The synthesis, spectroscopic and electrochemical investigation of thienyl derivatives of polyaromatic hydrocarbons

Colin J. Martin

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Doctor of Philosophy

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Declaration

This thesis has not been submitted as an exercise for a degree at this or any other university. Except where acknowledgement is given, all work is original and was carried out by the author alone. I agree that the library may lend or copy this thesis upon request.

Colin Martin
Summary

Part 1 gives an overview of the literature concerning both polyphenylenes and thiophenes. In particular it focuses on the variations known for the ligand-metal coordination of systems based on either species. The reactivity of these systems towards oxidative carbon-carbon bond formation leading to the formation of fused aromatics and polymers is discussed in detail.

Part 2 describes the synthesis and characterisation of a series of tri-thienyl polyphenylenes prepared via the cobalt catalysed cyclotrimerisation of the appropriate thienyl acetylene. Through varying the position of thiophene substitution, along with the other substituent on the acetylene, the ratios of products formed have been observed using in situ NMR spectroscopy. Computational analysis and solid state X-ray crystallography have been used to further examine the trimerisations taking place.

Part 3 discusses the synthesis and characterisation of sulfur containing polyphenylenes which have been prepared using Diels-Alder reactions, in order to study the changes in the hexabenzocoronene framework upon heteroatom substitution. Four novel compounds are discussed the reactivity of which under oxidising conditions using FeCl₃ been examined. The formation of dimeric species upon oxidation was proven spectroscopically and through careful substitution of the thiophene units a monomeric partially fused di-thienyl polyphenylene was prepared.

In Part 4 the photochemistry and electrochemistry of the di-thienyl monomers and dimers prepared in part 3, along with a series of mono-thienyl compounds previously prepared within the group are discussed. The effect of changes in the thienyl substitution on the UV/Vis and luminescence properties along with the concentration and temperature dependence of the fused systems is discussed. This chapter also investigates how the
availability of sites on the thiophenes for electrochemical bond formation, influences the electrochemical reactivity.

**Part 5** involves the synthesis and characterisation of polyphenyl-thienyl systems containing four and six thiophene groups. The chemical oxidation of these compounds leads to the formation of polymeric materials which are insoluble and could be examined only by thermal gravimetric analysis and powder diffraction. Using electrochemical and spectroelectrochemical methods the oxidative polymer formation was monitored and the effect of changes in the thienyl substituents, on the properties of the polymers have been investigated.

**Part 6** explores attempts to apply the reactivity of the thienyl moieties observed in earlier chapters toward the preparation of new systems. Three areas: thienyl based molecular switches, thienyl containing tetrazines and thiophene-metal coordination are described. Some potential future work into the development of these systems, along with other new methods for developments in the area of thiophene-phenylenes are also discussed.

**Part 7** gives a full account of the experimental work carried out in this thesis.
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Firstly I would like to thank my supervisor, Prof. Sylvia Draper for her help, advice and encouragement during my time working on this project. Also thanks to Prof. Sarath Perera for the huge amount of help and ideas he gave me when I first started. Thanks to Dr. Sunil Varughese and Dr. Longsheng Wang for all their help with crystallography and Dr.’s John O’Brien and Manuel Reuther for hours of assistance with tricky NMR data. Thanks also to Dr. Martin Feeney, Dr. Dilip Rai and Dr. Bernard Jean-Denis for Mass spectral analysis. Special thanks also to NíChaoimh Dewdney for computational calculations and Dr. Belén Gil Ibáñez for all her assistance with the photochemical studies.

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<td>2D</td>
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Part 1: Introduction
1.1 Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) consist of multiple aromatic units which have been fused together, leading to the formation of all carbon species with novel properties. These properties can be varied by changing the arrangement of the fused aromatic units in the structure. Linear PAH systems such as anthracene and phenanthrene (Figure 1-1) have been intensively investigated due to their applications in photochemistry and as they represent a basis for many naturally occurring compounds.\(^{1-2}\)

![Figure 1-1: Anthracene and phenanthrene, two simple PAH systems.](image)

The development of predefined all carbon aromatic frameworks based upon a central benzene ring around which other phenyl groups could be extended was initially investigated by Clar and Zander,\(^{3-4}\) in these works a correlation between the size and topology of the large aromatic systems and their electronic properties was observed. Difficulties in obtaining synthetic control over the structures of the PAHs, along with the harsh conditions required for their synthesis\(^{5}\) meant that systematic studies of larger PAH based systems were difficult.

Recently a synthetic strategy developed by Müllen et al.\(^{6}\) has allowed for the development of new polycyclic systems, such as those shown in Figure 1-2. These fully fused frameworks are prepared from polyphenylene precursors by addition of a Lewis acid such as iron trichloride or aluminium trichloride which can oxidise the systems to give PAH products. In these studies it was found that increasing the size of the aromatic platform leads to a decrease in the size of the HOMO-LUMO gap.
 Investigations into the effect of substitution on fused systems have been carried out for hexa-\textit{peri}-hexabenzocoronene (HBC) based frameworks in which 13 fused phenyl rings are present (Figure 1-2). As a result of the insolubility of the unsubstituted platforms (Figure 1-2, $R = H$) a number of alkyl substituted HBC systems have been developed.\textsuperscript{7} Upon substitution with long chain alkyl groups these form mesophases with potential liquid crystal properties. The size and shape of the platform in these systems is important in controlling the packing; however the columnar stacking which is often observed is induced by the substituent groups on the framework.\textsuperscript{8}

These HBC systems have been investigated both in terms of their own reactivity and as a model for graphene.\textsuperscript{9-11} These compounds have potential applications in semiconductor and transistor devices,\textsuperscript{6,12} charge-carrying processors,\textsuperscript{13} light emitting diodes and solar cells due to their electronic and charge mobility properties.\textsuperscript{14-15}

In our group we have reported the development of nitrogen containing derivatives of hexa-\textit{peri}-hexabenzocoronene, the nitrogen heterosuperbenzenes (N-HSB). In these systems nitrogen atoms have been placed around the periphery of the coronene framework.\textsuperscript{16} The fully cyclised N-heterosuperbenzene \textbf{I.2} has been prepared from the oxidation of the precursor compound \textbf{I.1} using a combination of aluminium chloride and copper chloride.
Nitrogen substitution means that these compounds are now polar, having lost the $C_6$ symmetry observed in the coronene systems. Resulting from this is an increase in solubility compared to the all carbon analogues, along with an observed increase in the electron accepting ability; a significant increase in the charge carrying ability compared to all carbon systems is also observed. The coordinating ligand characteristics of these compounds provide an opportunity to study the N-HSB systems both in terms of their metal coordination properties and their $\pi$-stacking ability in solution.

Metal coordinated N-HSB systems have been prepared within the group and the effect of metal coordination on the photochemical properties of the systems, compared to those of other similar species have been examined. Fully cyclised N-HSB I.2 has been coordinated to both palladium and ruthenium to give cationic species I.3 and I.4.
N-HSB I.2 is luminescent in toluene with an emission at $\lambda_{\text{max}}$ 494 nm which is quenched upon coordination to palladium to give I.3. This quenching results from an efficient radiationless decay process, indicated by a 60 nm red shift in the UV/Vis absorption spectrum of I.2 compared to I.3.\(^{17}\) For the ruthenium complex I.4 stacking of the planar N-HSB ligands is seen both through the photochemical properties in solution and the molecular structure in the solid state.\(^{18}\) The UV/Vis spectrum of I.4 shows a low-energy absorption band at 615 nm, this is red shifted compared to [Ru(bpy)\(_3\)]\(^{2+}\) indicating that a MLCT occurs between the metal centre and the N-HSB ligand as a result of its low lying $\pi^*$ acceptor orbitals. These low lying orbitals also mean that I.4 is a near IR emitter; further investigation into N-HSB metal complexes including iridium and osmium, are ongoing within the group.

By switching the oxidation method for I.1 from aluminium trichloride to iron trichloride the partially fused N-1/2HSB I.5 has been prepared.\(^ {19}\)

![I.5](image.png)

The photochemical properties of both I.5 and its ruthenium complex appear similar to those of I.2 and I.4 respectively. A loss of some fine structure is observed as a result of the decrease in planarity; a reduction in the absorption peaks resulting from intermolecular stacking is also seen in solution, due to the unfused phenyl groups present in the molecule.
1.2 Metal coordination to thiophene

In this thesis thiophene has been used in the synthesis of new polyphenylene derivatives to incorporate sulfur into the platforms previously prepared within the group. The ability of thiophene to form metal coordinated species has been investigated in the literature and patterns of reactivity have been observed. The standard nomenclature used for a substituted thiophene is to designate the thienyl group as either 2-thienyl or 3-thienyl depending on the carbon at which it is substituted to the core of the molecule (Figure 1-3). The other positions on the thiophene are then numbered around the ring (with the sulfur always designated as 1).

![Figure 1-3: The numbering nomenclature for 2-thienyl and 3-thienyl parts of a molecule.](image)

The majority of studies of thienyl-metal reactions are based upon the catalytic hydrodesulfurisation of naturally occurring organic materials including feedstock and natural gas. These reveal that thiophene systems can coordinate to metal centres \( \eta^1 \) through the sulfur, \( \eta^2 \) through two carbon atoms, \( \eta^4 \) through all four carbons and \( \eta^5 \) through the entire ring (Figure 1-4, I.6 - I.9).

![Figure 1-4: Examples of the different possible thiophene coordination modes.](image)
In the studies of Angelici the \( \eta^1 \) coordination ability of thiophene through the sulfur atom along with that of benzothiophene and dibenzothiophene was investigated (Figure 1-5).\(^{22-24}\) The kinetics of the displacement of these three from metal complexes by a series of coordinating ligands was examined, the tendency of the ligands to coordinate to metal ions was observed to increase in the order \( I.10 < I.11 < I.12 \).

![Figure 1-5: Thiophene I.10, benzothiophene I.11 and dibenzothiophene I.12 as studied by Angelici.\(^{22-24}\)](image)

The binding strength of the \( \eta^1 \) S-coordination in the metal complex \([\text{Cp(CO)}(\text{PPh}_3)\text{Ru}(\eta^1-\text{thiophene})]^+\) was found to be \( 7.1 \times 10^6 \) times weaker than that of the equivalent hydrated tetrahydrothiophene complex \([\text{Cp(CO)}(\text{PPh}_3)\text{Ru}(\eta^1-\text{terthiophene})]^+\).\(^{22}\) This indicates coordination of terthiophene is much more favourable than is observed for thiophene. It was also found that thiophene can be displaced in such systems by weakly coordinating ligands such as a methyl iodide to give \([\text{Cp(CO)}(\text{PPh}_3)\text{Ru}({\text{MeI}})]^+\) indicating the \( \eta^1 \) coordinating ability of thiophene is very weak. These studies indicate that in order to get \( \eta^1 \) coordination of a thiophene it is necessary to have sufficient aromatic substitution on the thiényl ring to stabilise the coordination. It has been noted that d\(^6\) metals such as Re(I), Ru(II) and Ir(III) give the most stable S-coordination complexes.\(^{25-26}\) Interestingly in all reported \( \eta^1 \) thiophene metal coordination systems the metal always lies out of the plane of the thiophene ring, indicating some sp\(^3\) hybridisation of the sulfur atom.\(^{27}\)

One of the major problems in the synthesis of \( \eta^1 \) thiophene species is the ability of thiophenes to react with coordinatively unsaturated electron-rich metal complexes to give products in which the metal inserts into a carbon-sulfur bond (Scheme 1-1).
The reaction pathway for the coordination of thiophene with the rhodium complex \( \text{Cp}^*\text{Rh}(\text{PMe}_3) \) was studied by Jones and coworkers\(^{28}\) and later modelled computationally by Sargent and Titus.\(^{29}\) The initial coordination of the thiophene is \( \eta^1 \) through the sulfur \( \text{I.11} \) although a \( \eta^2 \) coordination through two of the carbons is also observed \( \text{I.12} \) (Scheme 1-2).

The \( \eta^2 \) coordinated thiophene can undergo an oxidative addition to give \( \text{I.14} \) which is the kinetic reaction product; however this species is unstable and converts through \( \text{I.11} \) to the stable cyclometalated species \( \text{I.13} \). This metal insertion between carbon-sulfur bonds has been observed for a large number of metal centres and is one of the main reasons why \( \eta^1 \) metal coordinated thiophenes are uncommon.

When \( \eta^1 \) or \( \eta^5 \) coordinated to a metal thiophene can undergo further metalations to form di-metallic species in which the thiophene has different coordination modes to each metal, some examples \( \text{I.15}, \text{I.16} \) and \( \text{I.17} \) are shown in Figure 1-6.

The reactivity of metal coordinated thiophene varies drastically with the type of coordination present. In the case of $\eta^5$ species the electronic effect of the metal makes the thiophene ring susceptible to nucleophilic attack at the 2- and 5- positions on the ring to give thioallyl (a) or butadienethiolate (b) species or to give coordination to the sulfur atom (c) (Scheme 1-3).

For $\eta^1$ coordination through the sulfur the aromatic character of the ligand is disrupted making it susceptible to electrophilic attack, leading to the formation of mixed metal complexes as in the case of the rhenium species of Choi (Scheme 1-4).
IR studies on these complexes indicate that upon $\eta^4$ coordination to iron the sulfur becomes a better donor to rhenium with a decrease in $\nu$(CO) from 1934 and 1874 cm$^{-1}$ before iron coordination to 1922 and 1862 cm$^{-1}$ after. This results from the electronic density of the sulfur and diene parts of the thiophene becoming more distinct upon metal coordination to the diene.

1.3 Cyclodehydrogenation

1.3.1 Oxidation of polyphenylenes and coronenes

In the synthetic methods used for both the coronene derivatives and the nitrogen containing heterosuperbenzenes discussed in §1.1 the key step is the oxidative carbon-carbon bond formation between two aromatic rings (Scheme 1.5).

![Scheme 1-5: The general form of cyclodehydrogenation reactions.](image)

A number of possible metal based oxidants have been reported. Initial work on dehydrogenation reactions carried out by Copland and McNeil used a palladium-platinum-charcoal catalyst in a hydrogen atmosphere to oxidise a naturally occurring naphthalene derivative at high temperature (Scheme 1-6).$^{32}$

![Scheme 1-6: Cyclodehydrogenation of a naphthalene derivative reported by Copeland et al.$^{32}$](image)
In the 1960’s Kovacic examined the oxidation of benzene to para-polyphenyl at room temperature using a mixture of aluminium chloride and copper chloride. Soon afterwards it was also shown that the same oxidation could be achieved using iron trichloride. The oxidation mechanism (Scheme 1-7) resembles that of a catalysed olefin polymerisation, for which an acid is required.

![Scheme 1-7: Acid and metal catalysed polymerisation of benzene.](image)

In this polymerisation the initiation step is the protonation of a phenyl ring to give the reactive cation, this then undergoes propagation with another benzene ring to form a biphenyl cation. The non-cationic ring is then oxidised by the metal to regain its aromaticity with the loss of hydrogen bound to the metal, the cation on the other ring then undergoes reactions so that the polymerisation is further propagated. This cationic mechanism is only possible in the presence of a metal catalyst. Lewis acid catalysts such as iron trichloride or aluminium trichloride are used as they form weak Bronsted acids in dichloromethane solution and can act as the oxidant in the reaction. The reaction is quenched by the removal of the cationic species by the addition of methanol or a weak base.

In the work of King et al. the oxidation of smaller arene systems was studied. Here by examining the effect of changes in the substituent groups, the directed oxidation of
smaller oligophenyl arenes was achieved.\textsuperscript{36} For small unsubstituted oligophenylenes such as ortho-terphenyl I.18 (Scheme 1-8) oxidation results in the formation of triphenylene I.19 in a 20% yield. An insoluble powder was also formed in a 75% yield which was found to be a mixture of products (I.20 and I.21) on which annulation has occurred; a small amount (< 5%) of larger fused polyphenylenes was also observed.

![Scheme 1-8: Dehydrogenation products observed for the oxidation of ortho-terphenyl.](image)

The low concentrations of the larger fused polyphenylenes was due to the insolubility of the species I.20 and I.21, indeed the limiting factor in these oxidative coupling reactions is the solubility of the first products formed. In reactions where the fused products are insoluble further reactivity is not observed. These conditions have been used in the work of Mullen to prepare coronenes from their polyaromatic phenylene precursors, in these systems the oxidation leads to the formation of coronene systems which cannot undergo further oxidations due to their insolubility. Both aluminium and iron oxidation catalysts have been used in the synthesis of such systems in a condensation called the Scholl reaction (Scheme 1-9).\textsuperscript{37-38}

![Scheme 1-9: Mullen’s HBC synthesis using metal catalysts for dehydrogenation.](image)
The mechanism for the Scholl reaction of hexaphenylbenzene has been modelled computationally by King et al.\textsuperscript{39-40} In these studies two possible mechanisms for the reaction were proposed, the first goes via aromatic cation intermediates similar to those seen for the polymerisation of benzene and the other goes via radical cations. The aromatic cation mechanism (Scheme 1-10) is the more likely with each bond formation lowering the energy required for the next in a concerted cascade effect.

\textbf{Scheme 1-10:} The cationic Scholl mechanism for the oxidative dehydrogenation of hexaphenylbenzene.

In the case of the N-HSB systems, nitrogen atoms in the periphery increase the possibility of the formation of stable, partially cyclised systems such as N-1/2HSB I.5. There are three factors contributing to this: (i) protonation of the nitrogen atoms makes the pyrimidine rings more electrophilic, such that cationic bond formation involving pyrimidines are easier than those involving only phenyl groups. (ii) The nitrogen-protonated PAH core is a poor nucleophile making it difficult for it to attack ortho phenyl groups. (iii) The basicity of the pyrimidine nitrogens makes the protonation of the phenyl groups more difficult, again hindering the formation of bonds not involving the pyrimidine rings.
The conditions employed for cyclodehydrogenation to give HBC compounds are similar to those used for Friedel-Crafts reactions. In recognition of this, Rathore and Burns have shown that cyclodehydrogenation can be combined with Friedel-Crafts alkylation to give substituted HBC systems in high yields (Scheme 1-11).

(i) \text{tBuCl, FeCl}_3, \text{MeNO}_2, 22^\circ\text{C}

Scheme 1-11: Synthesis of a substituted HBC reported by Rathore and Burns.\textsuperscript{41}

1.3.2 Oxidation of thiophene systems

The oxidative polymerisation of thiophene has been widely reported using a number of metal catalysts including magnesium,\textsuperscript{42} nickel\textsuperscript{43} and palladium;\textsuperscript{44} however the best results are observed using iron trichloride.\textsuperscript{45} One of the reasons for the prevalence of iron in thiophene polymerisations is the high percentage (>80%) of head to tail thiophene linkages formed with thiophenes that are mono-substituted at the 3-position. Polymers with these linkages have been found to be more crystalline and to have better electron transport properties than irregular ones. Upon oxidation the polymerisation goes via a radical pathway. Depending on the orientation of the thiophene cation radicals to each other, three isomers of the dimer are possible, head to tail, head to head and tail to tail (Scheme 1-12).
In the case of aluminium trichloride, oxidation of thiophene results in the formation of irregular polymers in which thiophene, terthiophene and carbon linkages resulting from thiophene desulfurisation are present.\textsuperscript{47} This is due to the interactions between aluminium and the sulfur-carbon bonds on the thienyl ring, leading to the extraction of the sulfur. Thienyl oxidations using aluminium trichloride are uncommon due to the lack of control over the products and the gaseous hydrogen sulfide by-product formed.

