml) and the product was extracted into ethyl acetate (3 x 75 ml). The combined organic extracts were washed with water (2 x 100 ml) and dried ($MgSO_4$). The product was isolated by column chromatography (silica, dichloromethane) to afford **(124)** as a green/yellow solid (52%, 85 mg, 0.25 mmol).

mp 42-44 °C

$^1$H NMR ($CDCl_3$) δ 7.46 (2 h, dd, *J* = 1.33 and 4.29 Hz), 7.38 (2 H, dd, *J* = 1.10 and 5.13 Hz), 7.07 (2 H, m), 2.4 (6 H, s).

$\nu_{max}/cm^{-1}$ 1411, 1056, 835 and 686

HRMS (EI) calcd for $C_{14}H_{12}S_5$ 339.95425, found 339.95578

## 2,5-Bis-2-thienyl-3,4-bis(hexylsulfanyl)thiophene (125)

To a solution of **(100)** (120 mg, 0.36 mmol) in dry tetrahydrofuran (50 ml) under dry nitrogen at 0 °C was added potassium t-butoxide (80 mg, 0.78 mmol). The reaction was allowed to stir at this temperature for approximately 1 h, and 1-bromohexane was added (0.11 ml, 0.78 mmol). The reaction was allowed to warm to room temperature and was stirred for a further 3 h. Water was added (100 ml) and the product was extracted into ethyl acetate (3 x 75 ml). The combined organic extracts were washed with water (2 x 100 ml) and dried ($MgSO_4$). The product was isolated by column chromatography (silica, dichloromethane) to afford **(125)** as a dark orange oil (53%, 90 mg, 0.19 mmol).

$^1$H NMR ($CDCl_3$) δ 7.45 (2 H, d, *J* = 3.95 Hz), 7.39 (2 H, d, *J* = 4.87 Hz), 7.07 (2 H, m), 2.9 (4 H, t, *J* = 7.25 Hz), 1.6 (4 H, m), 1.3 (12 H, m), 0.9 (6 H, t, *J* = 6.59 Hz)

HRMS (EI) calcd for $C_{24}H_{32}S_5$ 480.11075, found 480.11060.

### 2,5-Bis(2-thienyl)-3,4-(ethylenedisulfanyl)thiophene (126)

To a solution of **(129)** (250 mg, 0.60 mmol) in dry tetrahydrofuran (30 ml) under dry nitrogen at 0 °C was added tetrabutyl ammonium hydroxide (1.31 mmol, 1.31 ml, 1.0 M solution in methanol). The mixture was stirred at 0 °C for 1 h, and 1,2-dibromoethane was added (0.057 ml, 0.66 mmol). The reaction was stirred for 2 h whilst warming to room temperature and poured into water (100 ml) before extracting the product into ethyl acetate (3 x 50 ml). The combined organic extracts were washed with water (3 x 50 ml) and dried ($MgSO_4$). The solvent was removed under reduced pressure and the product was isolated by column chromatography (silica, dichloromethane), to afford **(126)** as a pale yellow solid (59%, 120 mg, 0.35 mmol). Crystals of the product were grown by slow evaporation of a solution of **(126)** in dichloromethane.

mp 140-142 °C

$^1$H NMR ($CDCl_3$) $\delta$ 7.35 (2 H, d, $J$ = 1.15 Hz), 7.32 (2 H, d, $J$ = 1.56 Hz), 7.09 (2 H, t, $J$ = 1.36 Hz), 3.28 (4 H, s).

HRMS (EI) calcd for $C_{14}H_{10}S_5$ 337.93860, found 337.93731

Anal. calcd for $C_{14}H_{10}S_5$: C, 49.67; H, 2.98. Found: C, 49.85:H, 3.03

### 2,5-Bis(2-thienyl)-3,4-bis(2-cyanoethylsulfanyl)-thiophene (129)

A solution of compound **(100)** (0.75 g, 2.22 mmol) in dry tetrahydrofuran (30 ml) under dry nitrogen was cooled to 0 °C. Potassium *t*-butoxide (0.58 g 4.87 mmol) was added and the mixture was allowed to stir at 0 °C for 1 h. 3-Bromopropionitrile (0.41 ml, 4.87 mmol) was added and this was allowed to stir under dry nitrogen for approximately 2 h whilst warming to room temperature. The reaction was poured into water (50 ml) and the product was extracted into ethyl acetate (3 x 50 ml). The combined organic extracts were washed with water (2 x 100 ml) and dried ($MgSO_4$). The solvent was removed under reduced pressure and the product was isolated by column chromatography (silica, dichloromethane), to afford **(129)** as a dark orange solid (70%, 0.65 g, 1.55 mmol).

mp 132-134 °C

$\nu_{max}$/cm$^{-1}$ 2219, 1473, 1409, 1052, 840, 821, 728 and 709

$^1$H NMR (CDCl$_3$) δ 7.49 (2 H, dd, *J* = 0.97 and 3.62 Hz), 7.43 (2 H, dd, *J* = 0.94 and 5.15 Hz), 7.11 (2 H, m) 3.12 (4 H, t, *J* = 7.31 Hz), 2.58 (4 H, t, *J* = 7.35 Hz)

HRMS (EI) calcd for $C_{18}H_{14}S_5N_2$ 417.97604, found 417.97845.

## GENERAL PROCEDURE FOR POLYMERISATION OF MONOMERS

To a suspension of anhydrous $FeCl_3$ in dry dichloromethane was added a solution of the desired monomer in dichloromethane, dropwise over 1h. The mixture was allowed to stir under dry nitrogen for approximately 24 h, at which time the solution was filtered. The resulting solid residues were washed with methanol and dried under vacuum for 6 h. The product was extracted by soxhlet extraction with varying organic solvents (acetone, dichloromethane, toluene) and the extracts were treated with hydrazine upon cooling for 12 h. The volume of solvent was reduced in vacuo and water was added. The solid product formed was filtered under reduced pressure and dried to afford the neutral polymer.

# EXPERIMENTAL FOR CHAPTER 5

## Thieno[3′,4′-*d*:5,6][1,4]dithiino[2,3-*b*]quinoxaline (130)

To a stirred solution of **(78)** (1.5 g, 8.62 mmol) in ethanol (50 ml) at 0 °C was added NaOEt (2 equivalents from a freshly prepared 1.5 – 2.0 M ethanolic solution), and the mixture was stirred at this temperature for 45 min. Diethyl ether was added (200 ml) and the resulting precipitate was filtered under $N_2$ using a sintered Schlenk tube. The solid was washed with diethyl ether (100 ml), dissolved into THF (50 ml) and 2,3-dicloroquinoxaline was added (1.75 g, 8.79 mmol). The reaction was allowed to stir for 16 h, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica, ethyl acetate/petroleum ether [5:1 v/v]) and the product was recrystallised from dichloromethane/ethanol to afford a pale yellow crystalline solid (40%, 0.95 g)

mp 160 - 162 °C

# CHAPTER 7

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# APPENDIX 1

## Crystal Data for Compound (98)

University of Southampton · Department of Chemistry

## EPSRC National Crystallography Service

**Table 1.** Crystal data and structure refinement.

| | | |
|---|---|---|
| Identification code | **00src025** | |
| Empirical formula | $C_{20}H_{26}Br_2S_7$ | |
| Formula weight | 650.65 | |
| Temperature | 150(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | *P*–1 | |
| Unit cell dimensions | $a = 7.7910(16)$ Å | $\alpha = 96.69(3)°$ |
| | $b = 11.819(2)$ Å | $\beta = 98.74(3)°$ |
| | $c = 15.064(3)$ Å | $\gamma = 104.21(3)°$ |
| Volume | 1311.9(5) $Å^3$ | |
| *Z* | 2 | |
| Density (calculated) | 1.647 Mg / $m^3$ | |
| Absorption coefficient | 3.654 $mm^{-1}$ | |
| *F(000)* | 656 | |
| Crystal | Needle; orange | |
| Crystal size | $0.55 \times 0.075 \times 0.025$ $mm^3$ | |
| $\theta$ range for data collection | 2.09 – 27.44° | |
| Index ranges | $-10 \le h \le 8, -15 \le k \le 15, -19 \le l \le 19$ | |
| Reflections collected | 14353 | |
| Independent reflections | 5919 [$R_{int} = 0.0720$] | |
| Completeness to $\theta = 27.44°$ | 98.7 % | |
| Absorption correction | Semi–empirical from equivalents | |
| Max. and min. transmission | 0.939 and 0.755 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 5919 / 0 / 275 | |
| Goodness-of-fit on $F^2$ | 0.860 | |
| Final *R* indices [$F^2 > 2\sigma(F^2)$] | $R1 = 0.0430$, $wR2 = 0.1149$ | |
| *R* indices (all data) | $R1 = 0.0595$, $wR2 = 0.1308$ | |
| Extinction coefficient | 0.0112(12) | |
| Largest diff. peak and hole | 1.024 and –0.880 e $Å^{-3}$ | |

**Diffractometer:** *Enraf Nonius KappaCCD* area detector ($\phi$ scans and $\omega$ scans to fill *Ewald* sphere). **Data collection and cell refinement:** *Denzo* (Z. Otwinowski & W. Minor, *Methods in Enzymology* (1997) Vol. **276**: *Macromolecular Crystallography*, part A, pp. 307–326; C. W. Carter, Jr. & R. M. Sweet, Eds., Academic Press). **Absorption correction:** *SORTAV* (R. H. Blessing, Acta Cryst. A**51** (1995) 33–37; R. H. Blessing, J. Appl. Cryst. **30** (1997) 421–426). **Program used to solve structure:** *SHELXS97* (G. M. Sheldrick, Acta Cryst. (1990) A**46** 467–473). **Program used to refine structure:** *SHELXL97* (G. M. Sheldrick (1997), University of Göttingen, Germany).

**Further information:** http://www.soton.ac.uk/~xservice/strat.htm

**Special details:**

**Table 2.** Atomic coordinates [× $10^4$], equivalent isotropic displacement parameters [$Å^2 \times 10^3$] and site occupancy factors. $U_{eq}$ is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| Atom | *x* | *y* | *z* | $U_{eq}$ | *S.o.f.* |
|---|---|---|---|---|---|
| Br1 | 659(1) | 8689(1) | 4934(1) | 29(1) | 1 |
| Br2 | −1843(1) | 4370(1) | 1985(1) | 42(1) | 1 |
| S1 | −202(1) | 6897(1) | 3123(1) | 27(1) | 1 |
| S2 | −1878(1) | 6052(1) | 5606(1) | 26(1) | 1 |
| S3 | −3110(1) | 3903(1) | 4145(1) | 27(1) | 1 |
| S4 | −3756(1) | 4490(1) | 6992(1) | 27(1) | 1 |
| S5 | −4945(1) | 2389(1) | 5555(1) | 26(1) | 1 |
| S6 | −5373(1) | 3192(1) | 8388(1) | 31(1) | 1 |
| S7 | −6671(1) | 792(1) | 6755(1) | 30(1) | 1 |
| C1 | −367(4) | 7195(3) | 4248(2) | 23(1) | 1 |
| C2 | −1390(4) | 5440(3) | 3054(2) | 25(1) | 1 |
| C3 | −1884(4) | 5206(3) | 3855(2) | 23(1) | 1 |
| C4 | −1301(4) | 6223(3) | 4546(2) | 22(1) | 1 |
| C5 | −2996(4) | 4532(3) | 5283(2) | 23(1) | 1 |
| C6 | −3753(4) | 3889(3) | 5869(2) | 23(1) | 1 |
| C7 | −4842(4) | 3141(3) | 7301(2) | 24(1) | 1 |
| C8 | −5368(4) | 2188(3) | 6648(2) | 24(1) | 1 |
| C9 | −3146(5) | 3707(3) | 9107(3) | 33(1) | 1 |
| C10 | −2055(4) | 2804(3) | 9094(3) | 31(1) | 1 |
| C11 | −244(5) | 3239(3) | 9736(3) | 36(1) | 1 |
| C12 | 854(5) | 2344(4) | 9738(3) | 39(1) | 1 |
| C13 | 2615(5) | 2747(5) | 10414(3) | 52(1) | 1 |
| C14 | 3820(40) | 1980(30) | 10510(20) | 51(6) | 0.50 |
| C14 | 3540(40) | 1700(30) | 10340(20) | 54(6) | 0.50 |
| C15 | −5193(5) | −153(3) | 6525(3) | 32(1) | 1 |
| C16 | −3492(4) | 109(3) | 7228(3) | 31(1) | 1 |
| C17 | −2423(5) | −792(3) | 7080(3) | 35(1) | 1 |
| C18 | −692(5) | −512(3) | 7783(3) | 36(1) | 1 |
| C19 | 391(5) | −1414(4) | 7681(3) | 45(1) | 1 |
| C20 | 2094(5) | −1104(4) | 8413(4) | 54(1) | 1 |

Table 3. Bond lengths [Å] and angles [°].

| | |
|---|---|
| Br1–C1 | 1.859(3) |
| Br2–C2 | 1.857(3) |
| S1–C1 | 1.720(3) |
| S1–C2 | 1.727(3) |
| S2–C4 | 1.744(3) |
| S2–C5 | 1.767(3) |
| S3–C3 | 1.743(3) |
| S3–C5 | 1.768(4) |
| S4–C6 | 1.758(4) |
| S4–C7 | 1.763(3) |
| S5–C6 | 1.758(3) |
| S5–C8 | 1.759(3) |
| S6–C7 | 1.746(3) |
| S6–C9 | 1.819(4) |
| S7–C8 | 1.752(3) |
| S7–C15 | 1.832(3) |
| C1–C4 | 1.365(4) |
| C2–C3 | 1.359(5) |
| C3–C4 | 1.425(5) |
| C5–C6 | 1.341(5) |
| C7–C8 | 1.340(5) |
| C9–C10 | 1.520(5) |
| C10–C11 | 1.517(5) |
| C11–C12 | 1.515(5) |
| C12–C13 | 1.513(5) |
| C13–C14 | 1.46(4) |
| C13–C14 | 1.59(4) |
| C15–C16 | 1.507(5) |
| C16–C17 | 1.520(5) |
| C17–C18 | 1.522(5) |
| C18–C19 | 1.521(5) |
| C19–C20 | 1.528(6) |

| | |
|---|---|
| C1–S1–C2 | 91.14(16) |
| C4–S2–C5 | 94.43(16) |
| C3–S3–C5 | 94.47(15) |
| C6–S4–C7 | 95.50(16) |
| C6–S5–C8 | 95.32(16) |
| C7–S6–C9 | 101.62(16) |
| C8–S7–C15 | 102.24(15) |
| C4–C1–S1 | 112.1(2) |
| C4–C1–Br1 | 126.3(3) |
| S1–C1–Br1 | 121.69(17) |
| C3–C2–S1 | 112.1(3) |
| C3–C2–Br2 | 126.6(2) |
| S1–C2–Br2 | 121.33(19) |
| C2–C3–C4 | 112.3(3) |
| C2–C3–S3 | 130.6(3) |
| C4–C3–S3 | 117.1(2) |
| C1–C4–C3 | 112.4(3) |
| C1–C4–S2 | 130.5(3) |
| C3–C4–S2 | 117.1(2) |
| C6–C5–S2 | 121.6(3) |
| C6–C5–S3 | 121.5(3) |
| S2–C5–S3 | 116.89(17) |
| C5–C6–S5 | 122.6(3) |
| C5–C6–S4 | 123.1(3) |
| S5–C6–S4 | 114.24(18) |
| C8–C7–S6 | 125.4(3) |

| | |
|---|---|
| C8–C7–S4 | 116.9(3) |
| S6–C7–S4 | 117.2(2) |
| C7–C8–S7 | 125.4(3) |
| C7–C8–S5 | 117.6(2) |
| S7–C8–S5 | 116.7(2) |
| C10–C9–S6 | 114.2(3) |
| C11–C10–C9 | 112.8(3) |
| C12–C11–C10 | 113.5(3) |
| C13–C12–C11 | 113.7(4) |
| C14–C13–C12 | 120.6(10) |
| C14–C13–C14 | 14.1(17) |
| C12–C13–C14 | 106.4(10) |
| C16–C15–S7 | 114.0(3) |
| C15–C16–C17 | 112.3(3) |
| C16–C17–C18 | 112.1(3) |
| C19–C18–C17 | 113.9(3) |
| C18–C19–C20 | 111.8(4) |

Symmetry transformations used to generate equivalent atoms:

**Table 4.** Anisotropic displacement parameters [$Å^2 \times 10^3$]. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + \cdots + 2\,h\,k\,a^*\,b^*\,U^{12}]$.

| Atom | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Br1 | 30(1) | 19(1) | 37(1) | 3(1) | 6(1) | 4(1) |
| Br2 | 60(1) | 37(1) | 27(1) | −2(1) | 13(1) | 11(1) |
| S1 | 30(1) | 26(1) | 29(1) | 8(1) | 12(1) | 7(1) |
| S2 | 31(1) | 21(1) | 24(1) | 2(1) | 8(1) | 3(1) |
| S3 | 33(1) | 21(1) | 25(1) | 3(1) | 8(1) | 2(1) |
| S4 | 31(1) | 23(1) | 26(1) | 4(1) | 8(1) | 6(1) |
| S5 | 31(1) | 21(1) | 27(1) | 5(1) | 9(1) | 4(1) |
| S6 | 27(1) | 44(1) | 26(1) | 9(1) | 10(1) | 10(1) |
| S7 | 24(1) | 27(1) | 40(1) | 13(1) | 8(1) | 4(1) |
| C1 | 21(1) | 20(2) | 28(2) | 7(1) | 6(1) | 7(1) |
| C2 | 25(2) | 22(2) | 29(2) | 4(1) | 10(1) | 6(1) |
| C3 | 20(1) | 22(2) | 27(2) | 2(1) | 5(1) | 5(1) |
| C4 | 24(1) | 20(2) | 25(2) | 5(1) | 6(1) | 7(1) |
| C5 | 22(1) | 22(2) | 26(2) | 7(1) | 5(1) | 7(1) |
| C6 | 21(1) | 22(2) | 28(2) | 6(1) | 6(1) | 8(1) |
| C7 | 20(1) | 29(2) | 26(2) | 10(1) | 6(1) | 7(1) |
| C8 | 20(1) | 25(2) | 29(2) | 11(1) | 8(1) | 7(1) |
| C9 | 34(2) | 39(2) | 27(2) | 6(2) | 6(1) | 11(2) |
| C10 | 29(2) | 33(2) | 29(2) | 0(2) | 6(1) | 7(1) |
| C11 | 32(2) | 45(2) | 29(2) | 5(2) | 6(2) | 9(2) |
| C12 | 33(2) | 51(2) | 34(2) | 12(2) | 10(2) | 11(2) |
| C13 | 42(2) | 85(3) | 34(2) | 14(2) | 4(2) | 25(2) |
| C14 | 21(6) | 60(12) | 64(13) | 11(8) | −12(6) | 8(7) |
| C14 | 38(11) | 82(17) | 49(11) | 29(12) | 9(9) | 16(9) |
| C15 | 35(2) | 24(2) | 38(2) | 5(2) | 6(2) | 9(1) |
| C16 | 33(2) | 27(2) | 35(2) | 7(2) | 8(2) | 7(1) |
| C17 | 36(2) | 28(2) | 41(2) | 5(2) | 5(2) | 11(1) |
| C18 | 35(2) | 38(2) | 39(2) | 12(2) | 11(2) | 12(2) |
| C19 | 38(2) | 40(2) | 63(3) | 21(2) | 13(2) | 16(2) |
| C20 | 41(2) | 60(3) | 68(3) | 34(3) | 8(2) | 18(2) |

**Table 5.** Hydrogen coordinates [$\times 10^4$] and isotropic displacement parameters [$Å^2 \times 10^3$].

| Atom | *x* | *y* | *z* | $U_{eq}$ | *S.o.f.* |
|---|---|---|---|---|---|
| H9A | −2479 | 4411 | 8911 | 40 | 1 |
| H9B | −3281 | 3929 | 9728 | 40 | 1 |
| H10A | −2741 | 2085 | 9263 | 37 | 1 |
| H10B | −1860 | 2613 | 8480 | 37 | 1 |
| H11A | 444 | 3955 | 9563 | 43 | 1 |
| H11B | −442 | 3440 | 10348 | 43 | 1 |
| H12A | 139 | 1613 | 9877 | 47 | 1 |
| H12B | 1108 | 2177 | 9133 | 47 | 1 |
| H13A | 3299 | 3479 | 10263 | 62 | 1 |
| H13B | 2327 | 2941 | 11008 | 62 | 1 |
| H14A | 3155 | 1219 | 10610 | 76 | 0.50 |
| H14B | 4780 | 2325 | 11023 | 76 | 0.50 |
| H14C | 4309 | 1889 | 9970 | 76 | 0.50 |
| H14D | 4710 | 1934 | 10723 | 82 | 0.50 |
| H14E | 3672 | 1501 | 9717 | 82 | 0.50 |
| H14F | 2810 | 1017 | 10518 | 82 | 0.50 |
| H15A | −5857 | −972 | 6491 | 39 | 1 |
| H15B | −4869 | −60 | 5936 | 39 | 1 |
| H16A | −3801 | 114 | 7828 | 37 | 1 |
| H16B | −2744 | 890 | 7207 | 37 | 1 |
| H17A | −2129 | −806 | 6477 | 42 | 1 |
| H17B | −3163 | −1571 | 7111 | 42 | 1 |
| H18A | 56 | 259 | 7737 | 43 | 1 |
| H18B | −992 | −467 | 8386 | 43 | 1 |
| H19A | 723 | −1449 | 7085 | 53 | 1 |
| H19B | −353 | −2189 | 7720 | 53 | 1 |
| H20A | 2832 | −337 | 8377 | 81 | 1 |
| H20B | 2754 | −1682 | 8319 | 81 | 1 |
| H20C | 1767 | −1100 | 9002 | 81 | 1 |

# APPENDIX 2

## Crystal Data for Compound (122)

ble 1. Crystal data and structure refinement for 1.

| | |
|---|---|
| entification code | 98src182 |
| pirical formula | C15 H8 O2 S7 |
| rmula weight | 444.63 |
| mperature | 293(2) K |
| velength | 0.71069 A |
| ystal system | Monoclinic |
| ace group | P2(1)/n |
| it cell dimensions | a = 8.773(2) A<br>b = 20.104(4) A<br>c = 10.983(2) A<br>beta = 111.08(3) deg. |
| lume | 1807.5(6) A^3 |
| | 4 |
| nsity (calculated) | 1.634 Mg/m^3 |
| sorption coefficient | 0.878 mm^-1 |
| (000) | 904 |
| ystal size | 0.45 x 0.2 x 0.2 mm |
| eta range for data collection | 2.03 to 25.07 deg. |
| dex ranges | -8<=h<=9, -22<=k<=22, -12<=l<=11 |
| flections collected | 7039 |
| dependent reflections | 2657 [R(int) = 0.0620] |
| finement method | Full-matrix least-squares on F^2 |
| ta / restraints / parameters | 2656 / 0 / 217 |
| odness-of-fit on F^2 | 0.856 |
| nal R indices [I>2sigma(I)] | R1 = 0.0482, wR2 = 0.1037 |
| indices (all data) | R1 = 0.0802, wR2 = 0.1112 |
| rgest diff. peak and hole | 0.406 and -0.492 e.A^-3 |

Table 3. Bond lengths [A] and angles [deg] for 98src182.