Hohne and Spange investigated the reactivity of poly(2-vinylthiophene) under oxidative conditions (Scheme 1-13). Here only one orientation of product is possible and it was found that four equivalents of iron trichloride is enough to completely form the cross linked polymer in a quantitative yield.\textsuperscript{46}
The oxidation of thiophene systems in which polymerisation positions have been blocked in order to promote the formation of large sulfur-containing polycyclic aromatics has been examined by Tovar et al.\textsuperscript{48} Firstly the relative reactivity of the different positions on the thiophene ring were examined through the oxidation of I.22 which can undergo either a 2,2’ intramolecular oxidation to give I.23, a 4,4’ intramolecular oxidation to give I.24 or a 2,4’ intramolecular oxidation to give I.25.

![Scheme 1-14: The possible oxidation products of I.22 studied by Tovar.\textsuperscript{48}](image)

In this system only I.23 was found to be formed (in a 93\% yield) indicating that the 2,2’ intramolecular oxidation is the most favourable. The electrochemical oxidation product formed from I.22 shows similar electrochemical properties to the chemically formed product I.23.

In order to examine if the 3-position on the thiophene will undergo intramolecular oxidative bond formation two compounds I.26 and I.27 were prepared. These were found to oxidise with iron trichloride to give the intramolecularly fused compounds I.28 and I.29 in which phenyl-thienyl carbon-carbon bonds have been created (Scheme 1-15). Although in both cases oxidation occurred, it was found to require a significant excess of iron trichloride to drive the cyclisation due to the more demanding oxidation positions involved.
The reactivity of thiophenes towards carbon-carbon bond formations has been exploited in a number of synthetic procedures. In the work of Larsen and Bechgaard intramolecular thiophene oxidation has been used in the preparation of thiaheterohelicenes. This method has been found to be more efficient than the classic iodine cyclisation method as either the cis or trans ethylene can be used as the reagent (Scheme 1-16).

In the work of Zhou et al. a π-extended benzothiophene containing six sulfur atoms has been prepared via a thienyl oxidation (Figure 1-17). Using this compound an individual organic field effect transistor wire, with carrier mobility suitable for commercial applications has been synthesised.
1.4 Ligands containing thiophene

1.4.1 Bidentate ligands containing thiophene

In the study of metal coordinating systems a number of sulfur containing ligands have been coordinated to metal centres. As discussed in section 1.2 thiophene systems can coordinate to metal centres $\eta^1$ through the sulfur, $\eta^2$ through two carbon atoms, $\eta^4$ through all four carbons and $\eta^5$ through the entire ring. The incorporation of thiényl units into bidentate and tridentate ligands restricts the possible coordination modes available. This is due to the availability of stronger coordinations to other parts of the ligands (such as pyridyl nitrogens) controlling the coordination and the effect of the increased steric bulk on the ligands. As such only metal-sulfur $\eta^1$ coordination or metal-carbon bond formation have been observed for these ligands.
Two of the simplest systems are compounds $\text{I.30}$ and $\text{I.31}$ in which a single thiophene moiety is connected to another group such as pyridine or benzene.

\[ \text{I.30} \quad \text{I.31} \]

In the examination of metal complexes of $\text{I.30}$ two coordination modes are observed (Figure 1-7).

\[ \text{Figure 1-7: The two bidentate metal coordination modes seen for I.30.} \]

In the first the ligand coordinates through an $\eta^1$ lone pair donation from both the sulfur on the thiophene and the nitrogen on the pyridine. In the other the metal is bonded to the thiophene through the carbon at the 3-position, while the pyridine is still coordinated $\eta^1$ through nitrogen. For ligand $\text{I.30}$ cyclometallation is more common with complexes observed for a variety of metals including rhodium$^{51}$, platinum$^{52-53}$, palladium$^{54}$ and ruthenium$^{55}$.

In the work of Amari et al. a copper complex containing two coordinated 2-(2’-thienyl)pyridine ligands $\text{I.32}$ was formed and compared to the equivalent bipyridyl ligand $\text{I.33}$ (Figure 1-8).$^{56}$

\[ \text{Figure 1-8: The two thienyl coordinated copper complexes prepared by Amari.}^{56} \]
Again as in the case of $\eta^1$ thiophene, the sulfur coordinates out of the plane of the thiophene, with an observed angle between the Cu-S bond and the plane of the thiophene ring of 28.3(1)$^\circ$ compared to 7.5(1)$^\circ$ for the pyridine equivalent I.33. Also of note is the metal-sulfur distances in I.32 of 2.968(2) and 2.904(1) Å, these values are well outside the range seen for Cu-S single bonding (2.39 Å) and indicate that a $\eta^1$ coordination mode is present in I.32.

The iridium (III) complex I.34 in which three ligands of I.30 have been coordinated has been prepared by McGee and Mann. In this complex two of the ligands are cyclometalated through the thiophene while the third is coordinating through both the nitrogen and the sulfur. In this work it was noted that upon heating the complex to 90°C it rearranged to give the tris cyclometalated species I.35.

![Figure 1-9: The two thienyl coordinated iridium(III) complexes prepared by McGee and Mann.](image)

For 2-phenylthiophene I.31 only one example of a $\eta^1$ coordinated thiophene is reported. This is for the iridium (III) complex I.36 synthesised by Ren et al. Again as observed for ligand I.30 the metal-sulfur bond lies out of plane of the thiophene ring indicative of an sp$^3$ hybridised sulfur atom.
1.4.2 Tridentate ligands containing thiophene

Ligands containing three coordinating units, based on terpyridine (tpy) have been investigated due to the ease with which they can coordinate strongly to metal centres. As a part of this a number of tridentate systems in which one or two of the coordinating parts of the molecule are thiophene based have been prepared. The three main examples of this are I.37, I.38 and I.39 (Figure 1-11).

The reactivity of 6-(2-thienyl)-2,2'-bipyridine I.37 towards a series of metals was studied by Constable et al. As a result of the presence of two strongly coordinating nitrogens along with the weakly coordinating sulfur a number of possible coordination modes are observed in its d\textsuperscript{8} metal complexes (Figure 1-12).

Figure 1-12: Examples of the different coordination modes observed for I.37 with d^8 metal centres.\textsuperscript{60}

Reaction of I.37 with ruthenium trichloride gives the tris coordinated complex I.40 in which the weak η^1 S-coordination can be displaced by a coordinating solvent such as dimethylformamide to give the solvent coordinated complex I.41 (Scheme 1-18).

Scheme 1-18: The tris coordinated ruthenium(III) complexes studied by Constable.\textsuperscript{60}

When I.37 is reacted with ruthenium(terpyridine)trichloride it gives the complex I.42. The thienyl coordination of this complex can be reversibly changed between η^1 sulfur and orthometallation via the carbon at the 3-position on the thiophene, by the addition of weak acid or base (Figure 1-13).\textsuperscript{61}
I.38 and I.39 were reacted with a series of metals by Constable et al. and found to have metal-dependent behaviour. Upon reaction with K$_2$[PtCl$_4$] both I.38 and I.39 gave the $\eta^1$ sulfur coordinated complexes I.43 and I.44 (Figure 1-14).

Interestingly neither I.38 nor I.39 coordinated to gold, instead they both dimerised in the presence of Na[AuCl$_4$] to give I.45 and I.46 (Figure 1-15).
1.5 Polythiophenes

1.5.1 Introduction to polythiophenes

There are a large number of literature reports describing the properties of thienyl systems. In part this is due to the ease with which they can form polymeric products. Work in this area has been directed towards the preparation of monomers which contain multiple thiophene units. This is because of the increased solubility of polymers formed from multi-thiophene monomers; the starting material already contains exclusively 2-2’ linkages thus decreasing the percentage of 2-3’ defects in the polymer. The increased number of possible substitution sites on multi-thiophene monomers also allows for the properties of the polymers to be synthetically varied with greater ease than when monothienyl monomers are used.\cite{63-64}

In the work of Brocks, the properties of a series of thiophene based polymeric systems were studied using DFT calculations.\cite{65} Polymers which could be formed from the oxidation of thiophene monomers substituted in the 3- and 4- positions were modelled (Figure 1-16).

![Figure 1-16: Some of the thiophene polymers modelled using DFT methods by Brocks.\cite{65}](image)

It was found that there are two possible electronic arrangements between thiophene units in the polymer, in the first (aromatic) each thiophene retains its electronic structure, bonding to the next through a sigma-bond. In the second (quinoid) the aromaticity of the thiophene is lost and instead pi-bonds are formed between adjacent thiophenes in the polymer.
Figure 1-17: The aromatic and quinoid forms of thiophene based polymers.

Although most thiophene polymers are of the aromatic form it is possible to generate quinoid polymers. Polymerisation always occurs so as to maximise the bandgap of the polymer; in the case of phenyl substituted thiophene monomers (Figure 1-17, R = Ph) the system is found to exclusively favour the aromatic form. Further DFT calculations on aromatically substituted thiophene polymers have been carried out by Kwon. These concluded that for polymers containing a small number of thiophene units (less than eight) an increase in the steric bulk of the substituents on the monomer results in an increase in the steric strain observed in the polymer. This causes a decrease in the planarity of adjacent thiophene units and a decrease in the quinoid character of the polymer. For larger polymers (greater than eight thiophene units) the size of the substituents has less effect as the planar quinoid form is favoured due to an increase in electron delocalisation leading to enhanced stability.

1.5.2 Monomers containing two or three conjugated thiophenes

Monomers containing multiple $\pi$-conjugated thiophene units that allow for the development of polymeric systems in which the properties can be easily tuned have been reported. By using such monomers the number of defects in the polymer, resulting from irregular conjugations of monomers can be minimised. Also the oxidation potential required for electrochemical polymerisation decreases with increasing monomer conjugation length leading to easier polymer formation along with a decrease in the number of unwanted side reactions. One disadvantage of conjugated systems is the lower cation lifetime observed resulting in a decrease in the molecular weight of the polymer formed. Two of the most common frameworks that are used are bithienyls in
which two thiophene units are present and terthienyls containing three thiophene units (Figure 1-18).

![Figure 1-18: Bithienyl and terthienyl monomers for electrochemical polymerisation.](image)

Bithiophene (Figure 1-18, \( R = \text{H} \)) was the first multi-thienyl derivative to be successfully polymerised by Diaz in the late 1980’s.\(^68\) Its derivatives still used in polymerisation reactions due to the low oxidation potential required and the high conductivity of the polymers formed. In the work of Lambert and Ferraris it was discovered that substitution on the bridging carbon of bithienyl with an electron-withdrawing group, such as the ketone in \( \text{I.47} \), decreases the aromaticity of the system.\(^71\) This results in the formation of a quinoid type polymer with a bandgap lower than those observed for other polythiophene systems, while having little effect on the oxidation potential required for polymerisation. By changing the electron withdrawing effect of the substituents on the bridging carbon the bandgap can be tuned effectively. Another advantage of bithienyl systems is that they allow for tuning of the physical properties of the polymers formed, for example in the case of \( \text{I.48} \) developed by Roncali the polymer formed is soluble in aqueous media unlike polythiophene or poly(bithiophene).\(^72\)

![Figure 1-19: Bithienyl systems \( \text{I.47} \) and \( \text{I.48} \).](image)

Unlike bithienyls, terthienyls are not as useful in developing systems in which the polymer properties are easily tunable; however the polymers that are formed from terthienyls monomers allow for theoretical studies of polymerisations. By varying the
substituents on the middle thiophene, terthiophenes are used to examine the effects of concentration, pH and solvent on polymerisations.\textsuperscript{69-70} The major disadvantage of terthienyls systems is their low reactivity during polymerisation leading to the formation of polymers with much smaller molecular weights than those formed from mono-thienyl monomers.

\section*{1.5.3 Metal conjugated thiophene polymers}

Metal-conjugated polymers are ones in which a metal centre has been connected to the backbone of the polymer.\textsuperscript{73} One of the more successful systems in which metals have been incorporated uses thiophene polymers as the backbone, because of the ease with which they can be prepared and the high thermal stability of the polymers formed.\textsuperscript{74} The insertion of a metal into the polymer results in the coupling of the properties of the metal with those of the polymer backbone; metal-containing polythiophenes are classified based upon the location of the metal group (Figure 1-20).\textsuperscript{74}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{three_types_of_conjugated_polymer.png}
\caption{The three types of conjugated polymer.\textsuperscript{74}}
\end{figure}

In type I polymers there are pendent metal centres and an electronically insulating connecting group between the metal and the polymer backbone. Type II polymers have direct interaction between the metal centres and the polymer while type III polymers contain the metal in the backbone. Type III thienyl polymers are of great interest due to
the possible interaction of the metal with the delocalised $\pi$-electrons present in the polymeric system.

Direct metal-carbon bonded thienyl polymers $\mathbf{I.49}$ have been prepared by Hockemeyer et al. where germanium and tin are bridged by a bisthiophene (Figure 1-21).$^7$ From these materials low molecular weight polymers have been formed which absorb between 250-330 nm with no absorption observed in the visible region. Potential applications of these systems in photochemical devices have been proposed due to the small window of absorption wavelengths available. In the work of Lin et al. ferrocene capped palladium and platinum complexes with thiophene spacers have been prepared (Figure 1-21, $\mathbf{I.50}$). Examination of both the electrochemical reactivity and the $\pi \rightarrow \pi^*$ bands in the absorption spectra of these complexes shows an increase in charge transfer between the iron and palladium/platinum centres as a result of the thiophene bridge.$^7$

![Figure 1-21: Examples of direct metal-carbon conjugated polymers prepared by Hockemeyer$^7$ and Lin.$^7$](image)

The electron transport properties of thiophene allow for the synthesis of metal coordination ligands in which two coordination sites can be attached through a thienyl (or polythienyl) linker, allowing for increased interactions between metal centres. In the thienyl linked bipyridyl ligand $\mathbf{I.51}$ and the bipyridyl-thienyl polymer $\mathbf{I.52}$ (Figure 1-22) the absorption spectra of the ligands show a red shift in the thienyl $\pi \rightarrow \pi^*$ bands compared to thiophene and polythiophene indicating delocalisation of the thiophene electrons into the pyridine rings.$^7$ For the ruthenium complexes of $\mathbf{I.53}$ and $\mathbf{I.54}$ (Figure 1-22) a red shift is observed in the absorption spectrum; however no metal-metal
interactions could be observed in either the photochemical or electrochemical studies of the complex.

The mono and di bisthenyl containing ligands 1.55 and 1.56 and their ruthenium complexes have been prepared by Zhu and Swager, these complexes were then electropolymerised to form films, the conductivity of which was found to be higher than those of unmetallated films.

One problem with ruthenium tris-bipyridine coordination is the formation of diasteroisomers. This can lead to the formation of irregular linkages upon polymerisation decreasing the control over the properties of the polymers formed. This is
where terpyridine ruthenium complexes can offer an advantage. Using terpyridine (tpy) to coordinate to the metal Constable et al. have prepared a series of ruthenium and osmium di-metallic species containing a thienyl linker **I.57 - I.59**. Using this system the interaction of two adjacent metal centres has been investigated and the potential for the use similar systems in polymers explored.

![Diagram of terpyridine ruthenium complexes](image)

**Figure 1-24:** Thiophene linked terpyridine ruthenium complexes prepared by Constable.

The addition of the thiophene ring to the terpyridine ligand results in an increase in the luminescence lifetime and efficiency compared to \([\text{Ru(tpy)}_2]^{2+}\) as a result of increased conjugation. In the mixed ruthenium osmium complex **I.59** time resolved luminescence shows energy transfer between the two metal centres. The mono-terpyridine-thiophene ligand **I.60** and its ruthenium complexes have been prepared and electropolymerised by Hjelm et al. however no metal-metal interactions were observed in the polymers by cyclic voltammetry.

![Diagram of monothiophene terpyridine ligand](image)

**Figure 1-25:** The mono-thiophene substituted terpyridine ligand prepared by Hjelm.

In order to prepare systems in which the metal centre is directly coordinated to the thienyl polymer Wolf and co-workers have developed a system in which a phosphine substituent
is present on the oligothiophene backbone I.61. This allows bidentate coordination of a metal to the polymer. Upon reaction of I.61 with palladium dichloride, two complexes are formed depending on the metal: ligand ratio used I.62 and I.63 (Scheme 1-19). Both of these were found to electropolymerise to give thin films, which have been shown by energy dispersive X-ray analysis, to have the same palladium: sulfur ratio in the polymer as in the monomer.

\[
\begin{align*}
\text{(i) } & 1 \text{ eq. PdCl}_2; \hspace{1cm} \text{(ii) } 0.5 \text{ eq. PdCl}_2; \hspace{1cm} \text{(iii) AgBF}_4, \text{NH}_4\text{PF}_6
\end{align*}
\]

**Scheme 1-19:** The synthesis of oligothiophene coordinated palladium complexes I.62 and I.63.

The ruthenium coordinated oligothiophene has also been prepared by Wolf (Scheme 1-20). This complex is first formed as the unstable $\eta^1$ coordinated species which undergoes deprotonation in the presence of base to give the orthometallated complex I.65.

\[
\begin{align*}
\text{(i) } & \text{NaOH, MeOH, -HPF}_6
\end{align*}
\]

**Scheme 1-20:** The synthesis of oligothiophene coordinated ruthenium complex I.64.
Neither 1.64 nor any longer oligothiophene derivatives were found to undergo electropolymerisation and the absorption spectrum shows a dependence upon the length of the conjugated oligothiophene. EPR experiments on 1.64 and its derivatives show that the HOMO is of mixed metal-oligothiophene character with decreasing metal contribution as the oligothiophene increases in size, while the LUMO remains bipyridyl-based. The first oxidation of 1.65 occurs on the oligothiophene and has been monitored spectroelectrochemically. A thienyl based SOMO → LUMO, \( \pi \rightarrow \pi^* \) absorption is observed to appear with increasing lifetime as the oligothiophene length increases. This indicates that the oligothiophene cation undergoes a charge transfer to the bipyridyl based LUMO preventing polymerisation of the system.

### 1.6 Conclusion

The nitrogen-hexabenzocoronene systems which have been prepared previously within the group offer enormous potential as opto-electronic devices due to their extended electron distributions. By incorporating thienyl units into the polyphenylene precursors the development of new products with desirable photochemical and electrochemical properties were anticipated. The multiple coordination modes possible for simple thienyl systems indicate that a number of metal to S-polyphenylene and metal to S-hexabenzocoronene coordinations are possible. The recent development of bidentate and tridentate ligands containing thienyl units show that in complex systems thienyl units will tend towards \( \eta^1 \) coordination either through sulfur lone pair donation or \( \text{via} \) the formation of metal-carbon bonds to carbon atoms on the thiophene. This thesis details efforts to prepare sulfur-containing HBC and polyphenylenes through the incorporation of thienyl units. The development of sulfur containing HBC systems in which the sulfur atoms can potentially coordinate to metal centres is described.

Thiophene substituents have been shown to have a number of potential applications in materials chemistry. Systems based upon dithienyl units have been shown to undergo photochemically reversible molecular switching; the incorporation of these substituents
into simple polyphenylenes was investigated. Substitution of aromatic systems with thienyl groups leads to variations in the reactivity patterns and changes in the properties of the compounds formed. The development of both polyphenylene and tetrazine systems in which thienyl moieties have been incorporated in order to exploit these changes is discussed in this work.

Upon oxidation thiophene containing ligands are generally found to form polymers. Using existing methods of thiophene polymer formation, the oxidation of sulfur polyphenylenes was carried out. Although thiophene incorporation is predicted to lead to multiple intermolecular bond formations, the effect of changes in the substituents on both the extent of polymer formation and the properties of the polymers formed would be of interest. By using these reactions thienyl monomers based upon existing HBC frameworks have been prepared and oxidised in order to prepare polymeric systems.

1.7 References


58 Ren, X.; Giesen, D. J.; Rajeswaran, M.; Madaras, M. Organometallics 2009, 28, 6079-6089.

Part 2: Synthesis and cyclotrimerisations of thiophene acetylenes
2.1 Introduction

This chapter describes the synthesis and characterisation of a series of tri-thienyl polyphenylenes prepared via cyclotrimerisation of the appropriate thienyl acetylenes. The effect of varying the position of thiophene substitution, along with changes in the other substituent on the acetylene, on the ratios of the possible polyphenylene isomers formed was studied.