| | | | |
|---|---|---|---|
| S(1)-C(1) | 1.653(7) | S(1)-C(4) | 1.706(5) |
| S(2)-C(13) | 1.749(5) | S(2)-C(7) | 1.865(4) |
| S(3)-C(14) | 1.725(5) | S(3)-C(6) | 1.879(4) |
| S(4)-C(12) | 1.672(5) | S(4)-C(9) | 1.701(5) |
| S(5)-C(14) | 1.733(4) | S(5)-C(15) | 1.735(5) |
| S(6)-C(13) | 1.726(5) | S(6)-C(15) | 1.726(5) |
| S(7)-C(15) | 1.633(5) | O(1)-C(5) | 1.224(5) |
| O(2)-C(8) | 1.214(5) | C(1)-C(2) | 1.361(9) |
| C(2)-C(3) | 1.418(8) | C(3)-C(4) | 1.398(7) |
| C(4)-C(5) | 1.451(7) | C(5)-C(6) | 1.514(6) |
| C(6)-C(7) | 1.515(6) | C(7)-C(8) | 1.518(6) |
| C(8)-C(9) | 1.468(6) | C(9)-C(10) | 1.440(6) |
| C(10)-C(11) | 1.409(6) | C(11)-C(12) | 1.336(7) |
| C(13)-C(14) | 1.355(6) | | |

| | | | |
|---|---|---|---|
| C(1)-S(1)-C(4) | 92.1(3) | C(13)-S(2)-C(7) | 97.8(2) |
| C(14)-S(3)-C(6) | 101.2(2) | C(12)-S(4)-C(9) | 91.5(3) |
| C(14)-S(5)-C(15) | 97.4(2) | C(13)-S(6)-C(15) | 97.4(2) |
| C(2)-C(1)-S(1) | 113.7(5) | C(1)-C(2)-C(3) | 112.4(7) |
| C(4)-C(3)-C(2) | 110.2(6) | C(3)-C(4)-C(5) | 129.6(5) |
| C(3)-C(4)-S(1) | 111.6(4) | C(5)-C(4)-S(1) | 118.8(4) |
| O(1)-C(5)-C(4) | 121.9(5) | O(1)-C(5)-C(6) | 120.8(4) |
| C(4)-C(5)-C(6) | 117.3(4) | C(7)-C(6)-C(5) | 113.6(4) |
| C(7)-C(6)-S(3) | 115.6(3) | C(5)-C(6)-S(3) | 101.5(3) |
| C(8)-C(7)-C(6) | 111.9(4) | C(8)-C(7)-S(2) | 104.9(3) |
| C(6)-C(7)-S(2) | 116.2(3) | O(2)-C(8)-C(9) | 122.2(4) |
| O(2)-C(8)-C(7) | 120.4(4) | C(9)-C(8)-C(7) | 117.5(4) |
| C(10)-C(9)-C(8) | 129.6(4) | C(10)-C(9)-S(4) | 112.5(3) |
| C(8)-C(9)-S(4) | 117.9(4) | C(11)-C(10)-C(9) | 107.2(4) |
| C(12)-C(11)-C(10) | 115.5(5) | C(11)-C(12)-S(4) | 113.2(4) |
| C(14)-C(13)-S(6) | 116.7(4) | C(14)-C(13)-S(2) | 120.3(4) |
| S(6)-C(13)-S(2) | 122.8(3) | C(13)-C(14)-S(3) | 122.8(4) |
| C(13)-C(14)-S(5) | 115.7(4) | S(3)-C(14)-S(5) | 121.3(3) |
| S(7)-C(15)-S(6) | 124.1(3) | S(7)-C(15)-S(5) | 123.2(3) |
| S(6)-C(15)-S(5) | 112.7(3) | | |

# APPENDIX 3

## Crystal Data for Compound (126)

**Table 1.** Crystal data and structure refinement.

| | |
|---|---|
| Identification code | **99SRC252** |
| Empirical formula | $C_{14}H_{10}S_5$ |
| Formula weight | 338.52 |
| Temperature | 150(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Orthorhombic |
| Space group | $Cmc2_1$ |
| Unit cell dimensions | $a$ = 20.6948(7) Å |
| | $b$ = 8.7890(3) Å |
| | $c$ = 7.7472(3) Å |
| Volume | 1409.11(9) Å3 |
| Z | 4 |
| Density (calculated) | 1.596 Mg / m3 |
| Absorption coefficient | 0.803 mm−1 |
| *F(000)* | 696 |
| Crystal | Yellow block |
| Crystal size | 0.22 x 0.18 x 0.10 mm3 |
| $\theta$ range for data collection | 3.64 – 25.01° |
| Index ranges | $-24 \le h \le 24, -10 \le k \le 10, -9 \le l \le 9$ |
| Reflections collected | 6285 |
| Independent reflections | 1246 [$R_{int}$ = 0.0276] |
| Completeness to $\theta$ = 25.01° | 99.6 % |
| Absorption correction | Empirical, SORTAV |
| Max. and min. transmission | 0.9843 and 0.9393 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 1246 / 1 / 98 |
| Goodness-of-fit on $F2$ | 1.047 |
| Final $R$ indices [$F2 > 2\sigma(F2)$] | $R1$ = 0.0224, $wR2$ = 0.0579 |
| $R$ indices (all data) | $R1$ = 0.0231, $wR2$ = 0.0583 |
| Absolute structure parameter | 0.03(9) |
| Extinction coefficient | 0.0033(10) |
| Largest diff. peak and hole | 0.237 and −0.182 e Å−3 |

**Diffractometer:** *Enraf Nonius KappaCCD* area detector ($\phi$ scans and $\omega$ scans to fill *Ewald* sphere). **Data collection and cell refinement:** *Denzo* (Z. Otwinowski & W. Minor, *Methods in Enzymology* (1997) Vol. **276**: *Macromolecular Crystallography*, part A, pp. 307–326; C. W. Carter, Jr. & R. M. Sweet, Eds., Academic Press). **Absorption correction:** *SORTAV* (R. H. Blessing, Acta Cryst. A51 (1995) 33–37; R. H. Blessing, J. Appl. Cryst. 30 (1997) 421–426). **Program used to solve structure:** *SHELXS97* (G. M. Sheldrick, Acta Cryst. (1990) A46 467–473). **Program used to refine structure:** *SHELXL97* (G. M. Sheldrick (1997), University of Göttingen, Germany).

**Further information:** http://www.soton.ac.uk/~xservice/strat.htm

**Special details:** The end of the 6 membered ring is disordered over two puckered conformations each with an occupancy of 50%.

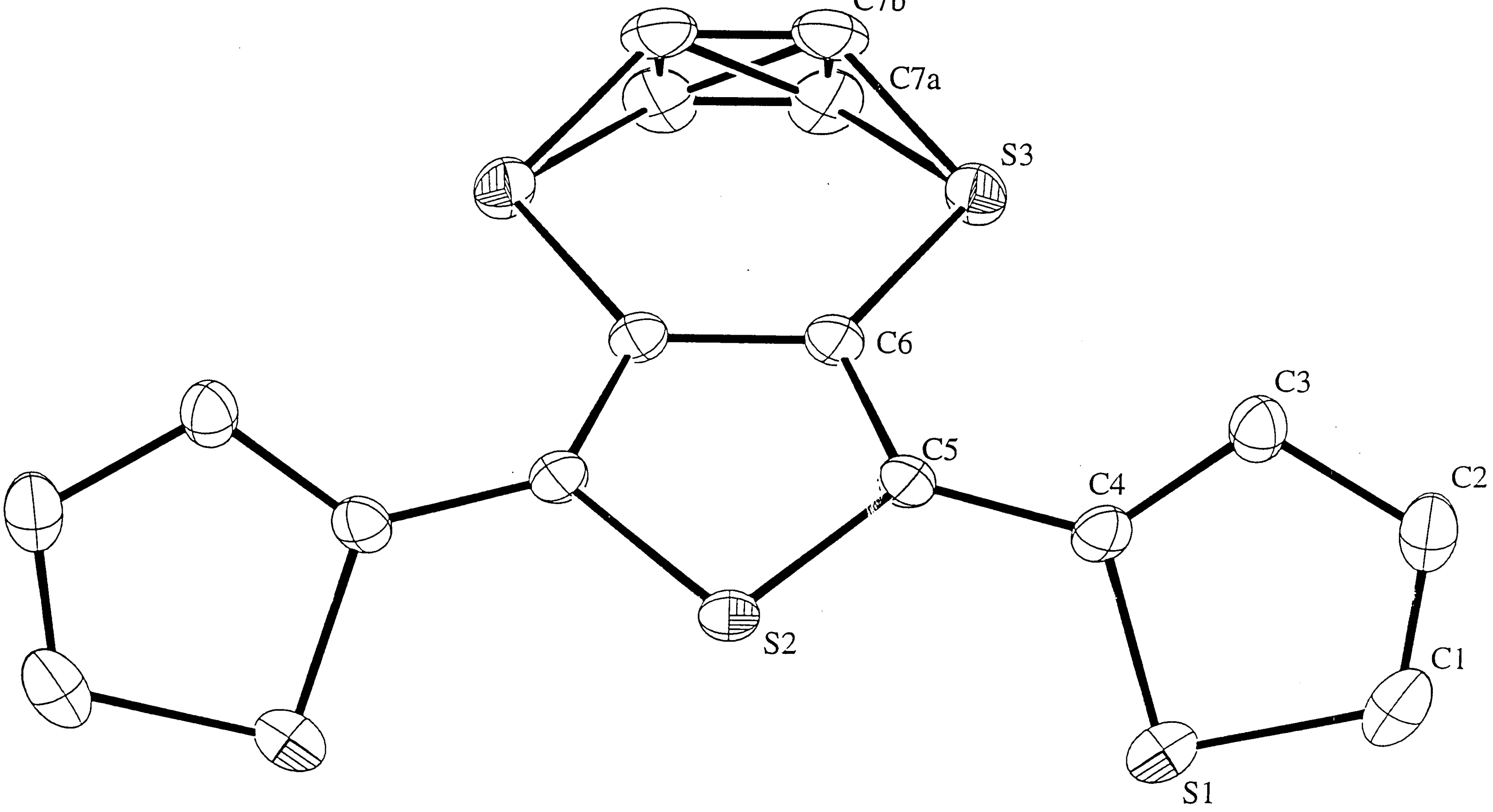
C7b
C7a
S3
C6
C3
C5
C4
C2
S2
C1
S1

Table 1. Torsion angles [°].

| | |
|---|---|
| C7B–S3–C6–C5 | −172.4(3) |
| C7A–S3–C6–C5 | 161.4(3) |
| C7B–S3–C6–C6$^{i}$ | 9.0(3) |
| C7A–S3–C6–C6$^{i}$ | −17.2(3) |
| C6$^{i}$–C6–C5–C4 | 179.4(2) |
| S3–C6–C5–C4 | 0.5(3) |
| C6$^{i}$–C6–C5–S2 | −0.88(18) |
| S3–C6–C5–S2 | −179.72(13) |
| C5$^{i}$–S2–C5–C6 | 1.2(2) |
| C5$^{i}$–S2–C5–C4 | −179.05(13) |
| C2–C3–C4–C5 | 177.46(19) |
| C2–C3–C4–S1 | 0.8(3) |
| C6–C5–C4–C3 | 43.0(4) |
| S2–C5–C4–C3 | −136.7(2) |
| C6–C5–C4–S1 | −140.6(2) |
| S2–C5–C4–S1 | 39.7(3) |
| C1–S1–C4–C3 | −0.14(19) |
| C1–S1–C4–C5 | −177.09(18) |
| C4–S1–C1–C2 | −0.61(17) |
| S1–C1–C2–C3 | 1.2(2) |
| C4–C3–C2–C1 | −1.3(3) |
| C6–S3–C7A–C7B$^{i}$ | 51.5(4) |
| C7B–S3–C7A–C7B$^{i}$ | −46.3(6) |
| C6–S3–C7B–C7B$^{i}$ | −9.2(3) |
| C7A–S3–C7B–C7B$^{i}$ | 78.8(6) |

Symmetry transformations used to generate equivalent atoms:
(i) −x+2,y,z

**Table 2.** Atomic coordinates [× $10^4$], equivalent isotropic displacement parameters [$Å^2$ × $10^3$] and site occupancy factors. $U_{eq}$ is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| Atom | *x* | *y* | *z* | $U_{eq}$ | *S.o.f.* |
|---|---|---|---|---|---|
| S3 | 9148(1) | 9358(1) | 532(1) | 28(1) | 1 |
| S1 | 8492(1) | 14386(1) | −973(1) | 29(1) | 1 |
| S2 | 10000 | 13765(1) | 336(1) | 19(1) | 1 |
| C6 | 9655(1) | 10963(2) | 474(3) | 18(1) | 1 |
| C5 | 9398(1) | 12406(2) | 387(3) | 18(1) | 1 |
| C3 | 8212(1) | 12361(2) | 1316(3) | 24(1) | 1 |
| C4 | 8725(1) | 12895(2) | 341(3) | 19(1) | 1 |
| C1 | 7713(1) | 14299(2) | −234(3) | 30(1) | 1 |
| C2 | 7634(1) | 13181(2) | 941(3) | 28(1) | 1 |
| C7A | 9692(3) | 7883(6) | −83(11) | 31(1) | 0.50 |
| C7B | 9688(3) | 7824(7) | 934(10) | 28(1) | 0.50 |

**Table 3.** Bond lengths [Å] and angles [°].

| | | | |
|---|---|---|---|
| S3–C6 | 1.7586(18) | C6–C5 | 1.376(2) |
| S3–C7B | 1.778(6) | C6–C6$^i$ | 1.429(4) |
| S3–C7A | 1.782(6) | C5–C4 | 1.460(2) |
| S1–C1 | 1.712(2) | C3–C4 | 1.384(3) |
| S1–C4 | 1.727(2) | C3–C2 | 1.427(3) |
| S2–C5 | 1.7259(18) | C1–C2 | 1.350(3) |
| S2–C5$^i$ | 1.7259(17) | C7A–C7B$^i$ | 1.507(5) |
| | | | |
| C6–S3–C7B | 103.77(19) | C4–C5–S2 | 118.98(13) |
| C6–S3–C7A | 101.55(19) | C4–C3–C2 | 111.1(2) |
| C1–S1–C4 | 91.81(10) | C3–C4–C5 | 128.2(2) |
| C5–S2–C5$^i$ | 92.33(12) | C3–C4–S1 | 111.45(14) |
| C5–C6–C6$^i$ | 112.68(10) | C5–C4–S1 | 120.26(15) |
| C5–C6–S3 | 120.70(14) | C2–C1–S1 | 111.87(16) |
| C6$^i$–C6–S3 | 126.61(6) | C1–C2–C3 | 113.8(2) |
| C6–C5–C4 | 129.87(16) | C7B$^i$–C7A–S3 | 115.0(4) |
| C6–C5–S2 | 111.15(13) | | |

Symmetry transformations used to generate equivalent atoms:
(i) −x+2,y,z

**Table 4.** Anisotropic displacement parameters [Å$^2$× 10$^3$]. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + \cdots + 2\,h\,k\,a^*\,b^*\,U^{12}]$.

| Atom | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| S3 | 23(1) | 14(1) | 46(1) | 0(1) | 0(1) | −4(1) |
| S1 | 28(1) | 24(1) | 34(1) | 5(1) | −2(1) | 6(1) |
| S2 | 20(1) | 11(1) | 27(1) | 0(1) | 0 | 0 |
| C6 | 20(1) | 14(1) | 19(1) | −1(1) | 0(1) | −2(1) |
| C5 | 18(1) | 15(1) | 22(1) | 0(1) | −1(1) | −3(1) |
| C3 | 17(1) | 18(1) | 37(1) | −3(1) | −1(1) | −1(1) |
| C4 | 20(1) | 14(1) | 24(1) | −2(1) | −2(1) | 2(1) |
| C1 | 25(1) | 28(1) | 37(1) | −7(1) | −7(1) | 9(1) |
| C2 | 17(1) | 26(1) | 41(1) | −8(1) | 0(1) | 1(1) |
| C7A | 35(3) | 10(2) | 48(4) | −5(3) | −8(3) | −2(2) |
| C7B | 36(3) | 17(3) | 31(3) | 6(3) | 5(3) | −1(2) |

**Table 5.** Hydrogen coordinates [× 10$^4$] and isotropic displacement parameters [Å$^2$ × 10$^3$].

| Atom | *x* | *y* | *z* | $U_{eq}$ | *S.o.f.* |
|---|---|---|---|---|---|
| H3 | 8241 | 11571 | 2111 | 29 | 1 |
| H1 | 7384 | 14945 | −598 | 36 | 1 |
| H2 | 7239 | 12965 | 1458 | 33 | 1 |
| H7A1 | 9473 | 6913 | 40 | 37 | 0.50 |
| H7A2 | 9798 | 8009 | −1294 | 37 | 0.50 |
| H7B1 | 9566 | 7438 | 2061 | 34 | 0.50 |
| H7B2 | 9566 | 7041 | 114 | 34 | 0.50 |

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# Novel Terthiophene and Bis(thienyl)furan Derivatives as Precursors to Highly Electroactive Polymers

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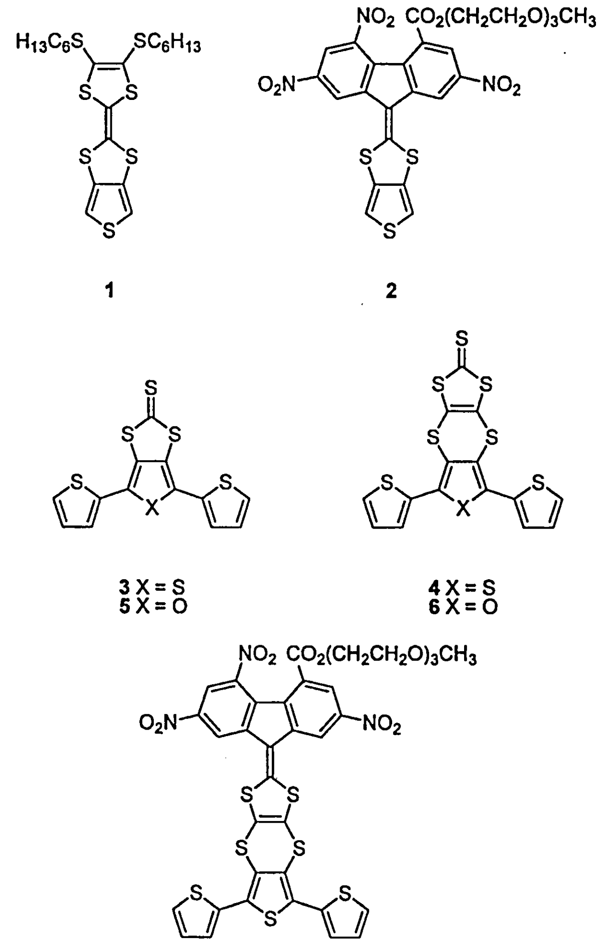
The syntheses of a series of 1,3-dithiole-2-thione derivatives (**3**−**6**), bearing fused terthiophene or bis(2-thienyl)-2,5-furan units, are reported. These novel heterocycles are readily polymerized electrochemically to give stable electroactive materials. The target compounds were obtained in moderate to high yield via the cyclization of the corresponding diketones or hydroxyketones, using phosphorus pentasulfide or acidic conditions. The ketones **12** and **17** were prepared directly from their hydroxy precursors by treatment with $MnO_2$. The trans configuration of diketone **20** was confirmed by X-ray crystallography.

## Introduction

The role of terthiophene systems in materials chemistry is 2-fold. First, unsubstituted 2,5 -derivatives can be used as efficient trimers for oxidative polymerization reactions. The corresponding poly(thiophene)s represent a major group in the highly topical field of conjugated polymers.[1] Due to the highly electroactive nature of poly(thiophene) and its derivatives, these materials can been used in applications such as batteries,[2] chemical[3] and biological[4] sensors, and light-emitting diodes.[5] Second, terthiophenes are useful synthetic precursors to sexithiophenes, which are materials currently being investigated as components in field-effect transistors.[6]

Recently, we have been investigating the syntheses of thiophene monomers bearing strongly redox-active subtituents, viz. the electron-donating tetrathiafulvalene in **1**[7] and the electron-accepting fluorene unit in **2** (Chart l).[8] Both species represent highly redox-active systems ith the potential of exhibiting unusual electronic proprties in conjunction with the conducting polymer.[9] Due o unfavorable electronic interactions, together with dditional steric reasons in **2**, we have been unable to polymerize these monomers. Subsequently, we have developed the syntheses of terthiophenes **3** and **4**, which are functionalized by a 1,3-dithiole-2-thione moiety; synthetically, this unit is extremely versatile and is a

### Chart 1



**1**

**2**

**3** X = S
**5** X = O

**4** X = S
**6** X = O

**7**

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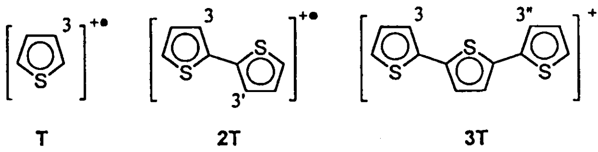
Chart 2



well-known precursor to tetrathiafulvalene systems.[10] The extended chains in terthiophenes **3** and **4** reduce the adversity of steric hindrance from substituents on the central ring, while in **4**, the cation radical intermediate obtained by oxidation will be affected less by the electronic behavior of the 1,3-dithiole unit, due to the fused 1,4-dithiino spacer group. Using this approach, we have succeeded in the preparation and electrochemical polymerization of fluorene derivative **7**, which has been the subject of a preliminary communication.[11]

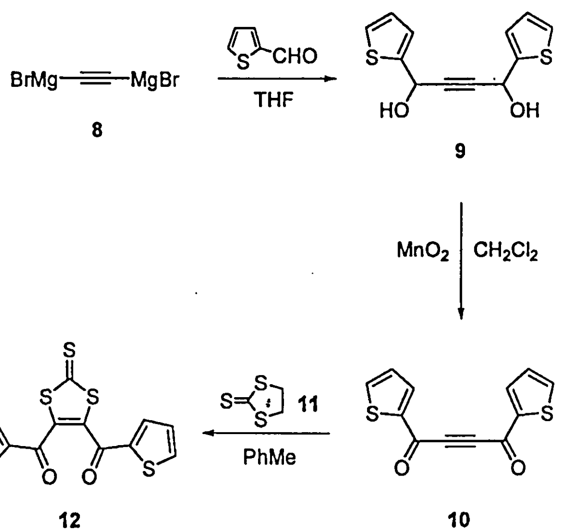
The synthesis and properties of mixed heterocyclopentadiene co-oligomers[12] and copolymers[13] are also of interest; in the latter case, theoretical studies have shown that the incorporation of mixed repeating units of different band gaps lowers the overall band gap ($E_g$) of the polymer.[14] This type of methodology can be used for tuning the value of $E_g$, which is an important criterion in the application of light-emitting devices.

According to Smith et al.,[15] density functional theory calculations (also supported by experimental ESR measurements in some cases) show that differences in the spin densities between the 2(5) and 3(4) positions in radical cations of thiophene (T), bithiophene (2T), and terthiophene (3T) decrease in the order T > 2T > 3T (Chart 2). Thus, for thiophene, $\rho_\pi(2,5) = 0.456$(DFT), 0.492 (ESR), $\rho_\pi(3,4) = 0.098$ (DFT), 0.095 (ESR); for terthiophene, $\rho_\pi(5) = 0.151$ (DFT), 0.127 (ESR); $\rho_\pi(3) =$ 0.075 (DFT), 0.077 (ESR). Consequently, there is a greater chance of α–α -coupling between bithiophene and terthiophene systems; this type of "imperfection" within poly(thiophene)s is detrimental to the conjugation in the polymer chain and results in a decrease in conductivity (compared to the corresponding polymer derived from exclusive α–α -coupling).[9] On the other hand, steric actors have not been taken into consideration and should be significant if, for example, the central ring in terthiophene is substituted at the 3 and 4 positions. Thus, compounds **3**–**6** are well-suited for the synthesis of ubstituted poly(terthiophene) and poly[bis(thienyl)furan] ystems with a good control of regiospecificity. Herein, 'e discuss the detailed syntheses and electrochemistry f **3** and **4**, together with the dithienyl furan analogues and **6**.