The reactivity of acetylenes towards metal-catalysed trimerisations is well known in organic synthesis and has been extensively studied in recent years. A number of different metal catalysts, (Cr, Dy, Fe, Ni, Pd and Ru)\(^1\)\(^-\)\(^4\) have been used to promote \([2 + 2 + 2]\) cyclotrimerisations; however the best yields for aromatically substituted acetylene trimerisations are obtained using either rhodium\(^5\) or cobalt\(^6\) catalysts. Of these cobalt based trimerisation catalysts have been the main focus of investigations.\(^6\)\(^,\)\(^8\)\(^,\)\(^10\) This is due to a number of factors including their low cost relative to other metals, the ease with which the catalyst can be removed from the reaction mixture and the high product yields compared to other systems, particularly in intramolecular trimerisations.

The mechanism for alkyne trimerisation as reported by Collman\(^7\) in 1980 is shown in Scheme 2-1. In this, two alkynes displace two of the ligands on the metal to give the \(\pi\)-coordination system \(a\); these then undergo an oxidative coupling to give the metallacyclopentadiene \(b\) in which the oxidation state of the metal is now two units higher than the precursor. A third acetylene then coordinates to the metal centre to give the highly reactive intermediate \(c\). This can then undergo either a Diels-Alder reaction to give the norbornadiene equivalent \(d\) or an alkyne-insertion to give the metallacycloheptatriene \(e\).
Part 2: Synthesis and cyclotrimerisations of thiophene acetylenes.

Scheme 2-1: The general mechanism for metal-catalysed alkyne trimerisation.

Computational calculations for the relative stabilities of the intermediates in this mechanism indicate\(^{6,8}\) that there are two possible routes to the phenyl product dependent on the reactivity of c. Although isolated examples of a, b, d and e have been widely observed no characterised versions of an alkyne coordinated metallacyclopentadiene of type c has been reported in the literature.

The construction of organic systems in which two of the acetylenes to be trimerised are linked intramolecularly, has allowed for the use of trimerisation in the synthesis of complex organic and medicinal compounds. In the synthesis of the natural hormone estrone, a cobalt catalyst is used to generate the Diels-Alder adduct which upon reaction produces the required compound with the correct stereochemistry (Scheme 2-2).\(^9\)

Part 2: Synthesis and cyclotrimerisations of thiophene acetylenes.

Upon trimerisation of an asymmetric acetylene two isomers of the polyphenylene product can be formed. In the symmetric (sym) isomer a C$_3$ rotational axis of symmetry is present while in the antisymmetric isomer (anti) no such rotational symmetry axis exists. Looking at the possible products of the trimerisation (Scheme 2-3) we see that four arrangements are possible; however for three of these the products formed are identical and as such we expect to observe a 1:3 ratio of the sym: anti products in the reaction mixture.

![Scheme 2-3: The symmetric and antisymmetric isomers formed from the trimerisation of an asymmetric alkyne.](image)

In the literature a number of studies into the effect on the sym: anti ratio caused by a change in the experimental setup have been carried out. The reaction is dependent on solvent, temperature, the ligands attached to the metal precursor, the size of the substituents on the alkyne being trimerised and the presence of any other metals in the reaction mixture. In recent publications Sigman and co workers\textsuperscript{10} have developed cobalt catalysts which can give trimerisation in aqueous media.

By varying the acetylene substituents ($R_1$ and $R_2$ in scheme 2-3) Hilt and co workers\textsuperscript{11-13} have shown that if they are both similar in size and electronic character the reaction tends towards the expected ratio of 1:3; however if the two substituents are different in nature then the relative concentration of the anti isomer increases.
Table 2-1: Effect of changes of the acetylene substituents on the sym:anti ratio observed after trimerisation using CoBr$_2$(Cy-dimine) and Zn dust in CH$_3$CN for 15 hr at 80ºC.$^{11}$

<table>
<thead>
<tr>
<th>Acetylene used</th>
<th>Sym: Anti ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Et Me</td>
<td>1: 3.5</td>
</tr>
<tr>
<td>Et CO$_2$Me</td>
<td>1: 6.1</td>
</tr>
<tr>
<td>nBu</td>
<td>1: 11.5</td>
</tr>
<tr>
<td>Me Ph</td>
<td>1: 24</td>
</tr>
</tbody>
</table>

Also in this work Hilt has studied the effect of increasing the size of a supporting nitrogen donor ligand on the metal catalyst, on the ratios of products observed (Figure 2-1).

![Figure 2-1: Catalysts used in the study of ligand effect (trimerisation conditions CoBr$_2$(L) and Zn dust in CH$_3$CN for 1 hr at 80ºC).][12]

An increase in the bulk of the ligand L results in an increase in the relative concentration of the antisymmetric isomer formed, with a ratio of 1: 7.0 for n-butyl (a) increasing to 1: 11.9 in the case of i-propyl (b), further increasing to 1: 29.0 (c) for t-butyl and 1: 31.1 (d) for biphenyl ligands. The effect of ligand size on the products formed is indicative of the trimerisation of acetylenes going via the norbornadiene-type intermediate in the reaction mechanism. This is the route expected for aromatically substituted alkynes.$^6$ As the norbornadiene-like intermediate is more sterically hindered at the two quaternary positions (Figure 2-2 *) the alkynes will trimerise in such a way as to minimise the hindrance at these positions. If the substituents on the alkyne are significantly different the smaller of the two will take up the quaternary positions (*) and as a result the antisymmetric isomer of the trimerised product is favoured.
2.2 Asymmetric thienyl-phenyl acetylenes

2.2.1 Preparation of the asymmetric acetylene derivatives

In this work a series of 3-thienyl (1-3) and 2-thienyl (4-6) phenylacetylenes with increasingly bulky para substituents on the phenyl ring have been prepared via a Sonogashira\textsuperscript{14} coupling.

\[ \text{Fc} = \text{Ferrocene} \]
Part 2: Synthesis and cyclotrimerisations of thiophene acetylenes.

(3-thienyl)phenylacetylene 1 and (2-thienyl)phenylacetylene 4 were synthesised via the palladium catalysed coupling of the relevant bromothiophene with commercially available phenylacetylene. Both were easily separated from the reaction mixture by column chromatography using hexane as the eluent ($R_f = 0.8$ in both cases) in good yields (1, 66%, 4, 58%).

\[
\begin{align*}
\text{(i) 3-bromothiophene (1, 2, 3)/2-bromothiophene (4, 5, 6), Benzene, CuI, Pd(PPh_3)_4, NaOH.}
\end{align*}
\]

Scheme 2-4: Sonogashira coupling of phenylacetylene and bromothiophenes.

The $^1$H NMR spectrum of 1 (Figure 2-3), shows the distinctive splitting pattern for a thiophene substituted at the 3 position, with a set of three correlated doublet of doublets each integrating for one proton at $\delta$ 7.63, 7.35 and 7.30 ppm with coupling constants $^4J_{2,4} = 1.0$, $^4J_{2,5} = 3.0$ and $^3J_{4,5} = 5.0$ Hz. The phenyl signals have the expected splitting pattern with signals integrating for the two ortho protons at $\delta$ 7.61 ppm and the two meta protons overlapping with the para proton at $\delta$ 7.42 ppm. The two signals in the $^{13}$C NMR spectrum at $\delta$ 88.6 and 84.3 ppm have been assigned to the acetylene carbons. Further evidence of acetylene formation is seen in the IR spectrum with the $\nu$(C≡C) visible at 2203 cm$^{-1}$.
The $^1$H NMR spectrum of 4 has been previously reported,\textsuperscript{15} here the spectrum is similar to that of 1 with a shift in the position of the thienyl signals to $\delta$ 7.37, 7.35 and 7.10 ppm. The thienyl splitting has changed to $^3J_{3,4} = 3.5$, $^4J_{3,5} = 1.0$ and $^3J_{4,5} = 5.0$ Hz resulting from the change in the position of the sulfur from 3- to 2-. In the $^{13}$C spectrum the acetylene carbons are present at $\delta$ 93.3 and 82.9 ppm while in the IR spectrum the v(C≡C) is seen at 2200 cm$^{-1}$. Both 1 and 4 were also characterised via electrospray mass spectrometry in acetonitrile and gave results of 108.0415 m.u. (1) and 108.0426 m.u. (4) with a calculated value of [M+H]$^+ = 108.0425$ m/z for both compounds.

The para-tert-butylphenyl-thienyl acetylenes (4-tert-butylphenyl)(3-thienyl)acetylene 2 and (4-tert-butylphenyl)(2-thienyl)acetylene 5 were prepared from coupling of the relevent bromothiophene with commercially available 4-tert-butylphenylacetylene. Both were separated from the reaction mixture by column chromatography using hexane as the eluent (R$_f$ = 0.8 for 2, 0.7 for 5) to give the acetylenes in good yields (2, 72%, 5, 64%).

The $^1$H NMR spectra of 2 (Figure 2-4) shows the standard splitting pattern for a 3-substituted thiophene as observed in 1 with three thiophene signals each integrating for one at $\delta$ 7.55, 7.33 and 7.26 ppm along with two phenyl signals each integrating for two hydrogens and having $^3J_{9,10} = 8.0$ Hz at $\delta$ 7.52 and 7.42 ppm. The $^1$H NMR also shows a signal integrating for nine protons at $\delta$ 1.38 ppm for the tertiary butyl group. The acetylene can be seen both in the $^{13}$C NMR with signals at $\delta$ 88.6 and 84.5 ppm and in the IR spectrum with a C≡C stretch at 2200 cm$^{-1}$.

![Figure 2-4](https://example.com/figure2-4.png)

*Figure 2-4*: The $^1$H NMR spectrum of 2 (400 MHz, CDCl$_3$, 25°C).
Part 2: Synthesis and cyclotrimerisations of thiophene acetylenes.

The $^1$H NMR spectrum of 5 is as expected with a set of three thienyl protons splitting for a 2-substituted thiophene as seen in 4 at $\delta$ 7.30 (2 overlapping signals) and 7.04 ppm. The phenyl signals can be seen each integrating for two protons at $\delta$ 7.48 and 7.39 ppm while the tertiary butyl group is seen integrating for nine protons at $\delta$ 1.36 ppm. The $^{13}$C NMR shows the acetylene carbons at $\delta$ 92.8 and 81.5 ppm and the IR spectrum shows the acetylene stretch at 2200 cm$^{-1}$.

To synthesise the 4-ferrocenyl substituted acetylenes first 4-ethynylphenylferrocene 7 was prepared from ferrocene by a modified version of the Rosenblum method (Scheme 2-5).$^{16-17}$

Ferrocene was oxidised to ferrocenium with concentrated sulfuric acid and the mixture was added to water, this was then added to a solution of sodium nitrite and 4-aminoacetophenone in water at 0°C and then copper powder was added to give, on workup 4-acetylphenylferrocene. This was treated with phosphorous oxychloride to yield $\alpha$-chloro-$\beta$-formyl-$\beta$-ferrocenylnstyrene, which was heated in a basic solution to give 7 in a 93% yield. The overall yield obtained was higher than that observed by Roberts$^{17}$ as result of increasing the reaction times used in parts (ii) and (iii) of the synthesis. The $^1$H NMR spectrum of 7 showed two coupled phenyl signals of $^3$J$_{HH} = 8.5$ Hz appearing at $\delta$ 7.48 and 7.43 ppm, one ferrocenyl signal integrating for five protons at $\delta$ 4.07 ppm and two ferrocenyl signals integrating for two protons each at $\delta$ 4.71 and 4.40 ppm. The alkyne signal integrating for one proton resonates at $\delta$ 3.19 ppm.
Part 2: Synthesis and cyclotrimerisations of thiophene acetylenes.

Coupling of 7 with 3-bromothiophene gave 4-(3-thienyl)ethylphenylferrocene 3 which was purified using column chromatography with hexane: dichloromethane (3:1, R_f = 0.6) in an 85% yield. ^1H NMR analysis of 3 (Figure 2-5) shows the same phenylferrocene pattern as was observed in 7 with one ferrocenyl signal integrating for five protons at δ 4.07 ppm and two ferrocenyl signals integrating for two protons each at δ 4.69 and 4.38 ppm.

The two phenyl signals overlap and appear as a singlet integrating for four protons at δ 7.47 ppm and the characteristic three signals for a substituted thiophene at the 3-position appear at δ 7.55, 7.33 and 7.24 ppm. The ^13C NMR spectrum shows the acetylene carbons at δ 84.1 and 83.8 ppm and the C≡C stretch can be seen in the IR spectrum at 2208 cm\(^{-1}\).

Coupling of 7 with 2-bromothiophene gave 4-(2-thienyl)ethylphenylferrocene 6 which was purified using column chromatography with hexane: dichloromethane (3:1, R_f = 0.5) in an 80% yield. Again the three ferrocene signals are seen in the ^1H NMR spectrum at δ 4.71, 4.39 and 4.08 ppm along with a set of three characteristic 2-substituted thiophene peaks at δ 7.33, 7.32 and 7.06 ppm and the two overlapping phenyl signals at δ 7.49 ppm.
Part 2: Synthesis and cyclotrimerisations of thiophene acetylenes.

Figure 2-6: The $^1$H NMR spectrum of 6 (400 MHz, CDCl$_3$, 25°C).

The acetylene carbons can be seen in the $^{13}$C NMR spectrum at δ 84.2 and 82.7 ppm and the C≡C stretch can be seen in the IR spectrum at 2216 cm$^{-1}$.

2.2.2 Solid-state characterisation

Single crystal X-Ray structures of 3 and 6 were obtained by slow evaporation of saturated dichloromethane / methanol solutions of the compounds. Due to the crystal mounting moving during the collection of 3 only some of the collected hemispheres were used in solving the data. As a result of this both the wR$_2$ (0.27) and the R$_{int}$ (0.25) values were high and could not be reduced any further. A R$_1$ value of 0.11 was obtained and the structure is consistent with the expected product and the NMR and mass spectral data observed.

Both 3 and 6 crystallise in the monoclinic space group P2$_1$/c and consequently are very similar each with four molecules in the asymmetric unit cell.
Part 2: Synthesis and cyclotrimerisations of thiophene acetylenes.

2.2.3 Trimerisation of asymmetric thienyl-phenyl acetylenes

Each of the six thienyl-phenyl acetylenes 1, 2, 3, 4, 5 and 6, described earlier (§ 2.2) were reacted with dicobalt octacarbonyl in refluxing dioxane to give after three days a mixture of isomers of cyclotrimerised products. In general the yields of the 3-thienyl trimerisations were higher than those of the 2-thienyl substituted equivalents. Isolation of a mixture of the two phenylene products was possible by column chromatography using dichloromethane: hexane (1:1) as the eluent (R_f between 0.7 and 0.5); however unlike in some other systems reported\(^{18}\) it was not possible to separate the two isomers chromatographically. This is due to the thienyl substituents which greatly increase the rate of flow of the products. Indeed separation of cyclotrimerisation isomers is best achieved in systems containing substituents, such as methoxy groups, which are known to slow the flow rate in the chromatography of polyphenyl systems.\(^ {18}\)
As a result of the inability to separate the sym and anti isomers of the products, *in situ* interpretation of the spectroscopic data was required. Looking at the $^1$H NMR spectrum of the cyclotrimerised product of 4-(2-thienyl)ethylphenylferrocene 3 to give the mixture of polyphenyl isomers 8 (Figure 2-10), a number of interesting features can be observed. Firstly looking at the cyclopentadienyl region of the spectrum (Figure 2-9) a total of eight signals can be seen.

![Figure 2-9: The cyclopentadienyl region of the $^1$H NMR spectrum of 8 (400 MHz, CDCl$_3$, 25°C).](image)

Four sharp signals each integrating for 15 protons are observed at $\delta$ 3.95, 3.94, 3.91 and 3.90 ppm, the position of these peaks indicates that these are the ferrocene cyclopentadienyl rings which remain unsubstituted (Figure 2-10, green). In the trimerisation of the precursor acetylene 3 to give 8, a 1:3 ratio of the symmetric:antisymmetric isomer is predicted. As such a three times excess of the antisymmetric isomer (Figure 2-10, 8a) in which all three unsubstituted cyclopentadienyl rings are inequivalent, over the symmetric isomer (8s) is expected; however in the symmetric isomer a C$_3$ axis of symmetry is present so the three unsubstituted cyclopentadienyl rings are equivalent in NMR analysis. As such three of the four signals for the unsubstituted cyclopentadienyl rings, represent the antisymmetric isomer (each having 5 protons for an integration of 15 each due to the reaction ratio) and the fourth the symmetric one (with 5 protons for each ring for an integration of 15 due to the symmetry of 8s).
Part 2: Synthesis and cyclotrimerisations of thiophene acetylenes.

![Image of isomers 8s and 8a]

**Symmetric** 1: 3 **Antisymmetric**

*Figure 2-10:* The two isomers 8s and 8a of the trimerised product 8.

Along with the unsubstituted ferrocene cyclopentadienyl rings four broader cyclopentadienyl signals can be seen at δ 4.60, 4.53, 4.27 and 4.21 ppm each integrating for 12 protons. Further examination of these peaks via TOCSY NMR shows there are two sets of mono-substituted ferrocene cyclopentadienyl rings: one set at δ 4.60 and 4.27 ppm and the other at δ 4.53 and 4.21 ppm. For the substituted cyclopentadienyl rings, only two sets of rings are seen with each signal appearing much broader compared to the sharp signals seen for the unsubstituted rings. This is due to similarities between the environments of the four substituted rings: two of the four rings are bound to a phenyl group which lies between two thiophenes on the central benzene ring (Figure 2-10, red), while the other two are bound to a phenyl group which lies between one thiophene and one phenyl group (Figure 2-10, blue). These substituted cyclopentadienyl rings give rise to overlapping of signals in the $^1$H NMR spectrum. The two “blue” rings which are both on 8a integrate for a total of 24 protons (4 protons for each ring which becomes 12 as a result of the ratio of 8a: 8s). The “red” rings, one of which lies on 8a and on one 8s also integrate for a total of 24 protons (4 protons for the ring on 8a, appearing as 12 protons due to the ratio of isomers and 4 protons for the rings on 8s, which becomes 12 protons due to the symmetry).
The unsubstituted cyclopentadienyl rings lie too far from the central ring to be affected by how they are connected to it and as such there is no overlap of their signals in the $^1$H NMR spectrum.

Looking at the aromatic region of the $^1$H NMR spectrum of 8 the overlap seen in the ferrocene cyclopentadienyls can again be observed (Figure 2-11).

![Figure 2-11: The aromatic region of the $^1$H NMR spectrum of the trimer 8 (400 MHz, CDCl$_3$, 25°C).](image)

The four phenyl rings (Figure 2-10, α-δ) appear as four sets of AB signals each integrating for 6 protons. One signal of each AB pair appears between δ 7.17 and 7.06 ppm and the other appears as part of the multiplet between δ 6.88 and 6.78 ppm (four signals with a total integration of 24 appearing as part of the multiplet which integrates for 30). The overlap of the phenyl signals is not exact unlike the case of the substituted cyclopentadienyl rings, so that the phenyl signals appear twinned (α with β and γ with δ) with each peak appearing next to its twin.

For the thiophene signals each set of ABC patterns (assigned by $^1$H-$^1$H TOCSY) is overlapping with its twin, as in the case of the substituted cyclopentadienyl rings (Figure 2-10, orange/pink). Two signals are observed for the protons at the 4-position on the thiophene ring with one at δ 6.90 ppm and the other as part of the multiplet between δ 6.88 and 6.78 ppm. Each of these signals integrates for 6 protons, the “pink” thiophenes have a contribution of 1 proton from the thiophenes on 8s which becomes 3 protons due to symmetry and 1 proton from the thiophenes on 8a which becomes 3 protons as a result.
Part 2: Synthesis and cyclotrimerisations of thiophene acetylenes.

of the product ratio. For the “orange” thiophenes the 4-positions each contribute one proton which again becomes 3 protons from each as a result of the ratio of isomers.