## Results and Discussion

**Synthesis.** The terthiophenes **3** and **4** were obtained n 70% and 57% yields, respectively, by heating the corresponding diketones **12** and **20** with phosphorus pentasulfide and sodium bicarbonate[16] in dioxane. The reaction proved to be suitable for the cyclization of saturated as well as unsaturated diketones, as previously seen for 1,2-dibenzoylnaphthalene.[17]

Scheme 1



We have explored two synthetic pathways toward compound **12**. First, the diketone was obtained by the reaction of acetylene **10** with ethylene trithiocarbonate **11**[18] by analogy with the synthesis of dimethyl 1,3-dithiole-2-thione-4,5-dicarboxylate.[19] The starting dithienoyl acetylene **10** was isolated in 55% yield, by the oxidation of the corresponding diol **9**, which was in turn obtained from the addition of acetylene dimagnesium bromide **8**[20] to 2-thiophenecarboxaldehyde (50% yield) (Scheme 1). The diol **9** was first reported as a byproduct in the synthesis of the monofunctionalized acetylene.[21] In the same work, several acetylenic monoketones were obtained by the oxidation of the corresponding monoalcohols with chromium trioxide; however, to the best of our knowledge, the synthesis of diketone **10** has not yet been described. Since, in the presence of acids employed in $CrO_3$ oxidations, one could expect **9** to undergo acid-catalyzed rearrangements (e.g. ring closure to the furan derivative), we chose manganese dioxide as the oxidizing agent which has been used for the synthesis of a number of acetylenic ketones of the thiophene series.[22] The yield of **10** was found to be essentially independent of the solvent choice (dichloromethane, diethyl ether, benzene), while the reaction efficiency increased with the quantity of manganese dioxide used (ca. 40% with $MnO_2$:diol = 6:1 w/w and 55% with 12:1). Dichloromethane was chosen for convenience, since it proved to be the best solvent for the subsequent purification of the product by column chromatography. The

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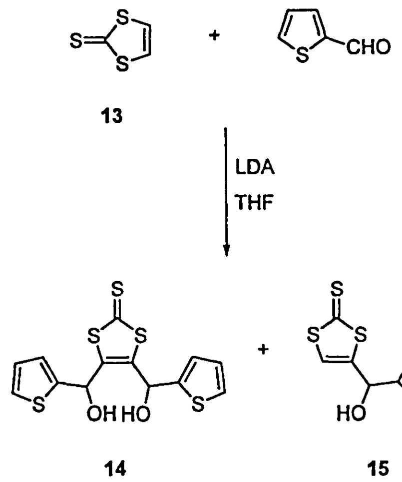
Scheme 2

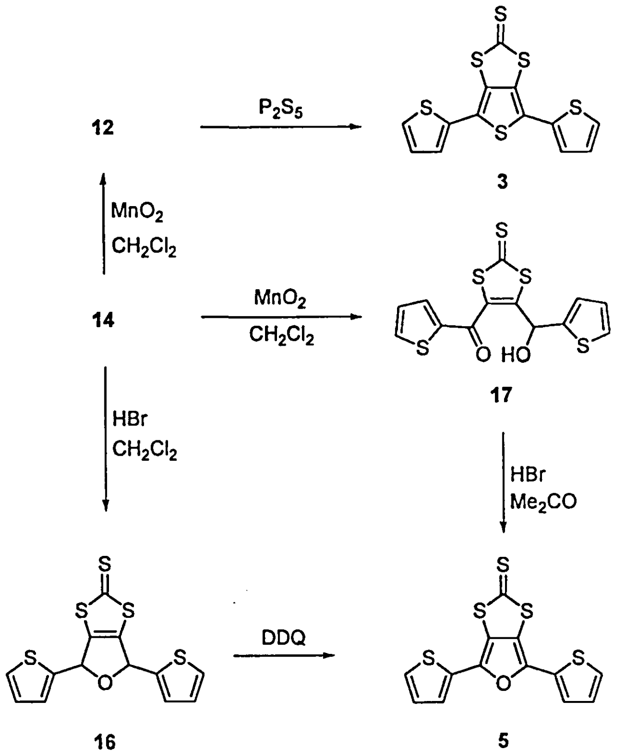


optimum reaction time for the oxidation process was very short (2 min), while prolonged treatment led to the decomposition of the product. Although diketone **10** was obtained in a satisfactory yield, its reaction with **11** gave a very low yield (8%) of the key intermediate **12**, which urged us to find an alternative synthetic strategy for the diketone **12**.

A much more efficient route to diketone **12** involved the oxidation of the diol **14**. Compound **14** was obtained in good yield (82%), via the lithiation of vinylenetrithiocarbonate[23] **13** and subsequent trapping of the carbanion species with thiophenecarboxaldehyde (Scheme 2). The reaction necessitated a stepwise process, such that 1 equiv of reagents was allowed to react with **13**, before the second equivalent was added. This exact procedure was necessary, since our attempts to obtain the dilithio derivative of **13**, in one step under mild conditions (THF, −60 °C), led to the predominant formation of the monofunctionalized product **15**, even in the presence of a large excess of LDA. The use of a less polar solvent (e.g. toluene and petroleum ether), which is known to favor the formation of dilithiothiophenes,[24] did not lead to an increase in the yield of **14**, while the use of *n*-BuLi or raising the reaction temperature (−30 °C) led to the decomposition of the starting material.

The diastereomers of **14** were separated easily by column chromatography, fraction **14a** having a higher $R_f$ value than **14b**. Whereas the NMR signal (acetone-$d_6$) of the methine proton in **14a** showed normal splitting due to coupling of the hydroxyl group ($J = 3.6$ Hz), the same peak for **14b** appeared as a broad singlet ($W_{1/2} = 3$ Hz). When the coupling of methine to hydroxyl protons was quenched (by the addition of a trace amount of acid or by using $CDCl_3$), both spectra showed methine doublets, due to the interaction with the 3-H proton of the thiophene ring ($J = 0.8$ Hz). Thus, the coupling constant between methine and hydroxyl protons in **14b** does not exceed 2 Hz, which suggests an unfavorable value for the H−C−O−H dihedral angle, possibly due to a dominant H-bonded conformation of the molecule.

Scheme 3



A quantitative yield was obtained for the conversion of **14** to the diketone **12**, using $MnO_2$ as the oxidizing agent (Scheme 3). For this reaction, a 10-fold excess (by weight) of $MnO_2$ was required to achieve an optimum yield, whereas the mono-oxidized derivative **17** was obtained by limiting the oxidizing reagent to a 3-fold excess (50% yield, with **12** as a side product). Under ambient conditions, the hydroxy ketone **17** underwent slow conversion to the furan **5**; the cyclization was efficiently catalyzed by the addition of acid (HBr or $HClO_4$) to give **5** in 89% yield. The same furan was obtained by the aromatization of dihydrofuran **16** with DDQ. Compound **16** was prepared in turn as a product of the acid-catalyzed rearrangement of **14**. The preparation of dithienyl furan **5** from diol **14**, via **17**, gave an overall yield of 45%; however, the overall yield via **16** was far lower (ca. 5%) and the product required further purification, proving that the latter method is an inferior route toward the synthesis of furan **5**. We discovered that, due to its allylic nature, diol **14** was able to undergo several acid-catalyzed rearrangement pathways, depending on the choice of acid and solvent; a study of the product distribution and kinetics of these processes, along with relevant mechanistic considerations, has recently been reported in a separate paper.[25]

The diketone **20** was obtained by the Diels−Alder coupling of oligo(1,3-dithiole-2,4,5-trithione) **19**[26] with 1,4-bis(2-thienyl)but-2-ene-1,4-dione **18**[27] (73% yield, Scheme 4). The efficiency of the cycloaddition step was complicated by side reactions between the product and the oligomer **19**. Consequently, the use of an excess of **19** led to a decrease in the product yield.

Diketone **20** proved to be quite stable and remained unchanged under the normal conditions used for the

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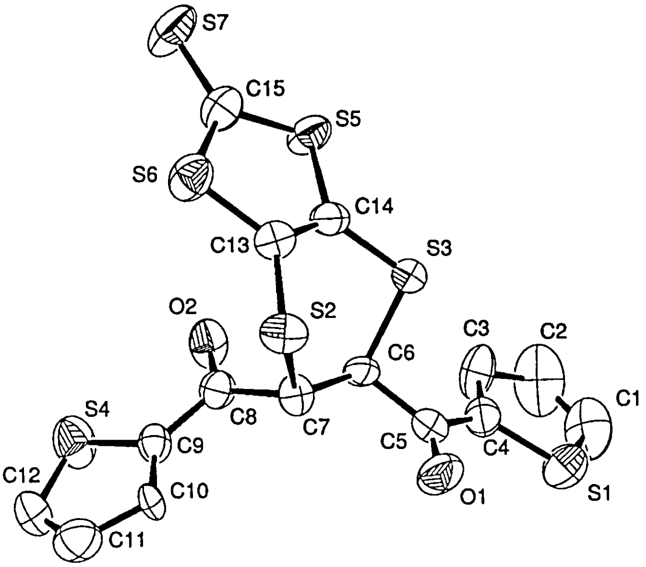
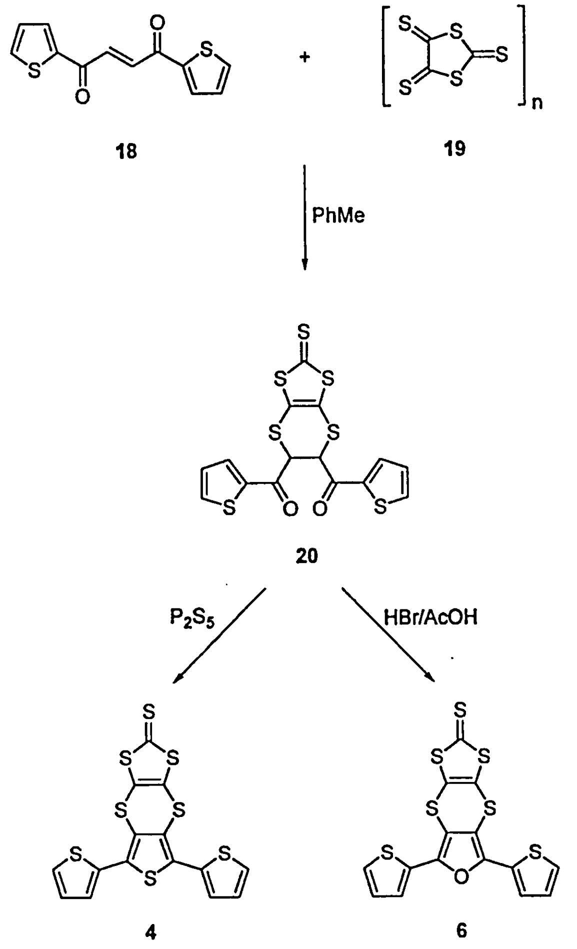


**Figure 1.** Molecular structure of *trans*-diketone **20**.

**Scheme 4**



reparation of thiophene derivatives from 1,4-diketones Lawesson's reagent in refluxing toluene or phosphorus entasulfide and sodium bicarbonate in ether at room emperature).[16] The inert behavior of **20** could be exlained by the trans arrangement of the carbonyl groups, 'ith respect to the dithiin ring, which was confirmed by ingle-crystal X-ray crystallography (Figure 1). The bsence of any classical intra- or intermolecular hydrogen onds in diketone **20** is noteworthy, since it is this type of arrangement which normally causes such stability in the solid state. Hence, we suspect that the low reactivity of **20** toward cyclization is due to steric hindrance arising from the conformation of the 1,4-dithiin ring, which limits the approach of the sulfur reagents. The structure of **20** consists of a 1,3-dithiole-2-thione fused to a 1,4-dithiin ring with 2,3-diketone substituents, each bearing a thienyl ring bound in the 2 position. The bond lengths and angles are within the expected ranges. In addition, the orientations of the thienyl rings are determined by the arrangement of the carbonyl groups, due to 1,4-intramolecular interactions between O1−S1 and O2−S4 (2.958 and 2.951 Å which, respectively, are 0.36 and 0.37 Å less than the sum of the contact radii). Similar 1,4-interactions between "nonbonded" O and S atoms have been observed previously.[28] When compared, the orientations of these substituents on the dithiin ring are somewhat different. The angle of the substituents to the mean plane of the dithiin ring are 17.64° (axial substituent) and 50.20° (bisectional substituent) for the C7−C8 and C6−C5 arms, respectively. A Cremer−Pople[29] puckering analysis of the rings showed them to be planar, apart from the dithiin ring. The lone pairs on the two sulfur atoms cause a puckering of the ring, with an angle between the two least squares mean planes (S2−C7−C6−S3 and S2−C13−C14−S3) of 116.25(12)°. Puckering analysis of this ring gave $\theta = 94.2$E and $= 184.27$E, which corresponds to a boat conformation.

Assuming the reaction stereochemistry of the cycloaddition mechanism, the conformation of **20** proves the suggested trans conformation of its precursor **18**.[27] Ultimately, the trans configuration of **20** did not render the cyclization impossible; terthiophene **4** was prepared successfully under more vigorous conditions ($P_2S_5$ + $NaHCO_3$, dioxane, 90 °C) in 57% yield.

Bis(thienyl)furan **6** was obtained by the acid-catalyzed cyclization of diketone **20** (35%). However, in parallel with the corresponding terthiophene **4**, the yield of **6** was substantially lower than that expected for a nonhindered system.[16,27]

**Electrochemistry.** The cyclic voltammogram (CV) of terthiophene **3** reveals two oxidation processes corresponding to $E_1^{1/2}$ (+1.23 V) and $E_2$ (+1. 73 V), with the latter being irreversible. Thiophene derivative **21**,[7] however, displays unusual redox behavior: a broad oxidation peak is observed between +1.30 and +1.70 V, which is accompanied by a distinct reduction peak at +0.81 V. The difference between these two peaks is quite large and does not correlate with the electrochemical behavior of terthiophene **3**. The overall redox properties of **3**, therefore, are probably independent of the central fragment (represented by **21**), and it can be assumed that the first redox process in **3** is due to the terthiophene moiety, while the second, irreversible peak arises from the fused 1,3-dithiole ring. This assumption is supported by the voltammogram of **5**, which shows only one redox wave ($E^{1/2}$ = +1.13 V): the absence of a second, irreversible peak (analogous to that of **3**), is probably due to the greater electron-withdrawing ability of the furan ring in

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(28) For example see: Eugster, C. H.; Balmer, M.; Prewo, R.; Bieri, J. H. *Helv. Chim. Acta* **1981**, *64*, 2636; Carpy, A.; Hickel, D.; Nuhrich, A. *Cryst. Struct. Commun.* **1981**, *10*, 1387; Ferguson, G.; Ruhl, B. *Cryst. Struct. Commun.* **1982**, *11*, 1033. Darocha, B. F.; Titus, D. D.; Sandman, D. J.; Warner, D. E. *Acta Crystallogr., Sect. B* **1982**, *38*, 2267.

(29) Cremer. D.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1354.

than that of the corresponding thiophene ring in **3**, uppressing the electroactivity of the 1,3-dithiole unit.

The CVs of compounds **4** and **6** are almost identical: n ill-defined oxidation peak is observed between +1.30 nd +1.90 V, together with the corresponding reduction aves at +0.85 and + 0.88 V, respectively. Again, the ifferences between these peak potentials is quite noticeble. The CV of thiophene derivative **22**[30] is also similar, his time with a clear oxidation peak at +1.48 V and a eduction peak at +0.94 V. In predicting the electroactive ites in compounds **4**, **6**, and **22**, one cannot discount the otential electroactivity of the 1,4-dithiino unit; therefore, assignment of the redox processes in **4** and **6** becomes omewhat ambiguous.

Although compounds **21** and **22** cannot be polymerized under electrochemical conditions, derivatives **3**–**6** form the corresponding polymers and copolymers via repetitive scanning in the range from 0.00 to +(1.60–2.00) V. The polymers are deposited at the working (Au) electrode as dark red films and appear to be stable over several scans, however, poly(**5**) permanently loses its electroactivity after cycling below −0.50 V and gives extremely broad oxidation waves above +0.90 V. The polyterthiophene erived from **3** gives an almost indistinguishable oxidation peak, but the reduction peak is quite pronounced and occurs in the region from +0.50 to +0.80 V, depending upon the anodic limit of the CV run. Successive cyclic voltammograms were taken from 0.00 V to maxima ranging from +1.00 to +3.25 V (at 0.25 V intervals). The current of the reduction peak is zero for the run from 0.00 to +1.00 V, but steadily increases to a maximum of +167 $\mu$A when the limit of the experiment reaches +2.50 V. Over the next two runs, the peak current for reduction falls steadily (+111 $\mu$A at $E_{max}$ = +2.75 V and −83 $\mu$A at $E_{max}$ = +3.00 V), and the polymer is finally destroyed at $E_{max}$ = +3.25 V. Despite the indeterminate nature of the oxidation peak in poly(**3**), these results indicate that the polymer is truly being oxidized over a broad range.

Although poly(**6**) is stable to cathodic analysis (up to −2.00 V), its electroactivity is poorly defined. Once more the oxidation process is broad and covers the range from +1.00 to +2.00 V with a more noticeable reduction at +0.44 V. The polyterthiophene prepared from **4**, however, gives a very stable polymer and is the only one in the series showing cathodic redox activity. A clear, almost irreversible oxidation peak is observed with a maximum at +1.79 V, while the polymer is reduced at −0.25 V (Figure 2). The band gap of poly(**4**) can be estimated from the onset potentials of these oxidation/reduction peaks (corresponding to p and n doping), and the resulting value observed (ca. 1.04 eV) is among the lowest reported for any polyterthiophene system.[31]

## Conclusions

We have presented the synthesis of a series of novel trimers based on terthiophene and bis(thienyl)furan derivatives (**3**–**6**), functionalized by a 1,3-dithiole unit. These materials are highly suitable precursors toward fascinating electroactive molecular species and conducting polymers incorporating strong redox active units.

We are currently investigating the reactivity and electrochemistry of the thiophene systems presented in this work. Early results have shown that trimers **3**–**6**, and their derivatives, are readily polymerized using chemical and electrochemical techniques.

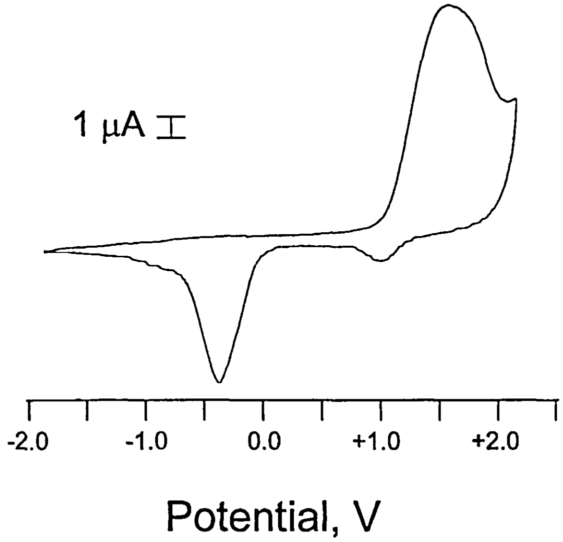
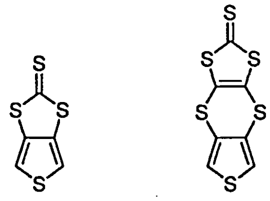


**Figure 2.** Cyclic Voltammogram of electrodeposited poly(**4**) on a gold working electrode in acetonitrile at a scan rate of 300 mV s$^{-1}$.

**Chart 3**



**21** **22**

## Experimental Section

**General.** All melting points are uncorrected. All solvents were dried and purified by standard methods. The reactions were carried out under dry N$_2$. All reagents were purchased from Aldrich unless referenced.

**Cyclic Voltammetry.** The measurements for compounds **3**–**6** and their electropolymerization were performed on a BAS CV50W voltammetric analyzer at a scan rate of 200 mVs$^{-1}$, with *iR* compensation, using anhydrous dichloromethane as the solvent, Ag/AgCl as the reference electrode, and platinum wire and gold disk as the counter and working electrodes, respectively. All solutions were degassed (N$_2$) and contained the substrate in concentrations ca. 10$^{-2}$ M, together with Bu$_4$NPF$_6$ (0.1 M) as the supporting electrolyte. Voltammograms of the polymer (scan rate 300 mVs$^{-1}$) films were obtained in monomer-free solutions (anhydrous acetonitrile) containing Bu$_4$NPF$_6$ (0.1 M) as the supporting electrolyte.

**Single-Crystal X-ray Structure Determination.** Crystal data for **20**: $C_{15}H_8O_2S_7$, $M$ = 444.63, monoclinic, space group $P2_1/n$ (alternative setting of $P2_1/c$, No. 14), $a$ = 8.773(2), $b$ = 20.104(4), $c$ = 10.983(2) Å, $\alpha$ = 111.08(3)°, $U$ = 1807.5(4) Å$^3$, $T$ = 293(2) K, $Z$ = 4, $\mu$(Mo-K$\alpha$) = 0.878 mm$^{-1}$, $F$(000) = 904, 7039 reflections collected, $\theta$ range 2.03–25.07° (index ranges; $h$ = −8 to 9, $k$ = −22 to 22 and $l$ = −12 to 11), which merged to give 2657 unique reflections ($R_{int}$ = 0.0620) to refine against 217 parameters. Final $R$ indices were $wR_2$ = 0.1037 and $R_1$ = 0.0482 [$I > 2\sigma(I)$] and 0.1112 and 0.0802 respectively for all data. Residual electron densities were 0.406 and −0.492 e Å$^{-3}$.

Data were collected for a crystal of size 0.45 0.2 0.2 mm on a Delft instruments FAST TV area detector diffractometer at the window of a rotating anode FR591 generator (50

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(30) Skabara, P. J.; Serebryakov, I. M.; Perepichka, I. F. Unpublished results.

(31) Roncali, J. *Chem. Rev.* **1997**, *97*, 173.

V, 55 mA), using a molybdenum target (λ(Mo−Kα) = 0.71069 ], controlled by a MicroVax 3200 and driven by MADNES[32] oftware.

The structure was solved by direct methods (SHELXS-97[33]) nd then subjected to full-matrix least squares refinement based on $F_o{}^2$ (SHELXL−97[33]). Non-hydrogen atoms were refined anisotropically with hydrogens included in idealized positions (C−H distance = 0.97 Å) with isotropic parameters free to refine. The weighting scheme used was $w = 1/[\sigma^2(F_o{}^2)]$. An absorption correction was deemed unnecessary, as the structure had been fully refined to a satisfactory standard.

Additional material, containing atomic coordinates, thermal parameters, bond lengths and angles are available from the Cambridge Crystallographic Data Center.[34]

**1,4-Bis(2-thienyl)but-2-yne-1,4-diol (9).** A solution of ethylmagnesium bromide was prepared from Mg (1.42 g, 59 mg-atom) and ethyl bromide (4.92 mL, 64 mmol) in THF (50 mL), under standard Grignard conditions. Acetylene gas was purified by passing the reagent through a trap cooled to −70 °C and a second trap with concentrated sulfuric acid; the gas was immediately transferred into the Grignard solution, over 2 h at 50 °C, at a rate of 2−3 L/min on vigorous stirring. After this time, the flow of acetylene was interrupted and a fraction of the solvent (10−15 mL) was removed by distillation at ambient pressure, to ensure the complete decomposition of acetylene monomagnesium bromide. 2-Thiophenecarboxaldehyde (5 mL, 54 mmol) was then added at room temperature and the mixture was allowed to stir overnight. The reaction contents were poured into 20% aqueous $NH_4Cl$ (200 mL) and the product was extracted with ethyl acetate (2 30 mL). The organic phase was dried over $MgSO_4$, the solvent was removed in vacuo, and the residue was purified by column chromatography (silica, $CH_2Cl_2$ with a gradual change to $CH_2Cl_2$:ethyl acetate = 2:1) to afford **5** (3.30 g, 50%), mp 110−113 °C (lit.[21] mp 116 °C).

**1,4-Bis(2-thienyl)but-2-yne-1,4-dione (10).** To a solution of **9** (50 mg, 0.20 mmol) in $CH_2Cl_2$ (5 mL) was added $MnO_2$ (600 mg). The mixture was stirred for 2 min at room temperature, slowly filtered through a (i.d.) 2 5 cm layer of silica and the silica was washed with dichloromethane (30 mL). Evaporation of the solvent under reduced pressure afforded **10** (28 mg, 55%): mp 133−135 °C; $^1$H NMR (acetone-$d_6$) δ 8.21 (dd, 2 H, $J$ = 3.9 and 1.1 Hz), 8.17 (dd, 2H, $J$ = 4.9 and 1.3 Hz), 7.36 (dd, 2H, $J$ = 4.9 and 3.9 Hz); $\nu_{max}$/cm$^{-1}$ (KBr) 1628 (C=O); HRMS calcd for $C_{12}H_6O_2S_2$ 245.98093, found 245.98165.

**4,5- Bis(2-thienoyl)-1,3-dithiol-2-thione (12). Method A.** A solution of **10** (33 mg, 0.13 mmol) and **11**[17] (20 mg, 0.15 mmol) in toluene (1 mL) was heated in a sealed tube under nitrogen at 100 °C for 16 h. The solvent was removed in vacuo and the residue was subjected to flash chromatography (silica, dichloromethane:petroleum ether = 1:1), affording **12** (4 mg, 8%).