Similar behaviour is observed for the protons at the 2- and 5- positions on the thiophene. These overlap with each other and appear as a large multiplet with a total integration of 24 protons between $\delta$ 6.64 and 6.52 ppm.

The overlap of signals in 8 can also be seen in the aromatic quaternary region of its $^{13}$C NMR spectrum in which the quaternary signals for the carbons at the 3-position on the thiophene rings (Figure 2-12, blue) are again paired and appear as two singlets at $\delta$ 136.3 and 136.1 ppm; however the other quaternary carbons are all seen, with eight signals seen for the central benzene rings (Figure 2-12, purple/orange) and a further eight signals seen for the quaternary carbons on the phenyl rings (Figure 2-12, yellow/green).

![Figure 2-12: The aromatic quaternary region of the $^{13}$C NMR spectrum of the trimer 8 (100.6 MHz, CDCl$_3$, 25°C).](image-url)
Upon trimerisation of 1 two possible isomers of the product 9s and 9a are observed in the \(^1\)H NMR spectrum while trimerisation of 2 gives 10s and 10a (Figure 2-13).

\[
\begin{align*}
9s/10s & \quad \text{Symmetric} \\
9a/10a & \quad \text{Antisymmetric}
\end{align*}
\]

\textbf{Figure 2-13:} The isomers s and a of the trimerised products 9 and 10.

Looking at the NMR spectra of 9 and 10 it can be seen that the peak overlap that was seen in 8 is again observed; however the \(^1\)H NMR spectra in these cases shows the overlap is not exact, so that rather than overlapping, the partner peaks appear next to each other. For 9 four sets of thiophenes \(\alpha, \beta, \gamma\) and \(\delta\) (Figure 2-14) have been identified via TOCSY experiments, \(\alpha\) and \(\beta\) appear as one set of twinned thiophenes and \(\gamma\) and \(\delta\) appear as the other.

\textbf{Figure 2-14:} The aromatic region of the \(^1\)H NMR spectrum of the trimer 9 showing the four sets of thiophene peaks \(\alpha, \beta, \gamma\) and \(\delta\) (400 MHz, CDCl\(_3\), 25°C).
Part 2: Synthesis and cyclotrimerisations of thiophene acetylenes.

Interestingly however the $^{13}$C NMR of both 9 and 10 show that the pattern of overlap observed in 8 is retained for the carbons, with each carbon and its twin appearing as a single peak, excluding those on the central benzene ring of the molecule.

In 10 the $^{13}$C NMR spectrum shows four signals for the carbons alpha to a phenyl substituent between δ 141.1 and 140.8 ppm (Figure 2-15, blue) and four signals for the carbons alpha to a thienyl substituent between δ 135.6 and 135.4 ppm (Figure 2-15, purple).

![Figure 2-15](image)

**Figure 2-15:** The aromatic region of the $^{13}$C NMR spectrum of the trimer 10 (100.6 MHz, CDCl$_3$, 25°C).

In the case of the 2-thienyl ferrocenylphenyl alkyne 6 a shift in the sym: anti ratio of the isomers formed (Figure 2-16) can be seen in the ferrocene signals observed in the $^1$H NMR spectrum of the trimerised product 11 (Figure 2-17).
Part 2: Synthesis and cyclotrimerisations of thiophene acetylenes.

11) R = Fc; 12) R = H; 13) R = tBu

Symmetric                           Antisymmetric

Figure 2-16: The symmetric and asymmetric isomers of 11, 12 and 13.

The pairing of the ferrocenyl signals in 11 is similar to that observed for 8; however due to a change in the ratio of the sym: anti isomers the relative integrations of the peaks seen are no longer the same.

For the four unsubstituted cyclopentadienyl ring signals between δ 3.96 and 3.89 ppm there is an increase in the integration of one signal at δ 3.93 ppm relative to the other
three (Figure 2-17, orange). This indicates that there has been an increase in the relative concentration of the symmetric isomer 11s, as only one of the signals has increased in intensity. Looking at the substituted cyclopentadienyl rings the overlapping of signals is similar to that observed in 8. An increase in intensity is observed for the pair of overlapping signals of the substituted cyclopentadienyl rings which are substituted with a phenyl ring lying between two thiophenes on the central benzene ring (Figure 2-17, purple); this is again consistent with an increase in the relative concentration of 11s. Using the difference in the two integration values for the substituted cyclopentadienyl rings the sym: anti ratio (11s: 11a) for 11 can be calculated.

From the 1H NMR spectrum a relative intensity ratio for the two pairs of substituted cyclopentadienyl rings of 1: 1.28 is seen. The contribution to the peak of larger integration is from three cyclopentadienyl rings on the symmetric isomer (3x) and one from the antisymmetric one (y), while the peak of smaller integration has a contribution from two cyclopentadienyl rings (2y) on the antisymmetric isomer. Giving a sym: anti ratio for 11 of 1: 1.92.

\[3x + y = 1.28 \text{ and } 2y = 1, \text{ therefore } x = 0.26 \text{ when } y = 0.5\]
\[x: y = 0.26: 0.5 \text{ or } 1: 1.92\]

From the integrations of the unsubstituted cyclopentadienone rings integration values of 1.93 and 1.22 are seen for the peaks. A similar calculation on these values gives a sym: anti ratio for 11 of 1: 1.90; however this value is less accurate than that seen for the substituted cyclopentadienyl rings due to overlap of these signals.

\[3x = 1.91 \text{ and } y = 1.21\]
\[x: y = 0.636: 1.21 \text{ or } 1: 1.90\]

The same calculation to estimate the sym: anti ratio can be carried out on the 1H NMR spectra of both 12 and 13 and the results are given in Table 2-2.
### Table 2-2: Sym: Anti ratios as calculated from the $^1$H NMR spectra of 8, 9, 10, 11, 12 and 13.

<table>
<thead>
<tr>
<th>Substituent Group</th>
<th>Ratio with 2-Th (Sym: Anti)</th>
<th>Ratio with 3-Th (Sym: Anti)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fc</td>
<td>1 : 1.92 (11)</td>
<td>1 : 3 (8)</td>
</tr>
<tr>
<td>H</td>
<td>1 : 2.07 (12)</td>
<td>1 : 3 (9)</td>
</tr>
<tr>
<td>tBu</td>
<td>1 : 1.86 (13)</td>
<td>1 : 3 (10)</td>
</tr>
</tbody>
</table>

Looking at the $^{13}$C NMR spectra for the 2-thiophene substituted trimers 11, 12 and 13, a change in the isomeric ratio from that seen for 8, 9 and 10 is again observed, with an increase in the intensity of the quaternary carbon signals for the symmetric isomer. In the case of 11 (Figure 2-18) this can be seen in both the quaternary core phenyl signals located alpha to a thiophene (green) from δ 136.7 -136.4 ppm and those located alpha to a phenyl ring (pink) from δ 138.1 - 137.8 ppm.

![Figure 2-18: The aromatic region of the $^{13}$C NMR spectrum of the trimer 11 (100.6 MHz, CDCl₃, 25°C).](image-url)
Part 2: Synthesis and cyclotrimerisations of thiophene acetylenes.

Upon trimerisation of the three 3-thienyl substituted acetylenes 1, 2 and 3 no deviation from the sym: anti ratio of 1:3 is observed; however in 4, 5 and 6 where the 2-thienyl acetylenes are used an increase in the relative concentration of the symmetric isomer is seen. This was unexpected as according to Hilt a change in the substituent groups of the precursor alkyne should result in an increase in the relative concentration of the antisymmetric isomer rather than the symmetric one. 11

The shift from 3- to 2- thienyl substitution results in a change in the steric and electronic character of the thiophene due to a change in the position of the sulfur atom and its lone pair which moves from pointing away from, to pointing toward the central benzene ring. In the cases described by Hilt 11-13 no such variation was investigated, indeed it is likely that the effect of the increase in electron density due to the sulfur has resulted in a shift from the norborne like trimerisation intermediate for (3-thienyl)acetylenes to the metallacycloheptatriene one for (2-thienyl)acetylenes (Figure 2-19). This metallacycloheptatriene intermediate minimises both the sulfur interactions with the cobalt catalyst and the energetically unfavourable sulfur-sulfur interactions by allowing the substituent groups to alternate around the seven member ring.

![Figure 2-19: A hexasubstituted metallacycloheptatriene intermediate and the resulting hexasubstituted phenyl product.](image)

Further evidence of the change in intermediate is the fact that between the 3-substituted systems 8, 9 and 10 no difference in the sym: anti ratio is observed; whereas increasing the size of the para substituent around the intermediates in 11, 12 and 13 does have an effect on the isomers formed. The more sterically demanding tertiary butyl substituted acetylene 5 gives, upon trimerisation the highest concentration of the symmetric isomer in 13, while the least sterically demanding acetylene 4, gives the lowest concentration of the symmetric isomer in 12. This agrees with the formation of a metallacycloheptatriene
intermediate thus allowing for favourable alternation of the substituent groups around the ring and an increase in the relative concentration of the symmetric isomer on increasing in steric bulk.

2.2.4 Computational calculations on thienyl-phenyl phenylenes

In order to confirm that the isomeric ratios were due to interactions in the transition state, Gaussian calculations were carried out on both isomers of the two para hydrogen substituted trimer products 9s, 9a, 12s and 12a using DFT B3LYP with a 6-31G(d) basis set to estimate the ground state energies (Figure 2-20 and Table 2-3).

Table 2-3: Minimum calculated energies for 9s, 9a, 12s and 12a.

<table>
<thead>
<tr>
<th></th>
<th>Hartrees (au)</th>
<th>kJ/mol</th>
<th>kJ/mol +6775900 (to clarify order)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9s</td>
<td>-2580.81697263</td>
<td>-6775934.962</td>
<td>-34.962</td>
</tr>
<tr>
<td>9a</td>
<td>-2580.81663218</td>
<td>-6775934.068</td>
<td>-34.068</td>
</tr>
<tr>
<td>12s</td>
<td>-2580.81468419</td>
<td>-6775928.953</td>
<td>-28.953</td>
</tr>
<tr>
<td>12a</td>
<td>-2580.81472598</td>
<td>-6775929.063</td>
<td>-29.063</td>
</tr>
</tbody>
</table>
From these calculations it can be seen that within error there is no difference between the symmetric and antisymmetric isomers of both 9 and 12. As there is little energetic difference between the isomer produced, the driving force for the formation of one isomer over the other is more likely to be due to the transition state.\(^7\) These calculations also show a small difference in the ground state energy of the 3- and 2-substituted thiophenes of 5-6 kJ/mol due to the effect of the positional change of the sulfur destabilising the ground state in the 2-substituted thiophenes.

2.3 Ethynyl thiophenes

2.3.1 Introduction

The cyclotrimerisation of mono substituted ethynes has been investigated in the past for a number of substituents indicating a preference for the antisymmetric trimerisation isomer\(^7\) (Figure 2-6, a); again as in the case of asymmetric acetylenes this is due to a minimisation of the sterics in the norbornadiene-like intermediate. By allowing two hydrogens to sit in the two quaternary substituted carbon positions the reaction results in the formation of the asymmetric isomer

\[
\text{Scheme 2-5: The two isomers s and a formed from the trimerisation of an ethylene.}
\]

2.3.2 Preparation of ethynyl thiophenes

3-thienylethylene 14 was commercially available while 2-thienylethylene 15 was prepared via the method of Beny.\(^19\) 2-thiophenecarboxaldehyde was added to a solution of triphenylphosphine and carbon tetrabromide in dichloromethane; this was filtered and recrystallised from acetone to give 2-(2,2-dibromovinyl)thiophene which was lithiated in
diethyl ether and quenched with water to give 15 in an overall 58% yield (Scheme 2-7).

(i) Triphenyl phosphine, carbon tetrabromide, dichloromethane, 5 min, 0°C.  
(ii) n-butyllithium, diethyl ether, -78°C, 2 hr, quench with H₂O.

Scheme 2-6: The synthesis of 2-thienylethylene 15.

2.3.3 Trimerisation of ethynyl thiophenes

Upon trimerisation with dicobalt octacarbonyl in refluxing dioxane, both 14 and 15 gave only the respective antisymmetric isomers 16 and 17 upon recrystallisation from methanol (Figure 2-21).

Figure 2-21: The labelling of the central phenyl core for the asymmetric products 16 and 17.

For 16 the ¹H NMR spectrum shows three sets of 3-thiophene signals which have been fully assigned by long range NMR. The most deshielded thiophene is observed at δ 7.55, 7.47 and 7.45 and through a HMBC experiment has been shown to lie at a position on the central ring between two hydrogens, as such this thiophene must be at position 4 (Figure 2-22). Similar HMBC analysis shows that the thiophene with protons at δ 7.24, 7.12 and 6.84 ppm lies at phenyl position 1 and the thiophene at δ 7.25, 7.17 and 6.88 ppm lies at position 2. The three phenyl protons are seen at δ 7.72 (position 3), 7.61 (position 5) and 7.55 (position 6) ppm.
Part 2: Synthesis and cyclotrimerisations of thiophene acetylenes.

Of the three thiophenes seen in the $^1$H NMR spectrum of 16 the most deshielded has been assigned to the thiophene on the 4-position of the central ring with hydrogen substituents either side of it. This is because of the shielding effect of the ring current on the other thiophene rings which are ortho to it. (Figure 2-23). This shielding effect on thiophenes ortho to other aromatic substituents is well documented.$^{15,20}$

For 17 again three sets of thiophene signals are observed in the $^1$H NMR spectrum, these have the expected splitting patterns for 2-substituted thiophenes. The furthest deshielded set of thiophene signals has been assigned via a HMBC experiment to be the thiophene ortho to two hydrogen atoms on the central phenyl ring, this is consistent with the assignment of 16. This is the thiophene at position 4 on the central ring and is observed at $\delta$ 7.41, 7.33 and 7.12 ppm (Figure 2-24). The thiophene at the 1 position is observed at $\delta$
Part 2: Synthesis and cyclotrimerisations of thiophene acetylenes.

7.30, 6.99 and 6.93 ppm, while the thiophene at the 2 position is seen at $\delta$ 7.33, 7.03 and 6.99 ppm. The three phenyl protons resonate at $\delta$ 7.77 (position 3), 7.63 (position 5) and 7.56 ppm (position 6).

![Figure 2-24: The $^1$H NMR spectrum of 17 (400 MHz, CDCl$_3$, 25°C).](image)

Single crystals of 16 and 17 suitable for X-ray crystallographic analysis were obtained from the slow evaporation of a saturated solution of the sample from a 1:1 mixture of methanol: dichloromethane. Both 16 and 17 crystallise in the same monoclinic space group P2(1)/c; however the packing of the two structures are different. In 16 there are four molecules in the unit cell.

![Figure 2-25: Perspective view of the molecular structure of 16, with selected atomic labelling shown. Selected bond lengths (Å) and angles (°): C3-C5 1.464(4), C5-C6 1.399(4), C6-C7 1.377(4), C6-C16 1.470(4), C7-C8 1.395(4), C8-C9 1.382(4), C8-C12 1.452(4), C9-C10 1.353(5), C5-C10 1.400(4), C1-S1-C4 93.2(2), C11-S3-C14 97.9(2), C15-S2-C18 93.1(2).](image)
Part 2: Synthesis and cyclotrimerisations of thiophene acetylenes.

Figure 2-26: Crystal packing along the a) a axis and b) c axis of 16.

For 17 the increased interaction of the sulfur atoms with the core of the molecule results in the structure packing in the solid state in such a way that a pair of molecules differing from each other by an 180° rotation of one of the three thiophenes is observed (S3 and S6, Figure 2-27).

Figure 2-27: Perspective view of two molecules of the molecular structure of 17, with atomic labelling shown. Selected bond lengths (Å) and angles (°): C21-C22 1.377(7), C22-C23 1.391(6), C23-C24 1.398(6), C24-C25 1.396(6), C25-C26 1.377(7), C21-C26 1.394(7), C11-C21 1.468(7), C23-C41 1.497(6), C24-C31 1.478(6), C11-S1-C14 93.1(3), C31-S2-C33 95.9(3), C41-S3-C44 97.3(4).

As a result of this there are a total of eight molecules in the unit cell. Between adjacent molecules along the b-axis of the cell two of the three thiophenes remain at the same orientation while the third rotates by 180° (Figure 2-28).
Each of the six sulfur atoms in 17 show disorder, with each thiophene having two possible orientations. This is due to a possible 180° rotation of each thiophene ring which results in an occupancy for each 2-position sulfur at the carbon 5-position on the same thiophene ring (values are between 22 and 45%). As such the goodness of fit on $F^2$ value for 17 is higher than normal (1.254).

Looking at the trimerisation yields and melting points of 16 and 17 some interesting observations can be made. The 3-thienyl 16 was obtained in 63% yield via trimerisation, whereas 2-thienyl 17 was only obtained in 23% under the same conditions of temperature and reaction time.

2.4 Conclusion

This chapter has shown that the cyclotrimerisations of thienyl containing acetylenes and ethylenes has been achieved. Six thiophene-phenylene acetylenes (1-6) were successfully synthesised using Sonagashira coupling and fully characterised by NMR, IR spectroscopy, Mass spectrometry and X-Ray crystallography.

These acetylenes were then trimerised using dicobalt octacarbonyl as catalyst to give six isomeric mixtures of phenylene systems (8-13). A series of complex NMR investigations
Part 2: Synthesis and cyclotrimerisations of thiophene acetylenes.

were carried out on the compounds obtained. Changing the substituents affects both the mechanism of the trimerisation reaction and the ratio of the symmetric and antisymmetric isomers formed. In the case of systems involving a 3-thienyl substituent the isomeric ratio of 1:3 expected from the norbornadiene like reaction intermediate is seen, while in the case of the 2-thienyl systems the effect of the greater sulfur interaction with the molecular core appears to drive the trimerisation to go via the metallacycloheptatriene intermediate resulting in an increase in the relative concentration of the symmetric isomer.

Two ethylenes 14 and 15 were trimerised to give 16 and 17 which were fully characterised by both NMR spectroscopy and X-Ray crystallography. In these cases as one of the acetylene substituents is a sterically undemanding hydrogen, trimerisation via the norbornadiene-like intermediate results in the exclusive formation of the asymmetric isomer.

2.5 References

Part 2: Synthesis and cyclotrimerisations of thiophene acetylenes.

20 Gregg, D. J.; Ollagnier, C. M. A.; Fitchett, C. M.; Draper, S. M. Chem. Eu. J. 2006, 12, 3043-3052.
Part 3: Synthesis and oxidation of di-thienyl polyphenylene derivatives
3.1 Introduction

As mentioned in Part 1, there is great interest in the development of large polycyclic aromatic hydrocarbons (PAH) due to their thermal stability and interesting optoelectronic properties as a result of the $\pi$-delocalisation around the aromatic framework. The synthesis of such systems has been successfully developed via the cyclodehydrogenation of polyphenylene precursors to form planar PAH compounds. In the past, a series of PAH in which a nitrogen group has been incorporated into the periphery have been synthesised by our group leading to a family of new compounds, the nitrogen heterosuperbenzenes (N-HSB).\textsuperscript{1-4}

This chapter discusses a series of di-sulfur containing polyphenylenes synthesised in order to study the effect of a heteroatom change on the hexabenzocoronene periphery. In the past, di-thienyl systems have been used in the synthesis of both polymers\textsuperscript{5} and as precursors for heteroaromatic systems.\textsuperscript{6} In these studies, di-thienyl units were found to increase the polarizability of the products, to enhance the electron density of the systems and to promote intermolecular interactions. The tuneability of the electronic properties of such systems makes them excellent frameworks for the development of new aromatic platforms. In the work of Ogura, di-thienyl frameworks have been prepared which, through variations in the substituents on the thiophene, can act as either electron donors or electron acceptors.\textsuperscript{7-8} An increase in the amount of cross linking present in the polymers due to the availability of multiple thiophene–thiophene intermolecular and intramolecular bond formations and significant shifts in the ground and excited state dipole moments of the polymers formed also arise from the use of such systems.

The propensity of mono-thiophene systems toward the formation of insoluble products, along with the difficulty in modifying the properties of the resulting polymers, have led to the strategy of using monomers containing two thiophene units in order to control the products formed. Substituted bisthiényl, dithienylethene and thiophene-oligomer monomers have given better control over both the bandgap and the conductivity of the polymers formed upon oxidation. In all of these systems, the focus has been on the effect
that structural changes to the monomer can have on the resulting polymer.\textsuperscript{9-10} In comparison little attention has been paid to the design of molecular systems containing multi-thiophenes where both inter- and intra- molecular oxidations are possible.

Scheme 3-1 shows the general synthesis of a hexaaryl polyphenylene in which, through design of the substituents (R\textsubscript{1}-R\textsubscript{4}) up to four different substituent groups can be placed on the periphery. Using 1,3-diarylacetones a made via the method of des Abbayes\textsuperscript{11} and 1,2 diaryldiketones b from the method of Muller-Westerhoff\textsuperscript{12} it is possible to synthesise 2,3,4,5-aryl-cyclopentadienones\textsuperscript{13} d which can be reacted with diaryl acetylenes c in [2+4] cycloadditions to give the polyphenylene products. Although the Knoevenagel condensation used in the synthesis of cyclopentadienones is well known\textsuperscript{13} it is worth noting that in the synthesis of cyclopentadienones where the 3 and 4 positions (R\textsubscript{1} in d, Scheme 3-1) are substituted with strong electronic groups such as thiophene, the classic potassium hydroxide condensation fails.\textsuperscript{14} In such cases either the method developed by Kawase,\textsuperscript{15} using a crown ether in dichlorobenzene or as in more recent work microwave irradiation is used to counter the electronic effects and force the reaction.\textsuperscript{16}

The following chapter discusses the steps involved in the incorporation of thiophene moieties onto the benzene core of polyphenyl precursors along with the cyclodehydrogenation of these precursors to give new PAH-based systems.
Section 3.2 deals with the synthesis and characterisation of new acetylenes which have been di-substituted with thiophene and were inspired by previous work in the group. This had shown that varying the acetylene is the simplest way by to moderate the substitution of the final phenylene.\textsuperscript{17}

Section 3.3 describes the synthesis and characterisation of a series of di-thienyl containing hexaarylbenzenes which have been prepared from the acetylenes described in section 3.2. The acetylenes readily undergo the Diels-Alder [2+4] cycloaddition step.\textsuperscript{1,17}

Sections 3.4 and 3.5 show the reactivity of the di-thienyl containing polyphenylenes toward oxidative cyclodehydrogenation as discussed in section 1.3. As a result of the reactivity observed in section 3.4 a new polyphenyl system was designed and the reactivity of this system is discussed in section 3.5.

3.2 Synthesis and characterisation of di-thienyl acetylenes

In order to synthesise di-thienyl containing polyphenylenes a series of di-thienyl acetylenes are required for the [2+4] cycloaddition step. In the case of the nitrogen containing species previously reported within the group\textsuperscript{18} the required diaryl acetylene has been prepared via the palladium coupling of 5-ethynylpyrimidine with 5-bromopyrimidine (Scheme 3-2). The ethynylpyrimidine is prepared via coupling of 5-bromopyrimidine with a protected acetylene such as trimethylsilylacetylene to give a protected pyrimidine acetylene which is then deprotected using a base such as sodium hydroxide. This is similar to the methods used in the synthesis of the monothienyl acetylenes seen in Section 2.2 and involves three steps including the difficult isolation of the volatile deprotected aryl acetylene for an overall yield of 36\%.\textsuperscript{18}

\[
\begin{array}{c}
\text{Th} \equiv \text{Br} \\
\text{+} \\
\text{Th} \equiv \text{C} \equiv \text{Br}
\end{array}
\quad \text{(i)}
\]

(i) \([\text{Pd}(\text{PPh}_3)_2\text{Cl}_2], \text{Et}_3\text{N}, \text{CuI}, \text{DMF}, 55^\circ\text{C}, 1 \text{ hour.}

**Scheme 3-2:** The synthesis of di-(pyramid-3,5-yl)acetylene.

As a result of the higher reactivity of substituted thiophenes compared to substituted pyrimidines it was possible to prepare the symmetric di-thienyl acetylenes in a one pot synthesis using the method of Carpita.\(^{19}\) In this the acetylene is formed *in situ* from the palladium tetrakis(triphenylphosphine) catalysed coupling of the bromothiophene with 2-methyl-3-butyln-2-ol in a mixture of benzene and aqueous sodium hydroxide (Scheme 3-3).

\[
\begin{array}{c}
\text{Th} \equiv \text{Br} \\
\text{+} \\
\text{Th} \equiv \text{C} \equiv \text{OH}
\end{array}
\quad \text{(i)}
\]

(iii) \([\text{Pd}(\text{PPh}_3)_4], \text{CuI}, \text{PhNEt}_3\text{Cl}, \text{a. NaOH}, \text{Benzene, Room temperature; (ii) and (iii) 80^\circ\text{C}}

**Scheme 3-3:** The one pot synthesis of di-thienyl acetylenes used in the synthesis of 18 and 19.

This is then heated to 80°C and more bromothiophene added to give the acetylene in modest yield (18: 14%; 19: 40%); however due to the low cost of both the protected acetylene and the bromothiophenes the di-thienyl acetylenes can be prepared on a large scale (~10 g). Mio has reported that it is possible to prepare both 18 and 19 in higher yield by using an iodo substituted thiophene and a silyl protected acetylene\(^{20}\) (a yield of 88% is reported for 18); however the inhibitive factors both in the cost of purchasing these reagents and the difficulty of synthesising the iodothiophenes meant this method was not used.
The $^1$H NMR spectrum of bis(2-thienyl)acetylene 18 has been previously reported within the group$^{17,21}$ and shows the characteristic signal splitting for a 2-substituted thiophene (§2.2.1) with three correlated doublet of doublet signals each integrating for two hydrogens at $\delta$ 7.33, 7.30 and 7.03 ppm. The $^{13}$C NMR spectrum of 18 shows one acetylene carbon (due to the $C_2$ symmetry in the molecule) at $\delta$ 85.7 ppm and the IR spectrum also shows the C≡C stretch at 2186 cm$^{-1}$.

A similar $^1$H NMR spectrum is observed for bis(3-thienyl)acetylene 19 in which three coupled thiophene signals are seen at $\delta$ 7.54, 7.32 and 7.21 ppm with coupling constants of $^3J_{2,4} = 4.8$ Hz, $^4J_{2,5} = 1.5$ Hz and $^3J_{4,5} = 3.0$ Hz (Figure 3-1). This data is consistent with published reports for the NMR spectrum of 19.$^{22}$

![Figure 3-1: The aromatic region of the $^1$H NMR spectrum of 19 (400 MHz, CDCl$_3$, 25°C).](image)

Again there is only one acetylene carbon seen in the $^{13}$C NMR at $\delta$ 85.7 ppm.

Single crystals of 18 and 19 suitable for X-ray crystallographic analysis were obtained from the slow evaporation of a saturated solution of the compound in a 1:1 mixture of methanol: dichloromethane. Both acetylenes are similar in the solid state crystallising in the orthorhombic centrosymmetric space group Pbcn with four molecules in the unit cell. The sulfur atoms of both 18 and 19 showed some disorder, with each thiophene having two possible orientations. This is due to a possible 180° rotation of each thiophene ring resulting in a partial occupancy for each sulfur at one of the carbon positions on the thiophene ring. This disorder is higher for 19 (31%) than 18 (20%). In the case of 19 the wR$_2$ value is higher than expected (0.254) this has been attributed to the small crystal size.
and resultant low intensity of the resulting X-ray data. One consequence of the disorder in the solid state is the appearance of a weak C≡C stretch in the IR spectrum for both 18 and 19 which are observed at 2186 and 2161 cm⁻¹ respectively.

![Figure 3-2: Perspective view of the molecular structure of 18, with atomic labelling shown. Selected bond lengths (Å) and angles (°): C1-C1A 1.271(15), C1-C2 1.417(8), C2-S1 1.722(7), S1-C3 1.732(4), C2-S1-C3 90.4(2).](image)

![Figure 3-3: Crystal packing along the a) c axis and b) a axis of 18.](image)

![Figure 3-4: Perspective view of the molecular structure of 19, with selected atomic labelling shown. Selected bond lengths (Å) and angles (°): C3-C3A 1.178(6), C3-C5 1.429(5), C2-S6 1.675(4), C4-S6 1.679(4), C2-S6-C4 96.6(2).](image)

In order to synthesise the mixed 2-thienyl-3-thienyl acetylene 21 the protected acetylene 4-(3-thienyl)-2-methyl-3-butyn-2-ol 20 was prepared from 3-bromothiophene and 2-methyl-3-butyn-2-ol in diethyl amine in a 25% yield. This was then heated to 80°C in basic solution and coupled in a Sonagashira reaction with 2-bromothiophene to give on workup 21 in 77% yield.

\[
\begin{align*}
\text{Br} & \quad + \quad \text{OH} \\
\text{S} & \quad \text{S} \quad \text{S} \quad \text{S}
\end{align*}
\]

(i) Pd(PPh$_3$)$_2$Cl$_2$, CuI, Et$_3$NH, Benzene, Room temperature; (ii) aq. NaOH, Benzene, 80°C; (iii) Pd(PPh$_3$)$_4$, PhNEt$_3$Cl, CuI, aq. NaOH, Benzene, 80°C.

**Scheme 3-4:** The synthesis of di-thienyl acetylene 21 from 20.

The $^1$H NMR spectrum of 21 contains six aromatic signals which have been shown through a 2D TOCSY experiment to be the two sets of thiophenes. The signals on the 2-thiophene substituted ring are seen at $\delta$ 7.30 (two signals) and 7.03 ppm. While the 3-substituted thiophene signals are seen at $\delta$ 7.55, 7.33 and 7.22 ppm. (In the case of di-
thienyl species the positions of thiophene substitution determine the ring labels; those atoms on the ring of lowest positional substitution are labelled 2, 3, 4 etc. while those on the higher substituted ring are 2’, 3’, 4’ etc.). The coupling of these sets of signals is as expected for both 2- and 3-substituted thiophenes.

![Image](image.jpg)

**Figure 3-6:** The aromatic region of the $^1$H NMR spectrum of 21 (400 MHz, CDCl$_3$, 25°C).

In the $^{13}$C NMR of 21 there are two acetylene carbons observed at δ 87.8 and 81.7 ppm, also the ν(C≡C) appears at 2163 cm$^{-1}$ in the IR spectrum. All three di-thienyl acetylenes 18, 19 and 21 have the same calculated exact mass of 189.9911; due to the difficulty in obtaining mass spectra for thienyl compounds as a result of rapid, complicated fragmentation occurring about the thiophene, the three samples could not be detected on the same machine. Nevertheless 18 and 19 were found by electrospray mass spec to have values of [M]$^+$ 189.9919 m.u. and 189.9916 m.u. respectively. [M]$^+$ was observed for 21 on an electron impact mass spectrometer at 189.9919 m.u.

### 3.3 Synthesis and characterisation of di-thienyl polyphenylenes

The [2+4] cycloaddition of 19 with commercially available 2,3,4,5-tetraphenyl cyclopenta-2,4-dien-1-one (tetracyclone) in benzophenone gave the polyphenyl compound 1,2-di(3-thienyl)-3,4,5,6-tetraphenylbenzene 22 in a 57% yield (Scheme 3-5).

(i) benzophenone, reflux, 1 hour.

Scheme 3-5: Diels-Alder cycloaddition of tetracyclone with acetylene 19.

The $^1$H NMR spectrum of 22 shows one set of 3-substituted thiophene signals and two sets of phenyl rings as a result of the $C_2$ symmetry axis present in the molecule. The thiophene signals each with an integration of two are observed at $\delta$ 6.56, 6.51 ppm and as part of the multiplet between $\delta$ 6.96 and 6.80 ppm which integrates for twenty two protons with two for the thiophene and five for each of the four phenyl rings.

Figure 3-7: The aromatic region of the $^1$H NMR spectrum of 22 (400 MHz, CDCl$_3$, 25°C).

The $^1$H NMR signals for the hydrogens at the 2- and 4- positions in the thiophene are deshielded compared to those of the acetylene precursor 19. This can be attributed to the shielding effect of the aromatic systems which lie ortho to the thiophenes. A similar effect was seen in the tri-thienyl benzenes (§2.3.2). For the 3- substituted thiophene under discussion there is a much smaller shift for H$_5$, this is a result of reduced interaction of this position on the thiophene ring with the rings ortho to it (Figure 3-8).

Figure 3-8: Two possible conformations of a thiophene ring ortho to a phenyl ring in 22, the hydrogens at positions 2- and 4- have more interaction with the shielding region of the phenyl ring than the hydrogen at position 5-.

Crystals of 22 suitable for single crystal X-Ray diffraction were obtained through precipitation of the sample from a warm solution of chloroform. 22 crystallises in the orthorhombic centrosymmetric space group Pna2₁ with four molecules in the asymmetric unit cell.

Figure 3-9: Perspective view of the molecular structure of 22, with selected atomic labelling shown. Selected bond lengths (Å) and angles (°): C29-C37 1.452(1), C32-C35 1.3920(1), C32-C38 1.4122(1), C33-C36 1.3893(1), C33-C38 1.4163(1), C34-C35 1.5105(1), C35-C37 1.4098(1), C36-C37 1.4005(1), C8-S2-C11A 101.76(2), C20-S1-C30 96.19(2).

Figure 3-10: Crystal packing along the a) a axis and b) c axis of 22.
Although the yield of 22 was reasonable (57%) the workup for this compound was difficult due to the insolubility of the product. Although 22 gave an R$_f$ value of 0.8 in 9:1 hexane: diethyl ether it was only sparingly soluble in this solvent and was purified instead by a series of repeated precipitations from warm dichloromethane solutions by the dropwise addition of methanol. The insolubility of 22 prompted the use of tert-butyl substituents; 2,3,4,5-tetrakis-(4-tert-butylphenyl)cyclopentadienone 25 was synthesised via a literature procedure$^{24}$ from 1,2-bis(4-tert-butylphenyl)ethane-1,2-dione$^1$ 23 and 1,3-bis(4-tert-butylphenyl)propane-2-one$^{24}$ 24 (Scheme 3-6).

Using 25 as the diene in the Diels-Alder [2+4] cycloaddition, three di-substituted polyphenylene systems, 1,2-di(2-thienyl)-3,4,5,6-tetra-(4-tert-butylphenyl)benzene 26, 1,2-di(3-thienyl)-3,4,5,6-tetra-(4-tert-butylphenyl)benzene 27 and 1-(2-thienyl)-2-(3-thienyl)-3,4,5,6-tetra-(4-tert-butylphenyl)benzene 28 were prepared. Each was purified via column chromatography using 9:1 hexane: diethyl ether as the eluent (all have R$_f$ = 0.8).

Of these three compounds 26 had been previously synthesised, spectroscopically characterised and its single crystal X-Ray structure obtained. Di(3-thienyl) phenylene 27 contains a \( \text{C}_2 \) symmetry axis and as such the \(^1\text{H} \) NMR spectrum shows four phenyl signals, each integrating for four hydrogens at \( \delta \) 6.90, 6.84, 6.74 and 6.65 ppm, which were fully assigned via a series of nOe experiments.

![Figure 3-11: The \(^1\text{H} \) NMR spectrum of 27 (400 MHz, CDCl\(_3\), 25°C).](image)

The three thiophene signals are seen with the expected splitting for a 3-substituted thiophene, \( ^3J_{2,4} = 5.0 \text{ Hz}, ^4J_{2,5} = 1.5 \text{ Hz} \) and \( ^3J_{4,5} = 3.0 \text{ Hz} \). Of these signals the 5- position is at higher ppm at \( \delta \) 6.83 ppm while the 2- and 4- positions are shielded by ortho interactions and are seen at \( \delta \) 6.56 and 6.51 ppm respectively. Also two tert-butyl signals each integrating for eighteen protons are seen at \( \delta \) 1.16 and 1.11 ppm.

Crystals of 27 were obtained within the group by Professor Sarath Perera via slow evaporation of a saturated dichloromethane solution of the compound. 27 crystallises in the triclinic space group P-1 (the same space group as reported for 26)\(^17\) with two molecules appearing in the unit cell along with two molecules of dichloromethane. Again as was observed for the thienyl acetylenes some disorder can be observed due to a possible 180° rotation resulting in an 48% occupancy for each 3-position sulfur at the carbon 4-position on the thiophene ring.

Figure 3-12: Perspective view of the molecular structure of 27, with selected atomic labelling shown. Selected bond lengths (Å) and angles (°): C2-C11 1.487(3), C6-C16 1.487(3), C11-C12 1.402(3), C11-C16 1.413(3), C12-C13 1.404(3), C13-C14 1.400(3), C14-C15 1.409(3), C15-C16 1.403(3), C1-S1-C4 86.94(5), C5-S2-C8 98.95(6).

Figure 3-13: Crystal packing along the a) b axis and b) a axis of 22 (Solvent has been removed for clarity).

The loss of the C₂ symmetry axis in 28 means that its ¹H NMR spectrum is more complicated. In this case three thiophene signals are seen for each of the two thiophenes. The 2-substituted thiophene signals (integrating for one proton each) appear at δ 7.00, 6.59 and 6.44 ppm and the 3-substituted thiophene signals appear at δ 6.86, 6.65 and 6.61 ppm. The splitting of the signals is as expected and those that point toward aromatic ortho groups (protons 3, 4, 2’ and 4’) are shielded.
Figure 3-14: The $^1$H NMR spectrum of 28 (400 MHz, CDCl$_3$, 25°C).

The $^1$H NMR spectrum shows a total of eight phenyl signals each integrating for two protons at δ 6.91 (two overlapping signals), 6.81 (three overlapping signals), 6.75 and 6.66 (two overlapping signals) ppm. From the overlap of the phenyl signals it can be seen that switching the substitution of the thiophenes has had minimal effect. The only signals which do not overlap have been shown through nOe and 2D correlation spectroscopy to be those signals which point towards the thiophene moieties (at δ 6.81 and 6.75 ppm). The tert-butyl signals present at δ 1.16 and 1.11 ppm show that only two environments with each signal integrating for eighteen protons.

The three tert-butyl di-thienyl polyphenylenes were all examined by electrospray mass spectrometry to give values of m/z = 771.4058 (26), 771.4048 (27) and 771.4050 (28) m.u. which fit with the calculated value for [M]$^+$ for each of m/z 771.4058 m.u.

### 3.4 Dehydrogenation of di-thienyl polyphenylenes

The reactivity of both thiophene$^{25}$ and polyphenylene species$^{26}$ towards carbon-carbon bond formation with the loss of hydrogen under oxidative conditions is well known and has been discussed in section 1.3.2. To date however little has been published into the effect of oxidative dehydrogenation on thiophene-containing species where bulky
substituents restrict the possibility of polymerisation. For this reason the reactivity of compounds 22, 26, 27 and 28 under oxidising conditions were investigated.

22 undergoes dehydrogenation upon the addition of iron trichloride, which acts as both oxidant and Lewis acid; however the product formed is a highly insoluble red polymeric species for which a $^1$H NMR spectrum could not be obtained.