**Method B.** To a solution of **14a** or **14b** (300 mg, 0.83 mmol) in dichloromethane (15 mL) was added $MnO_2$ (3.0 g). The mixture was stirred at room temperature for 2 min and immediately filtered through a layer of silica (2 (i.d.) 3 cm), while eluting with $CH_2Cl_2$ (25 mL). The solvent was removed in vacuo to afford **12** as a yellow tar which gradually solidified on standing (298 mg, 100%): mp 92 °C; $^1$H NMR ($CDCl_3$) δ 7.72 (m, 4H), 7.11 (dd, 2H, $J$ = 5.0 and 3.9 Hz); MS 354 (M$^+$, 100); $\nu_{max}$/cm$^{-1}$ (KBr) 1636 (C=O). Anal. Calcd for $C_{13}H_6O_2S_5$: C, 44.1; H, 1.7. Found: C, 44.1; H, 1.6.

***dl-* and *meso*-4,5-Bis(2-thienylhydroxymethyl)-1,3-dithiole-2-thione (14a and 14b) and 4-(2-Thienylhydroxymethyl)-1,3-dithiole-2-thione (15).** To a solution of vinylenetrithiocarbonate[22] (2.15 g, 16.1 mmol) in dry THF (60 mL), at −55 °C, was added lithium diisopropylamide (12.4 mL, 1.5 M solution in hexanes, 18.5 mmol); the mixture was stirred under dry nitrogen for 20 min. The reaction was then cooled to −70 °C, 2-thiophenecarboxaldehyde (1.50 mL, 16.1 mmol) was added over 1−2 min, and after stirring for 3 min, the second portion of LDA (11.6 mL, 17.4 mmol) was added. The mixture was stirred at −55 °C for 15 min, after which 2-thiophenecarboxaldehyde (1.50 mL, 16.1 mmol) was added over 1−2 min. The reaction was heated quickly to −30 °C and poured into saturated $NaHCO_3$ solution (200 mL), to which KBr (20 g) was added. The product was extracted with ethyl acetate (1 100 mL and 3 50 mL), and the combined organic layers were dried over $MgSO_4$. The solvent was removed in vacuo and the residue was purified by column chromatography (silica, $CH_2Cl_2$ with gradual change to $CH_2Cl_2$:ethyl acetate = 10:1), to afford essentialy pure (NMR evidence) **15**, **14a**, and **14b**, respectively, in order of elution. The analytical samples were obtained by treating the methanolic solutions with charcoal, removing the solvent in vacuo, and reprecipitation of the residues (only for **14a** and **15**) with petroleum ether from dichloromethane.

**14a**: pale green-yellow crystals (3.88 g, 67%); mp 109−110 °C; $^1$H NMR (acetone-$d_6$) δ 7.50 (dd, 2H, $J$ = 5.2 and 1.0 Hz), 7.20 (m, 2H), 7.03 (dd, 2H, $J$ = 5.2 and 3.6 Hz), 6.35 (d, 2H, $J$ = 3.4 Hz), 6.11 (d, 2H, $J$ = 3.8 Hz); $\nu_{max}$/cm$^{-1}$ (KBr) 3330 (O−H, br); MS 358 (M$^+$, 100). Anal. Calcd for $C_{13}H_{10}O_2S_5$: C, 43.6; H, 2.8. Found: C, 43.3; H, 2.6.

**14b**: yellow-brown tar (0.85 g, 15%); $^1$H NMR (acetone-$d_6$) δ 7.50 (dd, 2H, $J$ = 5.2 and 1.0 Hz), 7.20 (m, 2H), 7.03 (dd, 2H, $J$ = 5.2 and 3.6 Hz), 6.35 (d, 2H, $J$ = 3.4 Hz), 6.11 (d, 2H, $J$ = 3.8 Hz); $\nu_{max}$/cm$^{-1}$ (neat on KBr) 3330 (O−H, br); HRMS calcd for $C_{13}H_{10}O_2S_5$ 357.92844, found 357.92605.

**15**: pale green-yellow crystals (0.44 g, 12%); mp 67−69 °C; $^1$H NMR (acetone-$d_6$) δ 7.47 (dd, 1H, $J$ = 5.1 and 1.2 Hz), 7.33 (d, 1H, $J$ = 1.2 Hz), 7.14 (m, 1H), 7.02 (m, 1H), 6.21 (dd, 1H, $J$ = 4.4 and 0.9 Hz), 6.03 (dd, 1H, $J$ = 4.4 and 0.9 Hz); $\nu_{max}$/cm$^{-1}$ (KBr) 3363 (O−H, br); HRMS calcd for $C_8H_6S_4O$ 245.93015, found 245.93090.

**4,6-Bis(2-thienyl)-4,6-dihydrofuro[3,4-*d*]-1,3-dithiole-2-thione (16).** Two drops of concentrated HBr were added to a suspension of **14** (400 mg, 1.13 mmol) in dichloromethane (10 mL). After the mixture was stirred at room temperature for 20 min, the product was isolated by column chromatography (silica, $CH_2Cl_2$:petrol ether = 1:1). The major fraction was treated with cold acetone−water (10:1, 15 mL), and the insoluble yellow precipitate was filtered and washed with a small amount of cold acetone to give **16** (55 mg, 14%); mp 134 °C (dec); $^1$H NMR ($CDCl_3$) δ 7.40 (dd, 2H, $J$ = 5.1 and 1.0 Hz), 7.17 (dd, 2H, $J$ = 3.6 and 1.0 Hz), 7.02 (dd, 2H, $J$ = 5.1 and 3.6 Hz), 6.38 (s, 2H); HRMS calcd for $C_{13}H_8S_5O$ 339.91788, found 339.91634.

**4-(2-Thienoyl)-5-(2-thienylhydroxymethyl)-1,3-dithiole-2-thione (17).** To a solution of **14** (50 mg) in dichloromethane (2 mL) was added $MnO_2$ (150 mg), and the mixture was stirred at room temperature for 2 min. The product was purified directly from the reaction mixture by column chromatography, using silica and $CH_2Cl_2$ as the eluent. The solvent was evaporated under reduced pressure to afford **17** as a yellow tar (25 mg, 50%): $^1$H NMR ($CDCl_3$) δ 7.91 (dd, 1H, $J$ = 3.9 and 1.0 Hz), 7.81 (dd, 1H, $J$ = 5.0 and 1.0 Hz), 7.31 (dd, 1H, $J$ = 5.1 and 1.2 Hz), 7.19 (dd, 1H, $J$ = 3.9 and 5.0 Hz), 7.14 (m, 1H), 6.98 (dd, 1H, $J$ = 5.1 and 3.6 Hz), 6.41 (d, 1H, $J$ = 0.8 Hz), 3.6 (br, 1H); $\nu_{max}$/cm$^{-1}$ (neat on KBr) 3420 (O−H, br) and 1623 (C=O); HRMS calcd for $C_{13}H_8O_2S_5$ 355.91278, found 355.91103.

***trans*-5,6-Bis(2-thienoyl)-5,6-dihydro-1,4-dithiino[2,3-d]-1,3-dithiole-2-thione (20).** A mixture of **18** (1.0 g, 4.0 mmol), **19** (860 mg, 2.2 mmol) and toluene (100 mL) was stirred at 90−100 °C for 20−30 min. The product was purified from the hot solution by column chromatography (silica, toluene) The volume of the eluate from the second fraction was reduced in vacuo (to 30−40 mL), and left to crystallize affording **20** as red-brown crystals (960 mg, 53%): mp 174−179 °C (with fast decomposition at 182 °C). The remainder of **18** together with some amount of the product was eluted from

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[32] Pflugrath, J. W.; Messerschmidt, A. MADNES, version 11, Sep. 1989; Delft Instruments: Delft, The Netherlands, 1989.

[33] Sheldrick, G. M. SHELXL-97, Program for crystal structure refinement, University of Göttingen, Germany, 1997.

[34] The authors have deposited atomic coordinates for **20** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

the column with toluene:ethyl acetate mixture (10:1) and was used in an analogous synthesis affording additionally 360 mg (20%) of **20** (overall yield 73%): $^1$H NMR (CDCl$_3$, 50 °C) $\delta$ 7.92 (dd, 2H, $J$ = 4.6 and 0.8 Hz), 7.75 (dd, 2H, $J$ = 3.8 and 0.8 Hz), 7.21 (dd, 2H, $J$ = 4.6 and 3.8 Hz), 5.51 (s, 2H); $\nu_{max}$/cm$^{-1}$ (KBr) 1641 (C=O); MS 444 (M$^+$, 100). Anal. Calcd for $C_{15}H_8O_2S_7$: C, 40.5; H, 1.8. Found: C, 40.8; H, 1.9.

**4,6-Bis(2-thienyl)thieno[3,4-*d*]-1,3-dithiole-2-thione (3).** A mixture of **12** (1.0 g, 2.80 mmol), $P_2S_5$ (3 g, 13 mmol), and $NaHCO_3$ (1 g) in 1,4-dioxane (20 mL) was stirred under nitrogen while the temperature was increased from 60 to 100 °C over 1 h. The mixture was poured into water (150 mL) (**CAUTION!** $H_2S$ and $CO_2$ evolution) and the suspension was refluxed for 15−20 min. The crude product was filtered, dried, and purified by column chromatography (silica, toluene). The volume of the eluent was reduced in vacuo to 15−20 mL and petroleum ether (50 mL) was added to afford **3** as an orange powder (0.70 g, 70%): mp 195−196 °C; $^1$H NMR (CDCl$_3$, 55 °C) $\delta$ 7.38 (dd, 2H, $J$ = 5.1 and 1.0 Hz), 7.21 (dd, 2H, $J$ = 3.7 and 1.2 Hz), 7.11 (dd, 2H, $J$ = 5.1 and 3.7 Hz); MS 354 (M$^+$, 100). Anal. Calcd for $C_{13}H_6S_6$: C, 44.0; H, 1.7. Found: C, 43.6; H, 1.8.

**5,7-Bis(2-thienyl)thieno[3 ,4 :5,6]-1,4-dithiino[2,3-*d*]-1,3-dithiole-2-thione (4).** A suspension of **20** (1.0 g, 0.90 mmol), $P_2S_5$ (4.5 g, 20 mmol), and $NaHCO_3$ (1.5 g) in dry 1,4-dioxane (50 mL) was stirred at 90 °C for 1.5 h on vigorous stirring. After cooling, the mixture was diluted with water (100 mL) (**CAUTION!** $H_2S$ and $CO_2$ evolution), heated to 50 °C, and filtered. The precipitate was refluxed with water (50 mL) for 10 min, filtered, and dried. The solid was treated with boiling toluene (150 mL), filtered while still hot through a layer of silica (5 (i.d.)   5 cm) and the silica was washed with hot toluene (150 mL). The volume of the filtrate was reduced to ca. 40 mL in vacuo, affording **4** as yellow-orange needles (567 mg, 57%): mp 230−232 °C; $^1$H NMR (acetone-$d_6$, 50 °C) $\delta$ 7.67 (dd, 2H, $J$ = 5.2 and 1.0 Hz), 7.43 (dd, 2H, $J$ = 3.6 and 1.0 Hz), 7.21 (dd, 2H, $J$ = 5.2 and 3.6 Hz); HRMS calcd for $C_{15}H_6S_8$ 441.82352, found 441.82323.

**4,6-Bis(2-thienyl)furo[3,4-*d*]-1,3-dithiole-2-thione (5). Method A:** A mixture of **16** (25 mg, 0.073 mmol), DDQ (23 mg, 0.10 mmol), and toluene (10 mL) was refluxed for 3 h and the volume of the mixture was reduced to 2−3 mL. Flash chromatography (silica, toluene) afforded crude **5** (9 mg, 35%), mp 178−186 °C.

**Method B.** A solution of **17** (20 mg) and 3 drops of concentrated HBr in acetone (1 mL) was allowed to stand at room temperature for 24 h. Water (0.5 mL) was added and the precipitate was filtered and washed with a small amount of cold acetone: petroleum ether (1:3) mixture to afford **5** as scarlet thin needles (17 mg, 89%): mp 193−195 °C; $^1$H NMR (CDCl$_3$, 55°C) $\delta$ 7.39 (dd, 2H, $J$ = 5.1 and 1.0 Hz), 7.22 (dd, 2H, $J$ = 3.8 and 1.1 Hz), 7.14 (dd, 2H, $J$ = 5.0 and 3.8 Hz); HRMS calcd for $C_{13}H_6OS_5$ 337.90222, found 337.90424.