Oxidation of the 2,2’ dithiophene 26 with iron trichloride in dichloromethane produced after 30 minutes an orange species 29 which was isolated via silica plate chromatography with dichloromethane: hexane (1: 4). Looking at the $^1$H NMR spectrum of 29 a total of eleven aromatic signals are present.

![Figure 3-15: The $^1$H NMR spectrum of 29 (600 MHz, CDCl$_3$, 25°C).](image)

Eight of these signals show splitting values consistent with the presence of four phenyl AB patterns each integrating for four protons, indeed these can be paired off by TOCSY experiment and are observed at $\delta$ 7.35 and 7.21 ppm, $\delta$ 7.27 and 7.18 ppm, $\delta$ 6.83 and 6.77 ppm and $\delta$ 6.81 and 6.71 ppm. Looking at integration of the three remaining signals it can be seen that they each integrate for two hydrogens; from this it can be seen that no oxidation has occurred at the phenylene rings and that the compound has only lost hydrogens on the thiophene moieties. This oxidation has left three thiophene protons: an AB pattern at $\delta$ 7.44 and $\delta$ 7.32 ppm and a singlet at $\delta$ 7.41 ppm. In order for this to occur the starting material 26 must have undergone both an intramolecular carbon-carbon bond formation between the two thiophenes and an intermolecular dimerisation through one of the thiophenes. Four tert-butyl groups are also seen in the $^1$H NMR spectrum at $\delta$ 1.42, 1.32 and 1.08 (two overlapping signals) ppm, each integrating for eighteen protons.
This dimerisation is also observed in the MALDI mass spectrum for 29 where a peak is observed at m/z 1534.7516 m.u. which correlates with the calculated m/z value for [M]$^+$ of 1534.7490 m.u. From this data two possible structures for 29 are possible, shown in Figure 3-16.

![Figure 3-16: The two possible isomers of dimeric compound 29 (phenyl groups removed for clarity).]

These two isomers can be distinguished by long-range $^1$H-$^1$C NMR, looking at the long range interactions of the three thiophene signals it can be observed that they are all either alpha or beta to the quaternary carbon at $\delta$ 134.2 ppm. This is only possible if this carbon is the one at which intramolecular bond formation has occurred on the same thiophene as the AB protons and as such the singlet must be the proton at the 4’ position on the other thienyl ring; as such 29 must be 29a instead of 29b. This is also the dimer which is expected to be formed by standard thiophene reactivity,\textsuperscript{27} which predicts oxidative bond formation at the 2-position is preferable over the 3-position.

Oxidation of the 3,3’ di-thiophene 27 and the 2,3’ di-thiophene 28 with iron trichloride gave compounds 30 and 31 which are similar to the dimer 29. MALDI Mass spectral analysis of these two compounds shows a molecular mass indicative of the formation of dimers, with a value of 1534.7480 m/z for 30 and 1534.7480 m/z for 31. Comparing the $^1$H NMR spectra of the three species a number of common features can be observed again indicating the formation of dimeric species similar to 29 (Figure 3-17).

![Figure 3-17: The $^1$H NMR spectrum of 29 (600 MHz, CDCl$_3$, 25°C) 30 (600 MHz, CDCl$_3$, 25°C) and 31 (600 MHz, d$_2$-1,1,2,2-tetrachloroethane, 25°C).](image)

In the case of the 3,3’ dimer 30 a total of eight phenyl signals can be seen and as in the case of 29 these can be paired off via 2D TOCSY experiment as $\delta$ 7.34 and 7.11 ppm, $\delta$ 7.22 and 7.08 ppm, $\delta$ 6.83 and 6.66 ppm and $\delta$ 6.82 and 6.68 ppm. Also present are a thiophene AB pattern at $\delta$ 6.96 and 6.31 ppm with $^3$J$_{HH}$ = 3.8 Hz and a thiophene singlet at $\delta$ 6.38 ppm. There are a total of four possible dehydrogenated dimers which could be formed; however only one of these is seen in the $^1$H NMR spectrum. The position of two of the thiophene signals (between $\delta$ 6.45 and 6.25 pm) indicates that they point towards phenyl substituents located ortho to them on the core ring of the molecule. Also the splitting of the doublet is ~ 4 Hz which is indicative of the doublets in a 3-substituted
thiophene lying at the 4- and 5- positions on the ring. From this information there are only two structures possible for 30 (figure 3-18). These could not be distinguished via NMR; however from the theoretical reactivities of thiophene the most favourable isomer is 30a due to the fact that all oxidations have occurred at the more reactive 2- and 5- positions on the thiophene ring.

![Figure 3-18: The two possible structures of the dimeric compound 30 formed from the oxidative dehydrogenation of the 3,3' dithiophene polyphenylene 27.](image)

In the case of the 2,3’ dimer 31 there are a total of twelve possible structures for the dimer formed as a result in the decrease in symmetry in the starting material 28. Looking at the $^1$H NMR spectrum, again four sets of phenyl signal pairs are seen indicating that oxidation has occurred only on the thiophene rings. For the thiophene signals there is a singlet at $\delta$ 6.38 ppm and an AB doublet with both peaks as part of the multiplet between $\delta$ 7.41 and 7.34 ppm. This indicates that the singlet is pointing towards the core of the molecule and is located on the thiophene on which dimerisation has occurred. The absence of an AB signal in the more shielded region (~6.5 ppm) indicates that both the hydrogens on the other thiophene ring point away from molecule core, as such only two possible dimer structures are possible; 31a and 31b (Figure 3-19). Again as in 30 it is not possible to identify 31 fully from the NMR data.
In all three dimerisations the reaction went in a reasonable yield (29 - 55%; 30 – 60%; 31 – 52%). Of the three yields that observed for 30 is the highest, this is to be expected as this is the case in which all of the oxidations occur at the more reactive 2- and 5-positions on the thiophene rings.

3.5 Synthesis and dehydrogenation of blocked di-thienyl polyphenylenes

The prevalence of intermolecular dehydrogenation upon oxidation and the consequent problem of multiple isomeric dimeric products led to the possibility of exploiting steric hindrance in an attempt to direct the outcome of the dehydrogenation. As such the bisthienylacetylene 32 where the 5 and 5’ sites, at which dimerisation occurs in the phenylene oxidation, are blocked by methyl substituents was synthesised. Commercially available 2-bromo-5-methylthiophene was used for the Sonagashira coupling (Scheme 3-7). This reaction had to be carried out in the dark as 2-bromo-5-methylthiophene undergoes photo-decomposition.

Scheme 3-7: The one pot synthesis of the blocked di-thienyl acetylene 32.

After purification of the reaction mixture via column chromatography using 6: 1 hexane: dichloromethane as the eluent ($R_f = 0.5$) an overall yield of 42% of acetylene was obtained. As with the starting material the acetylene product was found to slowly decompose in light and so it was stored in an argon atmosphere in the dark.

Looking at the $^1$H NMR spectrum of 32 three signals are observed, two thiophene signals at $\delta$ 7.07 and 6.67 ppm each integrating for two hydrogens and a methyl signal with an integration for six protons at $\delta$ 2.50 ppm (Figure 3-20).

Looking at the splitting of the thiophene signals the doublet at $\delta$ 7.07 ppm has $^3J_{3,4} = 3.5$ Hz and is coupled with the other thiophene signal at $\delta$ 6.67 ppm; however this signal is
also coupled with the methyl protons and appears as an overlapping doublet of quartets with $^4J_{4,6} = 0.8$ Hz. As a result of this, this signal can be assigned as the H$_4$ beta to the methyl group which appears as a doublet. Electron ionisation mass spectrometry gave a value of m/z 218.0225 m.u. for 32 (compared to a theoretical [M]$^+$ value of 218.0225 m.u., also the IR spectrum shows a v(C≡C) at 2190 cm$^{-1}$.

Single crystals of 32 suitable for X-ray crystallographic analysis were obtained from the slow evaporation of a saturated solution of the compound in methanol. The acetylene crystallises in the orthorhombic centrosymmetric space group Pbca with eight molecules in the unit cell (Figure 3-21).

![Figure 3-21](image)

**Figure 3-21:** Perspective view of the molecular structure of 32, with atomic labelling shown. Selected bond lengths (Å) and angles (°): C1-C2 1.192(4), C1-C11 1.422(4), C2-C21 1.416(4), C14-C15 1.502(5), C24-C25 1.492(5), C11-S1-C14 92.2(2), C21-S2-C24 93.0(2).

![Figure 3-22](image)

**Figure 3-22:** Crystal packing along the a) c axis and b) a axis of 34.

This acetylene 32 underwent a Diels-Alder reaction in benzophenone with 2,3,4,5-tetrakis-(4-tert-butylphenyl)cyclopentadienone 25 to give the blocked di-thienyl polyphenylene 1,2-di(5-methyl-2-thienyl)-3,4,5,6-tetra-(4-tert-butylphenyl)benzene 33 in 41% yield.
In the $^1$H NMR spectrum of 33 a total of six aromatic signals are present as a result of the $C_2$ symmetry in the molecule, two sets of phenyl doublets with each signal each integrating for four protons at $\delta$ 6.92, 6.81, 6.80 and 6.62 ppm and two thiophene signals which overlap at $\delta$ 6.27 ppm. The methyl group is seen at $\delta$ 2.26 ppm integrating for six protons and the two tert-butyl signals are seen at $\delta$ 1.16 and 1.10 ppm, each integrating for eighteen protons.

Upon oxidation of 33 with iron trichloride in dichloromethane the partially fused phenylene 34 was isolated after chromatography using dichloromethane: hexane (1:3) as the eluent ($R_f = 0.6$). Due to the fact that there is one exclusive intramolecular bond formed in this oxidation the workup for this compound was simpler than that required for the dimeric systems and a much higher yield of 90% was obtained. The $^1$H NMR spectrum of 34 shows four phenyl signals each integrating for four protons which a TOCSY experiment show to be paired as $\delta$ 7.18 and 7.16 ppm and $\delta$ 7.09 and 6.72 ppm. A single thiophene signal is observed, integrating for two protons at $\delta$ 7.16 ppm. Also seen is the methyl signal integrating for six protons at $\delta$ 2.36 ppm and the two tert-butyl peaks at $\delta$ 1.24 and 1.00 ppm. MALDI mass spectral analysis of 34 gives a value of m/z 796.4168 m.u. for [M]$^+$ (calculated as 796.4136 m.u.).

Single crystals of 34 suitable for X-ray crystallographic analysis were obtained from the slow evaporation of a saturated solution a 1:1 mixture of hexane: dichloromethane. The molecular structure of this compound is in agreement with the spectroscopic data, showing the formation of an intramolecular carbon-carbon bond between the 3 and 3’ positions on the thiophene rings (Figure 3-23).

Figure 3-23: Perspective view of the molecular structure of 34, with atomic labelling shown. Selected bond lengths (Å) and angles (°): C11-C12 1.437(8), C12-C13 1.420(7), C13-C14 1.398(6), C14-C15 1.433(8), C15-C16 1.386(8), C11-C16 1.405(7), C11-C71 1.432(7), C71-C72 1.380(7), C62-C72 1.416(8), C61-C62 1.379(7), C12-C61 1.440(7), C71-S1-C74 92.1(3), C61-S2-C64 91.9(3).

Compound 34 crystallises in the monoclinic space group Cc with a total of four molecules of the compound in the unit cell. In the crystal packing an alternating abab pattern can be seen where the orientation of the sulfur containing part of each molecule in the two layers differs from the other by approximately 120° (Figure 3-24, a). This offset is due to the bulky nature of the tertiary butyl groups on the molecule which prevent the formation of any other orientation in the solid state, within each plane the sulfur containing parts of the molecules all have the same orientation (Figure 3-24, b). Unlike in other reported polyphenyl cases no π-π interactions are seen between the molecules in each layer and a minimum π-π distance of 4.95 Å is observed. This π-π distance is significantly longer than those seen for systems where stacking is observed, in which π-π distances between 3.55 and 4.00 Å are common.

![Diagram](image)

**Figure 3-24:** Crystal packing along the a) a axis and b) c axis of 34. Hydrogens have been removed for clarity.

From the structure of 34 it can be seen that it is possible to synthesise a monomeric di-thienyl 2,2’ polyphenylene. In order to examine the possibility of making a similar 3,3’ system the bromothiophene starting material 4-bromo-2-methylthiophene 35 was prepared from the commercially available 2-bromo-5-methylthiophene using the “halogen-dance” reaction. In this reaction the sterically hindered lithiation agent lithium diisopropylamine is reacted with 2-bromo-5-methylthiophene at -78°C in tetrahydrofuran. There is then a rearrangement of the thiophene substituents using 2-bromo-5-methylthiophene as a catalyst to give the more stable lithiated species 3-bromo-5-methylthienyl-2-lithium which is quenched with methanol after 2 hours to give 35 in an 82% yield (Scheme 3-8).

![Scheme 3-8](image)

(i) Lithium diisopropylamine, -78°C, THF, 2 hours; (ii) Methanol quenching.

**Scheme 3-8:** Synthesis of 35 via a halogen-dance reaction.

The Sonogashira coupling of 4-bromo-2-methylthiophene 35 with 2-methyl-3-butyn-2-ol was attempted in order to give bis(5-methyl-3-thienyl)acetylene 36; however instead the compound 3-(bis(5-methyl-3-thienyl)methylene)-2-methyl-5-(5-methyl-3-thienyl)pent-4-yn-2-ol 37 was obtained in a 52% yield (Scheme 3-9).

![Scheme 3-9: The Sonogashira coupling of 35.](image)

(i) 2-methyl-3-butyn-2-ol, Pd(PPh₃)₄, CuI, PhNEt₃Cl, Benzene, aq. NaOH, 3 days; (ii) 80°C, 3 days.

**Scheme 3-9:** The Sonogashira coupling of 35.

¹H NMR spectral analysis of 37 shows six thiophene signals all integrating for one proton at δ 7.15, 7.11, 7.03, 6.97, 6.76 and 6.66 ppm as well as four methyl signals two of the three thienyl methyl groups overlapping at δ 2.50 ppm integrating for three protons each, with the third at δ 2.47 ppm also integrating for three protons. The other methyl groups appear at δ 1.58 ppm integrating for six protons, while the hydroxyl signal is observed at δ 2.38 ppm integrating for one proton (Figure 3-25).

![Figure 3-25: The ¹H NMR spectrum of 37 (400 MHz, CDCl₃, 25°C).](image)
In order to synthesis 36 a Sonogashira coupling using trimethyl silyl acetylene was attempted; however this reaction was unsuccessful and the products formed could not be isolated. A crystal of 37 suitable for X-ray analysis was obtained via the slow evaporation of a saturated dichloromethane solution of the product. 37 crystallised in the monoclinic space group Cc with four molecules in the unit cell.

Figure 3-26: Perspective view of the molecular structure of 37, with atomic labelling shown. Selected bond lengths (Å) and angles (°): C1-C2 1.197(4), C1-C12 1.421(4), C3-C5 1.354(3), C5-C22 1.485(3), C5-C32 1.481(3), C6-O1 1.436(4), C11-S1-C14 92.75(4), C21-S2-C24 91.84(5), 92.39(4).

As a result of the complicated reactivity of 3-bromo-5-methylthiophene 35 which precludes the synthesis of acetylene 36 incorporation of the fused 3,3’ di-thienyl unit into the precursor without using the acetylene was attempted. (See §6.4).
3.6 Conclusion

The synthetic routes used in this chapter have led to the successful synthesis of three new acetylenes and four di-thieryl substituted polyphenylenes, three of which are novel.

The [2+2] Diels-Alder reaction which has been used in the synthesis is a good route for the preparation of such compounds. It gives the products in reasonable yields and allows for variations of the substituents, through changes on both the acetylene and the cyclopentadienone used which are not possible using other synthetic methods. The reaction times for the Diels-Alder reaction are significantly shorter than those of other synthetic methods for hexa-substituted polyphenyl benzenes (1 hour for the Diels-Alder compared to 72 hours for cyclotrimerisation).

Comparisons of the $^1$H NMR spectra of the polyphenylene compounds reveal some trends in the shift of the thiophene signals dependant on the substituents ortho to them on the central benzene ring. This will make the $^1$H NMR spectral analysis of later compounds easier.

X-ray crystallographic analysis shows seven of the structures and allows for examinations of both the packing and the orientation of the thiophene ring relative to the central benzene ring of the molecules in the solid state. These showed no $\pi$-$\pi$ interactions in the solid state, probably due to the uncyclised phenyl rings which lie out of the plane of the central benzene ring. As liquid crystal and aggregation effects are dependant on these interactions, such properties are not expected for these systems.

Cyclodehydrogenation with iron trichloride has been found to be a successful method for the dehydrogenation of thienyl substituted polyphenylenes. It gives newly formed inter and intramolecular carbon-carbon bonds on the thiophene parts of the molecules, leading to the formation of dimeric partially fused thienyl compounds. Understanding the reactivity of such systems allows for the development of more complicated di-thienyl substituted compounds, some such systems will be discussed in Chapter 6.

In the following chapters investigations into the photochemical and electrochemical properties of both the monomeric di-thienyl polyphenylenes and their partially fused dimers will be presented with interesting results. Also investigations into expanding the thienyl substitution towards tetra- and hexa-thienyl substituted systems have been carried out.

3.7 References


Part 4: Photochemistry and electrochemistry of mono- and di-thienyl polyphenylenes
4.1 Introduction

In Part 3 the synthesis and characterisation of a number of novel di-thienyl polyphenylenes was described; the range of structural variations observed for these systems has led to a systematic study of their optical properties. Along with these the properties of a family of mono-thienyl polyphenylene compounds which have been previously prepared within the group will be discussed.

The electrochemical and photochemical properties of conjugated thiophene systems similar to those prepared in part 3 have been investigated by a number of groups. Examination of the absorption and emission properties of oligo-thiophenes has been carried out by Taliani and Egelhaaf. In this study it was found that when the oligothiophene conjugation length is between three and six, UV/Vis examination shows a broad absorption is observed between 330 and 410 nm in dichloromethane. Along with this a vibrationally structured fluorescent emission is seen between 405 and 570 nm (λexc 380 nm). For polythiophene similar absorption and emission properties can be seen, however unlike in oligothiophenes the photochemical properties of polythiophene vary greatly depending on the temperature or solvent employed. The frequencies of the absorptions observed for polythiophene can vary between 400 and 600 nm depending on the conditions used. Looking at oligo-4-thiophene (Figure 4-1) which contains four conjugated thiophenes, similar to the dimeric structures 29-31, a broad absorption with λmax 392 nm is seen. Upon exciting into this band a structured fluorescence emission with λmax 454 and 476 nm and a shoulder at λ 513 nm are observed.

![Figure 4-1: Oligo-4-thiophene studied by Egelhaaf.](image)

The fused di-thienyl systems a and b shown in Scheme 4-1 have been prepared using the photochemically induced cyclisation of the corresponding di-thienyl alkenes in the presence of elemental iodine by Kellogg et al.
Unlike in the case of oligothiophenes these systems only absorb in the ultraviolet region with highly structured bands observed out to 320 nm. Luminescence studies on the di-2-thienyl compound in dichloromethane (Scheme 4-1, a) were carried out by Hu; these showed a fluorescence emission between 310 and 375 nm with $\lambda_{\text{max}}$ at 335 nm.²

Building on this work Nishide and co-workers have developed a series of oligomers based upon a fused di-thiophene framework (Figure 4-2).⁵ Synthesis of these species was carried out via a series of Suzuki, Stille and Sonogashira couplings. In order to counter the insolubility of the tetramer and pentamer analogues, these systems have been substituted with long chain hydrocarbon groups.

UV/Vis studies on these systems in toluene show the formation of a series of vibrationally structured absorptions each with two bands with $\lambda_{\text{max}}$ between 380 and 445 nm. For the dimeric oligothiophene which contains four thiophene rings, these
absorptions appear with $\lambda_{\text{max}}$ 380 and 403 nm. As the length of the oligothiophene increases the absorption peaks are red shifted, with the absorption shifting to $\lambda_{\text{max}}$ 420 and 445 nm in the pentamer. The vibrational structure observed in the absorption spectrum is retained as the oligomer length increases. Luminescence spectroscopy of these systems shows a structured set of emissions between 420 and 550 nm. Again as was observed in the absorption spectra a red shift in the emissions is seen as the oligomer length increases. Looking at the dimer, whose structure is similar to that of compound 29, a structured set of emissions with $\lambda_{\text{max}}$ 413 and 437 nm along with a shoulder at 465 nm can be observed.

Cyclic voltammetric examinations of the oligothiophenes in benzonitrile ($10^{-4}$ M, electrolyte: 0.1 M tetrabutylammonium perchlorate) show a very weak reversible oxidation ($i_{\text{ox}} = 0.03$ mA) with $E_{1/2} = 0.63$ V ($E_{\text{pa}} = 0.67$ V, $\Delta E_p = 80$ mV) vs. Fc/Fc$^+$. This oxidation is very weak and could not be observed at slow scan rate; however at a scan rate of 100 mV/s it was detected.

An extended system containing two fused thiophenes along with two free thiophene units has been developed by Song and Swager (Figure 4-3).

![Figure 4-3: The thienyl system developed by Song and Swager.](image)

Luminescence studies on this compound again show a series of structured emissions between 415 and 510 nm with $\lambda_{\text{max}}$ 430 and 465 nm as was the case with other fused thiophene systems.
4.2 Mono-thienyl systems

Three mono-thienyl polyphenylenes have been previously prepared in the group by Prof. Sarath Perera. The thienyl polyphenylene 1-(3-thienyl)-2,3,4,5,6-penta(4-tert-butylphenyl)benzene \( 38 \) was prepared via the Diels-Alder reaction of (4-tert-butylphenyl) (3-thienyl)acetylene \( 2 \) with 2,3,4,5-tetrakis-(4-tert-butylphenyl) cyclopentadienone \( 25 \) (Scheme 4-2).

Upon cyclodehydrogenation of \( 38 \) the reason behind the choice of 3-thiophene becomes self-evident; it provides two carbon sites (2- and 4-) for oxidative carbon-carbon bond formation. On complete cyclisation only one isomer of the product can be formed, irrespective of the twist of the thiophene about its point of attachment to the polyphenylene fragment. This allows for the formation of the planar graphene-like superaromatic thiophene \( 39 \) and its 5,5' dimer \( 40 \); no intermolecular dimerisation of \( 38 \) is observed prior to intramolecular cyclodehydrogenation, inferring dimerisation can only occur after the precursor polyphenylene has been oxidised and flattened. This result implies that in \( 38 \) the intramolecular cyclodehydrogenations between the thiophene 2- and 4- positions and the polyphenylene core are more facile than the intermolecular dimerisation at the 5- position. Although these species were made prior to this thesis no investigation into their electrochemical and photochemical properties had been carried out. Due to the similarities between these compounds and those prepared in Part 3, they were studied as part of investigations into di-thienyl polyphenylene species.
4.3 Photochemical properties

4.3.1 UV/Visible spectroscopy of thienyl phenylenes

There are significant similarities in the normalised UV/Vis spectra of the five thienyl polyphenylene precursors shown earlier 26, 27, 28, 33 and 38 in chloroform (10^-4 M) (Figure 4-4, Table 4-1).

![Figure 4-4: The UV/Vis spectra (10^-4 M chloroform) and structures of the thienyl polyphenylenes.](image)

Four of the five compounds have two broad absorption bands between 255-260 nm and 275-280 nm. These bands are in the same region and are similar in nature to those seen for the phenylene precursor of hexabenzocoronene in which two broad bands are observed at $\lambda_{\text{max}}$ 247 and 276 nm (in 1,2-dichloroethane). The small shift in the first of
these compared to the thienyl-polyphenylenes is most likely due to the change in solvent used to measure the spectra. These broad unstructured signals are indicative of a lack of planarity within the structures, this is to be expected as in similar nitrogen containing and all carbon\textsuperscript{8-11} systems the phenyl substituents lie out of the plane of the central benzene ring. This orientation was also seen for 26 and 27 in the crystal structures reported earlier. In the case of the methyl substituted system 33, a small bathochromic shift is observed for the lower-energy band. This is consistent with the effect of alkyl substitution on extended thienyl aromatic systems reported by Brusso\textsuperscript{12} which shows a shift of between 5 and 10 nm depending on the alkyl substituent used and is a result of the increase in electron density on the thienyl rings. For the unsubstituted systems a small increase in the structure of the lower-energy band can be observed, this band is more clearly observed for 26, decreasing in intensity from 28 to 27 with the weakest bands seen in 38. This trend can be related to the possible interaction of the sulfur lone pairs with the phenyl parts of the molecule as they rotate. In 26 two sulfur atoms point towards the phenyl part and as such an increase in the rigidity of the system is observed. As the sulfur interactions decrease the system gets less rigid and changes in the absorption bands are observed.

**Table 4-1:** UV/Vis absorption data for thienyl substituted polyphenylene compounds.

<table>
<thead>
<tr>
<th></th>
<th>(\lambda) [nm]</th>
<th>(10^3 \varepsilon) [mol(^{-1})L cm(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>monomers</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>256 (8.1), 281 (6.5), 338(sh) (0.8).</td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>256 (5.2), 279(sh) (3.9)</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>256 (3.9), 277 (3.0).</td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>249 (3.5), 289 (3.3), 355(sh) (0.3)</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>297 (7.4), 323(sh) (1.4)</td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>257 (4.1), 277(sh) (2.9).</td>
<td></td>
</tr>
<tr>
<td><strong>S-graphenes</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>241 (9.0), 340(sh) (4.7), 358 (8.0), 369 (8.4), 408 (2.1), 432 (2.0)</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>243 (16.1), 358 (14.0), 369 (14.7), 409(sh) (5.4), 433(sh) (3.6), 464(sh) (2.2) (tail till 530)</td>
<td></td>
</tr>
<tr>
<td><strong>dimers</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>266 (5.9), 321 (5.3), 375 (3.6), 396 (4.1), 418 (3.5), 447(sh) (1.0) (tail till 510)</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>289 (5.1), 394 (2.0), 415 (2.3), 443 (2.1), 494(sh) (0.7) (tail till 600)</td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>270 (7.9), 288 (7.4), 379 (2.6), 399 (3.7), 421 (3.0), 455(sh) (0.9) (tail till 540)</td>
<td></td>
</tr>
</tbody>
</table>
Part 4: Photochemistry and electrochemistry of mono- and di-thienyl polyphenylenes

Looking at the absorption spectra of the superaromatic thiophene compound 39 and its dimer 40, two intense absorptions are seen for both at $\lambda_{\text{max}}$ 358 and 369 nm. (Figure 4-5, Table 4-1) These are similar to those observed in the symmetrical hexa-alkyl substituted hexabenzocoronenes where peaks are seen at $\lambda_{\text{max}}$ 348 and 364 nm.\textsuperscript{13-15} The absence of significant changes in the absorption maxima and similarities in the $\lambda_{\text{max}}$ values indicate that the addition of sulfur to the system has had minimal effect on the absorption spectra.

![Figure 4-5: The UV/Vis spectra of superaromatic thiophenes 39 and 40 (10\textsuperscript{-4} M chloroform).](image)

The dimeric compound 40 shows a similar absorption profile to its monomer 39 but has less structure and has a new absorption tail between 460 and 530 nm. This new low energy absorption is independent of concentration, precluding the formation of any aggregated ground state complexes (range of 10\textsuperscript{-3} – 10\textsuperscript{-5} M). Instead it may be due to the fact that as a result of dimerisation there is an increase in conjugation length arising from the two monomeric subunits when they are aligned coplanar to each other (Figure 4-6).\textsuperscript{16}

![Figure 4-6: The increased planarity seen in 40 (Bu- groups not shown for clarity), isomer drawn is the one in which lone pair interactions are minimised.](image)
Part 4: Photochemistry and electrochemistry of mono- and di-thienyl polyphenylenes

Looking at the absorptions of the three partially fused dimeric di-thienyl systems \(29, 30\) and \(31\), a tail between 450 and 550 nm similar to the one observed for \(40\) is observed (Figure 4-7, Table 4-1).

![UV/Vis spectra of 29, 30, and 31](image)

**Figure 4-7:** The UV/Vis spectra and possible isomers of dimeric di-thienyl compounds \(29, 30\) and \(31\) \((10^{-4} \text{ M, chloroform})\).

In many ways \(29, 30\) and \(31\) are showing the characteristics of both polyphenylenes \((\lambda_{\text{max}} 250-300 \text{ nm})\) and structured graphenes \((\lambda_{\text{max}} 370 \text{ nm})\). A series of absorptions due to the phenyl rings twisted out of the plane of the molecule, similar to those seen in the precursor compounds are observed between \(\lambda 240\) and \(350\) nm. In addition there is a set of structured high-energy absorptions between \(\lambda 350\) and \(450\) nm similar to those seen in fused thiophene systems\(^5\) and a shoulder with a tail out to longer wavelengths \((\lambda 550\) nm) similar to that observed for \(40\). The new sharp structured bands are in agreement with the presence of a high-energy barrier of rotation for the monomeric subunits around the newly formed bond which links them (Scheme 4-3).\(^{17-20}\)
Part 4: Photochemistry and electrochemistry of mono- and di-thienyl polyphenylenes

![Diagram of perpendicular (A) and coplanar (B) orientations in dimeric systems.]

**Scheme 4-3**: The perpendicular (A) and coplanar (B) orientations possible in dimeric systems.

It appears that the position of the sulfur atoms and the direction of their lone pairs may play an important role in the barrier for rotation around this newly formed bond. In the case of **29**, where all of the sulfur atoms point toward the phenylene core the bands appear at the shortest wavelength of the three dimers (\(\lambda_{\text{max}}\) 375, 396 and 418 nm). In dimer **31** where two of the four sulfurs point toward the core these bands appear at \(\lambda_{\text{max}}\) 379, 399 and 421 nm while in **30** where all four sulfurs point away from the core, the bands are the most red shifted (\(\lambda_{\text{max}}\) 394, 415 and 443 nm).

Again as in **40** the low energy absorption tail is due coplanar orientation of the two units of the dimer when it is formed in solution. Using it, an estimate of the percentage of coplanar molecules (Scheme 4-3, B) in solution could be made. The UV/Vis spectrum of **40** (Figure 4-5) shows a new tail between \(\lambda\) 460 and 530 nm not present in the spectrum of its monomer **39**. Comparing the area before and after the appearance of the tail (at 460 nm) an estimate of 8% has been calculated for the percentage of the planar conformation observed in **40** (Table 4-2). Similar estimates have been made for **29**, **30** and **31** based upon the position at which the tail is observed to commence. Looking at the excitation spectra of **29-31** at \(10^{-5}\) M (Table 4-3) the contribution from the twisted contribution can be seen to disappear at 450 nm for **29**, 460 nm for **30** and 440 nm for **31**. From these estimates it can be seen that the planar conformation appears easiest to retain in solution in dimer **30** (24%). The percentage of planar, low energy absorptions seen in the spectrum can be related to the interactions between the sulfur atoms and the phenylene core of the molecule, with **29** and **40** showing more interaction than is seen in **30** and **31** and hence a smaller percentage of lower energy absorptions.
Table 4-2: Estimated comparisons of the percentage of the twisted and planar conformations in the UV/Vis spectra of the dimers 29, 30, 31 and 40.

<table>
<thead>
<tr>
<th></th>
<th>Twisted conformation</th>
<th>Planar conformation</th>
<th>Percentage of Planar conformation</th>
</tr>
</thead>
<tbody>
<tr>
<td>29</td>
<td>(Area under 350-450 nm region)</td>
<td>(Area under 450-510 nm region)</td>
<td>56.7</td>
</tr>
<tr>
<td>30</td>
<td>(Area under 350-460 nm region)</td>
<td>(Area under 460-600 nm region)</td>
<td>42.0</td>
</tr>
<tr>
<td>31</td>
<td>(Area under 350-440 nm region)</td>
<td>(Area under 440-600 nm region)</td>
<td>43.5</td>
</tr>
<tr>
<td>40</td>
<td>(Area under 300-460 nm region)</td>
<td>(Area under 460-550 nm region)</td>
<td>119.4</td>
</tr>
</tbody>
</table>

Given that these percentages are based upon extrapolation from recorded spectra some error (~3%) is present in these calculations; however they give an estimate of the relative conformations observed.
Part 4: Photochemistry and electrochemistry of mono- and di-thienyl polyphenylenes

Comparing the UV/Vis spectra of the blocked precursor 33 to that of the fused monomer 34 prepared from it, the effect of the increase in planarity as a result of the 3,3′ thiophene-thiophene bond formation can be seen. A decrease in intensity of the band due to the twisted aromatic rings at 249 nm is observed and an intense peak is seen at $\lambda_{\text{max}}$ 297 nm coming from the new fused thiophene system.

![Figure 4-8](image)

**Figure 4-8:** The UV/Vis spectra of 33 and 34 (10$^{-4}$ M, chloroform).

### 4.3.2 Luminescence of thienyl phenylenes in solution

The emission spectra of the thienyl precursors 26, 27, 28 and 33 in chloroform each show two broad weak bands which do not change with concentration, indicating that the compounds are quite structurally flexible in both the ground and excited states (Figure 4-9, Table 4-3).

![Figure 4-9](image)

**Figure 4-9:** The high (a) and low (b) energy emission spectra of 26, 27, 28 and 38 (10$^{-3}$ M chloroform).
Table 4-3: Luminescence and lifetime data for thienyl substituted polyphenylene compounds in chloroform.

<table>
<thead>
<tr>
<th>T[K]</th>
<th>Φem</th>
<th>λem [nm]</th>
<th>Φexc</th>
<th>λexc [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>26 10⁻⁵ M 298</td>
<td>330th, 345sh, 358, 383 (λem, 420)</td>
<td>423 (λem, 330)</td>
<td>444em (λem, 380)</td>
<td>465, 495 (λem, 425)</td>
</tr>
<tr>
<td>77</td>
<td>311th, 346em, 363 (λem, 390)</td>
<td>390em, 345h, 443h, 520th (λem, 330)</td>
<td>3.3(37%), 11.5(63%) (λem, 370-λem, 450)</td>
<td></td>
</tr>
<tr>
<td>27 10⁻⁵ M 298</td>
<td>324 (λem, 405)</td>
<td>405 (λem, 360)</td>
<td>405sh, 485em, 512th (λem, 395)</td>
<td>2.7(28%), 10.2(72%) (λem, 340-λem, 435)</td>
</tr>
<tr>
<td>77</td>
<td>325sh, 365em, 395sh (λem, 510)</td>
<td>420em, 490, 522 (λem, 330)</td>
<td>3.3(26%), 14.2(74%) (λem, 370-λem, 480)</td>
<td></td>
</tr>
<tr>
<td>28 10⁻⁵ M 298</td>
<td>295sh, 315th (λem, 390)</td>
<td>430 (λem, 360)</td>
<td>495th, 532th (λem, 290-420)</td>
<td>3.3(38%), 7.6(62%) (λem, 340-λem, 390)</td>
</tr>
<tr>
<td>77</td>
<td>290th, 330th, 355, 410 (λem, 490)</td>
<td>380em, 515 (λem, 290)</td>
<td>6.2(42%), 16.1(58%) (λem, 370-λem, 490)</td>
<td></td>
</tr>
<tr>
<td>29 10⁻⁵ M 298</td>
<td>315, 370, 445, 460, 480, 490, 499th, 519th (λem, 550)</td>
<td>545em, 580 br (λem, 365)</td>
<td>2.3(54%), 14.2(46%) (λem, 460-λem, 545)</td>
<td></td>
</tr>
<tr>
<td>77</td>
<td>325, 380, 400, 425 (λem, 495)</td>
<td>495, 547, 620th (λem, 380)</td>
<td>6.20br (λem, 510)</td>
<td></td>
</tr>
<tr>
<td>10⁻⁵ M 298</td>
<td>366, 477, 510th, 540 (λem, 510)</td>
<td>620br (λem, 510)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>77</td>
<td>283sh, 315em, 375, 395, 420 (λem, 440-495)</td>
<td>438, 465em, 495, 532th (λem, 290-420)</td>
<td>1.4(51%), 13.2(49%) (λem, 370-λem, 445)</td>
<td></td>
</tr>
<tr>
<td>30 10⁻⁵ M 298</td>
<td>290, 310, 415, 430, 450 (λem, 490)</td>
<td>437, 486, 535th, 570th (λem, 310-390)</td>
<td>229.4(20%), 1268.1(80%) (λem, 370-λem, 570)</td>
<td></td>
</tr>
<tr>
<td>77</td>
<td>367, 433, 476, 515 (λem, 575)</td>
<td>457, 490, 530, 570th, 605th (λem, 310-390)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10⁻⁵ M 298</td>
<td>310, 398, 420em, 448 (λem, 490)</td>
<td>520th, 605th (λem, 475)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>77</td>
<td>284em, 305sh, 370, 429, 454 (λem, 490)</td>
<td>457, 486, 515, 560, 595th (λem, 370)</td>
<td>2.2(43%), 12.8(57%) (λem, 370-λem, 460)</td>
<td></td>
</tr>
<tr>
<td>31 10⁻⁵ M 298</td>
<td>315, 360, 446, 456, 475, 486 (λem, 525)</td>
<td>430, 460, 495, 535th (λem, 310-420)</td>
<td>282.2(66%), 1315.9(73%) (λem, 370-λem, 525)</td>
<td></td>
</tr>
<tr>
<td>77</td>
<td>310, 375, 398, 420 (λem, 460)</td>
<td>430, 460, 495, 535th (λem, 310-420)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10⁻⁵ M 298</td>
<td>285sh, 370, 387th, 405, 425 (λem, 490)</td>
<td>430, 460, 490th (λem, 360)</td>
<td>1.2(49%), 10.5(51%) (λem, 295-λem, 430)</td>
<td></td>
</tr>
<tr>
<td>77</td>
<td>290sh, 370, 420 (λem, 480)</td>
<td>430, 460, 490 (λem, 290)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>33 10⁻⁵ M 298</td>
<td>447, 457em, 475 (λem, 535)</td>
<td>533 (λem, 460)</td>
<td>3.3(66%), 8.1(34%) (λem, 460-λem, 545)</td>
<td></td>
</tr>
<tr>
<td>77</td>
<td>289sh, 312em, 352, 370th (λem, 400)</td>
<td>400, tail till 600 (λem, 300-350)</td>
<td>1.5(51%), 15.4(49%) (λem, 340-λem, 450)</td>
<td></td>
</tr>
<tr>
<td>14 10⁻⁵ M 298</td>
<td>298th, 301, 325, 400-495 (λem, 495)</td>
<td>376, 395, 415, 495 (λem, 340)</td>
<td>173.7(18%), 1096.6(82%) (λem, 370-λem, 490)</td>
<td></td>
</tr>
<tr>
<td>38 10⁻⁵ M 298</td>
<td>325 (λem, 357)</td>
<td>375 (λem, 320)</td>
<td>2.7(28%), 10.2(72%) (λem, 340-λem, 375)</td>
<td></td>
</tr>
<tr>
<td>77</td>
<td>325sh, 364 (λem, 445)</td>
<td>375sh, 420th, 445sh, 475th (λem, 360)</td>
<td>4.3(38%), 14.2(64%) (λem, 370-λem, 450)</td>
<td></td>
</tr>
<tr>
<td>39 10⁻⁵ M 298</td>
<td>290sh, 311, 341, 365 (λem, 475)</td>
<td>346, 442th, 472em, 508 (λem, 285)</td>
<td>11.1(47%), 234.0(53%) (λem, 370-λem, 495)</td>
<td></td>
</tr>
<tr>
<td>77</td>
<td>290th, 320, 355, 392, 408, 433em (λem, 475)</td>
<td>430sh, 448, 482 (λem, 485)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40 10⁻⁵ M 298</td>
<td>527 (λem, 580)</td>
<td>580 (λem, 525)</td>
<td>3.3(37%), 15.7(63%) (λem, 460-λem, 580)</td>
<td></td>
</tr>
<tr>
<td>77</td>
<td>365, 397, 410, 452sh, 440, 555, 595th (λem, 640)</td>
<td>567, 600th, 637 (λem, 430)</td>
<td>10.9(23%), 24.8(77%) (λem, 370-λem, 485)</td>
<td></td>
</tr>
<tr>
<td>10⁻³ M 298</td>
<td>290th, 360em, 410, 430, 463 (λem, 495)</td>
<td>472, 485, 494th, 504, 528, 565 (λem, 360)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>77</td>
<td>290th, 360em, 428, 470 (λem, 529)</td>
<td>470, 503sh, 529, 540th, 560sh, 623, 647 (λem, 360)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The high energy bands which are observed between $\lambda$ 360 and 430 nm are related to the polyphenylene core of the molecule. For 26 and 28 the phenylenes can interact with the sulfur lone pairs on the 2-substituted thiophenes resulting in a red shift compared to 27. For 38 the high-energy band appears blue shifted (~375 nm) due to the presence of only one thiophene substituent, compared to two on each of the other species. The low energy emission bands that are observed between 450 and 520 nm are due to the thiophene substitution of the precursors. These emissions are not observed in all-carbon phenylenes but are characteristic of systems in which thienyl substituents are present.\textsuperscript{17-20}