**5,7-Bis(2-thienyl)furo[3 ,4 :5,6]-1,4-dithiino[2,3-*d*]-1,3-dithiole-2-thione (6).** To a solution of **20** (20 mg) in boiling acetic acid (7 mL) was added concentrated HBr (0.5 mL) and the mixture was allowed to reflux for 3 h. After addition of water (3 mL) the precipitate was filtered, dried, and chromatographed (silica, toluene) to afford **6** as a yellow powder (7 mg, 35%): mp 180−210 °C (dec); $^1$H NMR (CDCl$_3$, 50 °C) $\delta$ 7.42 (m, 4H), 7.14 (dd, 2H, $J$ = 5.1 and 3.7 Hz); MS found 426, required for 425.84637. Anal. Calcd for $C_{15}H_6S_7O$: C, 42.2; H, 1.4. Found: C, 42.3; H, 1.7.

**Acknowledgment.** We thank The Royal Society and NATO for a Former Soviet Union Postdoctoral Fellowship (I.M.S.) and The Royal Society for Cyclic Voltammetry equipment (P.J.S.) and for funding the visit to Sheffield (I.F.P.).

**Supporting Information Available:** X-ray data for diketone **20**; $^1$H NMR spectra for compounds **4**, **5**, **10**, **15**, and **16**; cyclic voltammograms for compounds **3**−**6** and their polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

JO990198+

# The development of an electropolymerisable unit for TTF-thiophene fused monomers

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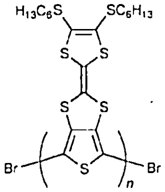
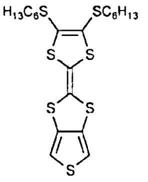
**A novel poly(terthiophene) species provides the first example of an annelated TTF-thiophene derivative which can be polymerised electrochemically.**

In general, the electropolymerisation of a conducting polymer is of particular interest for the following reasons: (i) the process is relatively cheap and can be performed on a small scale; (ii) the 'clean' reaction proceeds in the absence of a catalyst or other chemical reagents; (iii) the electrochemistry of the polymer can be investigated almost immediately and (iv) the electronic bandgap of the polymer can be measured by cyclic voltammetry and is usually comparable to the optical bandgap measured by UV–VIS spectroscopy.

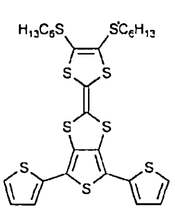
Although we have recently prepared polymer **1** using chemical coupling methods,[1] the electropolymerisation of thiophene units bearing fused **2**[2] or covalently attached[2,3] TTFs has so far eluded the field. The consensus of opinion points towards the fulvalene acting as a radical scavenger which, together with some degree of intramolecular coulombic repulsion between charged oxidised intermediates, renders the thiophene moiety inert to oxidative coupling reactions. The electrosynthesis of polythiophenes, linked to TTF units *via* saturated spacer groups, has been well established by the group of Roncali,[4] yet the successful electropolymerisation of conjugated TTF-thiophene monomers remains a challenge. In response to this, we have prepared compounds **3** and **4**, which are terthiophene analogues of **2**. The propensity towards electropolymerisation for these derivatives should be improved by the increased donor ability of the thiophene functionality (the oxidation potential of oligothiophenes decreases with an extension of the chain length).



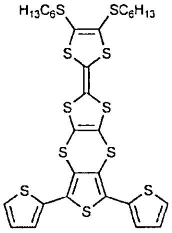
**1**



**2**

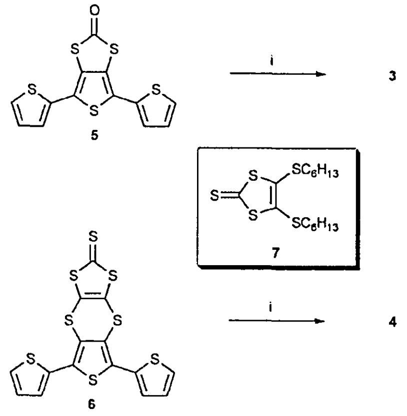


**3**



**4**

The target compounds were prepared using standard phosphite-mediated cross-coupling reactions of 1,3-dithiole-2-chalcogenones (Scheme 1).[5] Thus, terthiophenes **5**[6] and **6**[7] were reacted with dithiole **7**[8] in the presence of triethyl phosphite at 120 °C, to afford compounds **3** and **4** (30–40% yield in both cases).‡



**Scheme 1** *Reagents and conditions*: i, $P(OEt)_3$, **7**, 120 °C, 6 h.

The electrochemical behaviour of compounds **2**–**4** is summarised in Table 1.§ All three compounds show two sequential reversible oxidation waves corresponding to the formation of the TTF radical cation and dication, respectively. It is noteworthy that the oxidation values for the two terthiophene derivatives are almost identical, thereby indicating that any inductive effect due to the 1,4-dithiin ring is negligible. However, each oxidation of the TTF moiety in **2** is shifted to a more positive value by *ca.* 100 mV, compared to derivatives **3** and **4**. The electronic effect of the fused thiophene ring upon the TTF unit can be explained by a σ electron-withdrawing effect in **2**, which is reduced by a counter-active π-resonance effect of the two peripheral thiophene rings in **3** and **4**.

The high value for the irreversible oxidation of the thiophene ring in **2** ($E_3$ = +2.18 V)[9] is unfavourable for electropolymerisation, however, the corresponding oxidation processes for compounds **3** and **4** are reduced to +1.55 and +1.52 V, respectively. These values are relatively high for terthiophene derivatives in general and are probably due to an electron withdrawing effect of the TTF dication. For electropolymerisation experiments, repetitive scanning over the range 0.0 to +1.6 V was performed, using a Ag/AgCl reference electrode and a gold disk working electrode in a dichloromethane–hexane (2 : 1) solution containing tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte. As we have observed previously,[9] monomer **2** failed to polymerise; however, we were quite surprised to discover different electrochemical reactivities

**Table 1** Cyclic voltammetric data for compounds **2**–**4**

| Compound | $E_1^{1/2}$/V | $E_2^{1/2}$/V | $E_3$/V[a] |
|---|---|---|---|
| 2 | +0.74 | +1.10 | +2.18 |
| 3 | +0.64 | +1.02 | +1.55 |
| 4 | +0.64 | +0.99 | +1.52 |

[a] Irreversible peaks.

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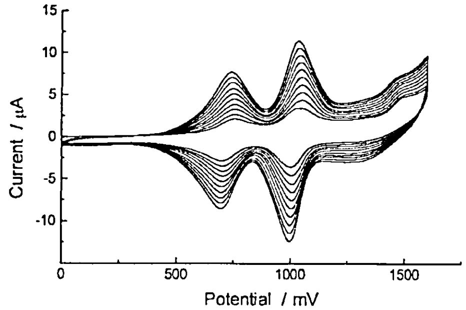

**Fig. 1** Electropolymerisation of 4 in dichloromethane–hexane (2 : 1).

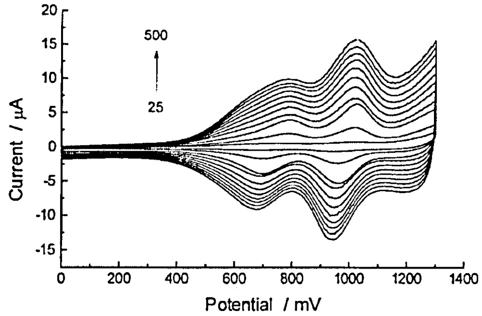

**Fig. 2** Cyclic voltammograms of poly(4) in monomer-free acetonitrile solution at scan rates of 25, 50, 100, 150, 200, 250, 300, 350, 400, 450 and 500 mV s$^{-1}$.

for compounds 3 and 4, despite the close similarity in redox potentials. Although, in the case of 3, we observed the formation of a red film on the surface of the electrode, cyclic voltammetry clearly showed that this was not of polymeric nature. Conversely, reproducible films of poly(4) were obtained under identical conditions; a typical trace showing polymer growth over 10 cycles can be seen in Fig. 1. The proportionally higher increase in current between scans for $E_2{}^{\frac{1}{2}}$, compared to the first oxidation wave, has been seen previously in poly(bithiophenes) linked to TTF units *via* saturated spacer groups.[4c] This type of behaviour shows that the second oxidation of the TTF species develops independently of charge-transport through the film, which is not the case for $E_1{}^{\frac{1}{2}}$.

Fig. 2 features cyclic voltammograms of poly(4) at various scan rates (25–500 mV s$^{-1}$) in monomer-free acetonitrile solution. The relationship between the maximum peak current and the scan rate (100–500 mV s$^{-1}$) is linear with a high correlation coefficient ($r > 0.996$). This behaviour is typical of an electroactive polymer attached to an electrode surface and exemplifies the stability of poly(4) towards p-doping up to +1.3 V. At higher potentials the CV behaviour becomes ambiguous. Although the polymer does not appear to decompose or break down in the range −1.5 to +2.0 V, the CVs obtained within these limits are poorly defined and irreproducible.

Poly(4) was prepared on ITO glass and the electronic spectrum of the film was recorded. Two broad peaks are observed at $\lambda_{\max} = 459$ and 833 nm ($\lambda_{\max}$ for compound 4 in dichloromethane is at 344 nm, Fig. 3). The latter peak indicates that the as-grown polymer remains in the oxidised state, however, since doped polythiophene and TTF$^{\bullet+}$ species absorb in this region, the identity of the oxidised species is uncertain. Rinsing the polymer film thoroughly with hydrazine had no effect on the electronic spectrum of poly(4), showing that the polymer is quite stable in the doped state. However, after repetitive cycling of the polymer film over the range −0.3 to 0.0 V for 2 h, we were able to obtain the electronic spectrum of the neutral polymer (Fig. 3). A broad band is observed ($\lambda_{\max} = 449$ nm), extending to *ca.* 736 nm, which is typical behaviour for a polythiophene system. The absence of a second peak above 800 nm confirms the neutral state of poly(4) and the optical bandgap of the neutral polymer (1.69 eV) was found to be somewhat higher than the bandgap determined electrochemically (1.39 V).

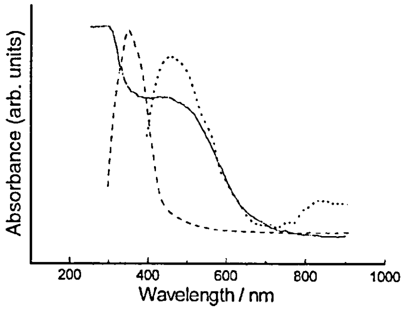

**Fig. 3** Electronic absorption spectra of compound 4 in dichloromethane (- - - - -), oxidised poly(4) on ITO glass (······) and neutral poly(4) on ITO glass (——).

In summary, we have presented a logical strategy towards the design of a polymerisable fused TTF-thiophene derivative. Beginning with a monomer unit 2 which has been acknowledged as being *a priori* for the formation of a regiospecific TTF-thiophene polymer,[10] we have highlighted the problems which arise from unfavourable interactions between the two redox units towards electropolymerisation. On one hand, the use of a terthiophene building-block is essential for a low oxidation value of the polymerisable moiety. Secondly, since 3 cannot be polymerised electrochemically, the incorporation of a fused 1,4-dithiin bridging unit in 4 presumably ensures a favourable spin density distribution in the radical trication for polymerisation to take place. We conclude that, in order to understand the nature of poly(4) at higher and lower potentials, a detailed spectroelectrochemical investigation would be extremely worthwhile.

We thank The Royal Society and NATO for a Postdoctoral Fellowship (to I. M. S.).

## Notes and references

‡ Satisfactory elemental analysis, mass spectra and $^1$H NMR spectra were obtained for all new compounds.

§ Data were obtained in dichloromethane *vs.* Ag/AgCl reference electrode, Au working electrode, Pt counter electrode at 20 °C using 0.1 M NBu$^n{}_4$PF$_6$ supporting electrolyte, 10$^{-3}$ M substrate and 100 mV s$^{-1}$ scan rate with *iR* compensation.

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5 See, for example: N. Svenstrup and J. Becher, *Synthesis*, 1995, 215.

6 The synthesis of compound 5 directly from the trithiocarbonate derivative and mercury(II) acetate is inefficient (20% yield); an improved method for the preparation of 5 will be reported elsewhere.

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