The emission of the superaromatic thiophene 39 is highly structured and shows no change in shape or position when the concentration of the sample or the excitation and emission wavelengths are varied (Figure 4-10, Table 4-3) which is consistent with its all carbon equivalents.\textsuperscript{13-15}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{spectrum.png}
\caption{The emission and excitation spectra of 39 (10\textsuperscript{-4} M chloroform).}
\end{figure}

The highly structured nature of the emission spectra of 39 is indicative of the presence in solution of several excited states, each close in energy and having their own vibronic progression. When the emission lifetime of 39 is examined (Table 4-3) a bi-exponential lifetime of 11.1 ns (47\%) and 234 ns (53\%) is observed. These lifetimes are short, indicating the system is undergoing fluorescence emission while the bi-exponential lifetime indicates the presence of multiple excited states. Comparing the fluorescence of
with that of alkyl substituted HBC\textsuperscript{13} it can be seen, as was the case in the absorption spectra, that the addition of the sulfur has had a minimal effect on the optical properties. For HBC two strong fluorescence emissions are observed at $\lambda_{\text{max}}$ 489 and 498 nm (compared to $\lambda_{\text{max}}$ 475 and 495 nm for 39) and a second weaker emission at $\lambda_{\text{max}}$ 524 and 534 nm ($\lambda_{\text{max}}$ 530 and 537 nm in 39) along with a tail out to $\lambda$ 625 nm which is also seen in 39.\textsuperscript{21}

For the dimeric systems 29, 30, 31 and 40 a dual luminescence is observed depending on the concentrations examined. In dilute solutions (chloroform, $10^{-5}$ M), the excitation spectra correspond to the absorption spectra with the absence of the tail seen in the UV/Vis. Taking 30 as an example (Figure 4-11) it can be seen that the tail in the UV/Vis from 460 – 550 nm is not observed in the excitation spectrum in $10^{-5}$ M chloroform solution. This indicates that in dilute solution the dimers are highly twisted (Scheme 4-3, A) and cannot easily take up the coplanar orientation (Scheme 4-3, B) which is responsible for the tail.\textsuperscript{17-20}

![Figure 4-11](image)

**Figure 4-11:** The UV/Vis (black), emission (blue) and excitation (red) spectra of 30 ($10^{-5}$ M chloroform).

The emission spectra at this concentration (chloroform, $10^{-5}$ M), show a well structured high-energy band which is similar in location to that of the high-energy thiophene related band in the starting materials. These bands are now more vibronically structured due to the increased rigidity around the thiophenes in the dimers. They appear unchanged in
energy from the starting materials, indicating there is little change in the delocalisation of
electronic density around the thiophenes and that the twisted conformation is prevalent at
low concentrations.

At higher concentrations (10^{-3} M, chloroform), the dimers show a new broad lower-
energy band in their emission spectra. Again taking 30 as an example (Figure 4-12), it
can be seen that this new band corresponds to the low-energy absorption which is seen in
the UV/Vis spectrum. This suggests that this new emission is related to the planar
conformation of the dimer (Scheme 4-3, B). In the excitation spectra at higher
concentrations a new low-energy band appears (between \( \lambda \) 460 and 550 nm) matching the
tail described in the UV/Vis spectrum. This suggests that the planar conformation is
observed in concentrated solution.

Figure 4-12: The UV/Vis (black), emission (blue) and excitation (red) spectra of 30 (10^{-3} M chloroform).

The planar arrangement of the two fused (or partially fused) thiophene units is difficult to
retain in solution; however at high concentration the increased molecular density of the
solution leads to the excited state of the planar conformation forming excimeric
species.\textsuperscript{22-23}
Comparing the emission spectra of the four dimers a number of observations can be made. Although the four dimers all form excimeric species (Figure 4-13) the nature of the excimers are not the same; in the case of 40 the low-energy excimeric emission can be seen even at low concentration with a peak visible at $\lambda_{\text{max}}$ 567 nm. This is not surprising as 40 is the only dimeric system in which the entire phenylene core has been fully dehydrogenated, giving a flat aromatic platform throughout the molecule, as such it is easier to form excimers in this case.

Looking at the lifetimes observed for the four dimers the excited states appear different in nature (Table 4-3). Although all four species have bi-exponential lifetimes, in 29 and 40 the emissions in concentrated solutions come from a singlet state (nanosecond range) while in 30 and 31 they come from a triplet state (microsecond range). This difference is indicative of the formation of longer lived excimers in both 30 and 31 due to the fact that these species can adopt a planar conformation with greater ease. Comparing this with the relative amount of planar conformation implied by the UV/Vis spectra it can again be seen that the planar conformation is more favourable in 30 and 31 than in 29 and 40.

The dual luminescence related to the twisting of monomeric aromatic subunits has been described previously in the literature. In some cases, it is dependent on the polarity of the...
solvent\textsuperscript{24} and in others is related to excimeric processes where the temperature has a key role\textsuperscript{13}. In our case, the excimeric species only form in the dimeric systems and are not observed in any of the monomeric compounds. For the blocked compound 34 no excimeric emissions are observed and two emissions are seen (Figure 4-14). Unlike in the other examples they vary with temperature rather than with concentration.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{The emission and excitation spectra of 34 at 295 K (red) and 77 K (blue) (10\textsuperscript{-3} M chloroform).}
\end{figure}

At room temperature an emission is seen with $\lambda_{\text{max}}$ 400 nm and a tail to longer wavelength out as far as $\lambda$ 600 nm. At low temperature a new structured band is seen which overlaps with the tail observed at room temperature ($\lambda_{\text{max}}$ 495 nm, 525 nm). The lifetime of the tail was found to be in the microsecond range indicating an emission from the triplet state. As no dimer is present in 34, excimer formation, as was observed for the other fused systems is not possible. Instead the system is undergoing phosphorescence at low temperature.
4.3.3 *Solid state luminescence of thienyl phenylenes*

In the solid state each of the monomeric precursors shows a broad emission between 450 and 500 nm.

The emissions of the substituted thienyl monomers 26, 27, 28 and 38 appear similar with $\lambda_{\text{max}}$ 460-475 nm. The excitation of mono-thienyl compound 38 is slightly blue shifted to 370 nm due to the difference in its thienyl substitution. The emissions of 28 and 38 are broader than those of 26 and 27, related to the ease with which the compounds can obtain a flattened structure in the solid state.
### Table 4-4: Luminescence and lifetime data for thienyl substituted polyphenylene compounds in the solid state.

<table>
<thead>
<tr>
<th>T[K]</th>
<th>$\lambda_{em}$ [nm]</th>
<th>$\lambda_{em}$ [nm]</th>
<th>$\tau$ [ns]</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>298 405 ($\lambda_{em}$ 475)</td>
<td>475 br ($\lambda_{exc}$ 400)</td>
<td>61.2(36%), 352.7(64%) ($\lambda_{exc}$ 370-$\lambda_{em}$ 440)</td>
</tr>
<tr>
<td>27</td>
<td>298 370sh, 385, 406 ($\lambda_{em}$ 450)</td>
<td>450 max, 482 sh br ($\lambda_{em}$ 360)</td>
<td>48.9(13%), 465.9(87%) ($\lambda_{exc}$ 370-$\lambda_{em}$ 480)</td>
</tr>
<tr>
<td>28</td>
<td>323sh, 374 max, 390 ($\lambda_{em}$ 425)</td>
<td>470 br ($\lambda_{exc}$ 390)</td>
<td>37.0(18%), 407.6(82%) ($\lambda_{exc}$ 370-$\lambda_{em}$ 460)</td>
</tr>
<tr>
<td>29</td>
<td>380 ($\lambda_{em}$ 470) broad</td>
<td>470 br ($\lambda_{exc}$ 440), 482 sh br ($\lambda_{exc}$ 330)</td>
<td>40.3 (78%), 20.5 (22%) ($\lambda_{exc}$ 295-$\lambda_{em}$ 360)</td>
</tr>
<tr>
<td></td>
<td>310 max, 363, 430 ($\lambda_{em}$ 500)</td>
<td>460, 495, 530, 560 sh ($\lambda_{exc}$ 366)</td>
<td>226.9 (20%), 1197.1 (80%) ($\lambda_{exc}$ 370-$\lambda_{em}$ 495)</td>
</tr>
<tr>
<td>30</td>
<td>310 ($\lambda_{em}$ 375)</td>
<td>370 ($\lambda_{exc}$ 300)</td>
<td>307 310 sh, 370, 400 sh ($\lambda_{em}$ 480)</td>
</tr>
<tr>
<td></td>
<td>307, 450, 525 ($\lambda_{em}$ 600)</td>
<td>373 ($\lambda_{exc}$ 315)</td>
<td>243.6(20%), 1215.4(80%) ($\lambda_{exc}$ 370-$\lambda_{em}$ 600)</td>
</tr>
<tr>
<td>31</td>
<td>310 ($\lambda_{em}$ 370)</td>
<td>370 ($\lambda_{exc}$ 300)</td>
<td>315, 370, 415 sh ($\lambda_{em}$ 500)</td>
</tr>
<tr>
<td></td>
<td>303, 370, 485, 517 sh ($\lambda_{em}$ 550)</td>
<td>360 br, 430, 460, 495, 547, 600 sh ($\lambda_{exc}$ 305)</td>
<td>25.8 (30%), 42.6 (70%) ($\lambda_{exc}$ 295-$\lambda_{em}$ 360)</td>
</tr>
<tr>
<td></td>
<td>344 304 ($\lambda_{em}$ 365)</td>
<td>364 ($\lambda_{exc}$ 310)</td>
<td>203.0 (20%), 1148.4 (80%) ($\lambda_{exc}$ 370-$\lambda_{em}$ 555)</td>
</tr>
<tr>
<td>32</td>
<td>310 ($\lambda_{em}$ 460)</td>
<td>457 ($\lambda_{exc}$ 370)</td>
<td>360, 375 max, 400 sh ($\lambda_{em}$ 465)</td>
</tr>
<tr>
<td></td>
<td>597 br ($\lambda_{exc}$ 445)</td>
<td>415, 436 max, 465 ($\lambda_{exc}$ 370)</td>
<td>53.7 (19%), 471.2 (81%) ($\lambda_{exc}$ 370-$\lambda_{em}$ 460)</td>
</tr>
<tr>
<td>33</td>
<td>344 297 sh, 310 ($\lambda_{em}$ 395)</td>
<td>360 sh, 377, 394 max, 450 sh ($\lambda_{exc}$ 310)</td>
<td>14.2 (8%), 42.7 (92%) ($\lambda_{exc}$ 295-$\lambda_{em}$ 380)</td>
</tr>
<tr>
<td></td>
<td>285, 312, 330 ($\lambda_{em}$ 395)</td>
<td>374, 393 max, 415, 525 max, 565 ($\lambda_{exc}$ 310)</td>
<td>11.5 (44%), 108.0 (56%) ($\lambda_{exc}$ 340-$\lambda_{em}$ 450)</td>
</tr>
<tr>
<td></td>
<td>313, 370 ($\lambda_{em}$ 525)</td>
<td>525 max, 565 ($\lambda_{exc}$ 370)</td>
<td>371 br ($\lambda_{em}$ 465)</td>
</tr>
<tr>
<td></td>
<td>325 ($\lambda_{em}$ 360)</td>
<td>460 br ($\lambda_{exc}$ 360)</td>
<td>323, 375 br ($\lambda_{em}$ 495)</td>
</tr>
<tr>
<td></td>
<td>594 (12%), 529.6 (88%) ($\lambda_{exc}$ 370-$\lambda_{em}$ 460)</td>
<td>460 max, 519 ($\lambda_{exc}$ 320)</td>
<td>404 (12%), 529.6 (88%) ($\lambda_{exc}$ 370-$\lambda_{em}$ 460)</td>
</tr>
<tr>
<td>39</td>
<td>314 max, 365, 385, 402 ($\lambda_{em}$ 530)</td>
<td>368, 390 sh ($\lambda_{exc}$ 305)</td>
<td>307 ($\lambda_{em}$ 370)</td>
</tr>
<tr>
<td></td>
<td>308 ($\lambda_{em}$ 370)</td>
<td>509 max, 533 ($\lambda_{exc}$ 370)</td>
<td>308, 366, 399 sh ($\lambda_{em}$ 480)</td>
</tr>
<tr>
<td></td>
<td>308 max, 399 sh ($\lambda_{em}$ 480)</td>
<td>373 max, 485 (br) ($\lambda_{exc}$ 310)</td>
<td>39, 435, 491 max, 531 sh ($\lambda_{exc}$ 365)</td>
</tr>
<tr>
<td>40</td>
<td>307 ($\lambda_{em}$ 365)</td>
<td>366 ($\lambda_{exc}$ 305)</td>
<td>308 max, 370, 397 ($\lambda_{em}$ 480)</td>
</tr>
</tbody>
</table>
Comparing the fluorescence spectra in the solid state of the partially fused dimers 29, 30 and 31 to that of their respective starting materials 26, 27 and 28 a red shift in the emission is observed (Table 4-4). Taking 28 / 31 as an example (Figure 4-16) the emission of the monomer 28 has $\lambda_{\text{max}}$ 460 nm. The partially fused dimer 31 has an emission with $\lambda_{\text{max}}$ 557 nm, resulting from this a stokes shift of 3787 cm$^{-1}$ between the monomer and dimer has been calculated (Table 4-5).

Looking at the stokes shifts observed between the three sets of monomers / partially fused dimers (Table 4-5); the smallest shift of 2150 cm$^{-1}$ is observed for 26 / 29. In this pair of compounds all the sulfur atoms point towards the phenyl part of the molecule, as such dimerisation has less effect on the rotation of the system as interactions between the sulfurs and the phenyl rings are retained. As a result of this the difference between the monomer and the dimer in the solid state is smaller than that of the other partially fused dimeric systems. The pair which shows the largest shift between the monomer and dimer is 27 / 30 in these compounds all the sulfurs point away from the core of the molecule. Upon dimerisation the sulfur interaction with the molecular core decreases leading to a larger stokes shift.
Table 4-5: The emission maxima and Stokes shift for the monomers 26-28 and their corresponding dimers 29-31 in the solid state.

<table>
<thead>
<tr>
<th>Monomer / dimer</th>
<th>$\lambda_{\text{max}}$ of monomer (nm/cm$^{-1}$)</th>
<th>$\lambda_{\text{max}}$ of dimer (nm/cm$^{-1}$)</th>
<th>Stokes shift (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>26 / 29</td>
<td>475 nm (21053 cm$^{-1}$)</td>
<td>529 nm (18903 cm$^{-1}$)</td>
<td>2150 cm$^{-1}$</td>
</tr>
<tr>
<td>27 / 30</td>
<td>470 nm (21275 cm$^{-1}$)</td>
<td>600 nm (16666 cm$^{-1}$)</td>
<td>4609 cm$^{-1}$</td>
</tr>
<tr>
<td>28 / 31</td>
<td>460 nm (21740 cm$^{-1}$)</td>
<td>557 nm (17953 cm$^{-1}$)</td>
<td>3787 cm$^{-1}$</td>
</tr>
</tbody>
</table>

Observing the differences between the solid state emissions of the two superaromatic thiophenes 39 and 40 to precursor 38 (Figure 4-17, Table 4-4) a number of changes can be observed. The emission observed in 38 ($\lambda_{\text{max}}$ 460 nm) has been replaced by two emissions for the superaromatic thiophenes. A strong high-energy UV emission is seen for both 39 and 40 at $\lambda_{\text{max}}$ 368 nm (39) and 366 nm (40). This emission is similar to those observed in HBC systems$^{13}$ and has been attributed to emissions from the all-carbon part of the molecules. A second low-energy emission as a result in the increased planarity of the species is also observed at $\lambda_{\text{max}}$ 509 nm for 39 and at $\lambda_{\text{max}}$ 543 nm for 40.

Figure 4-17: The solid state emission spectra of 38, 39 and 40.
These low-energy emissions seen for 39 and 40 correspond to the vibrationally structured emissions seen in the liquid state. For all four dimers 29, 30, 31 and 40 the low-energy solid state emission comes from a triplet state (microsecond lifetime range) (Table 4-4), indicating the formation of the planar conformations as seen in the concentrated solutions of 30 and 31.

The emission spectrum of the methyl substituted system 33 is blue shifted compared to 26 as a result of the substitution on the thiophene (Figure 4-18). Looking at the excitation spectra for 33 it can be observed that unlike in the other unfused precursor compounds there are two excitation maxima observed. One at higher energy at $\lambda_{\text{max}}$ 310 nm and a lower energy excitation, similar to those seen in the other thienyl monomers at $\lambda_{\text{max}}$ 370 nm.

![Figure 4-18](image)

**Figure 4-18:** The solid state emission (solid line) and excitation (dashed line) spectra of 26 and 33.

In the blocked, fused-thiophene system 34 the solid state fluorescence shows a temperature dependent emission similar to that seen in solution. At room temperature a high energy emission is observed at $\lambda_{\text{max}}$ 394 nm (in solution it is at $\lambda_{\text{max}}$ 400 nm) while at 77 K a structured emission is observed at $\lambda_{\text{max}}$ 525 and 565 nm (in solution it is at $\lambda_{\text{max}}$ 495 and 525 nm). Again as was observed in solution, the low temperature luminescence has a microsecond lifetime (Table 4-4) indicating it is phosphorescence from a triplet state.
Part 4: Photochemistry and electrochemistry of mono- and di-thienyl polyphenylenes

The emission seen at room temperature is relatively unaffected upon changing from solution to solid (Figure 4-19, black and green) although the low temperature emission is red shifted by ~ 35 nm (Figure 4-19, blue and red). This is possibly due to solvent interactions with the triplet excited state in solution which cause a shift in the frequency at which the phosphorescence is observed.

4.4 Electrochemical properties

4.4.1 Cyclic voltammetry of thienyl phenylenes

In order to shed light on the electronic character of the thienyl polyphenylenes synthesised earlier a series of solution cyclic voltammetry experiments were carried out. The cyclic voltammogram of the monomeric superaromatic thiophene 39 (Figure 4-20, blue) shows three single electron oxidations vs. Fc/Fc' with $E_{1/2} + 0.32$ V ($E_{pa} + 0.37$ V, $\Delta E_p = 110$ mV), + 0.51 V ($E_{pa} + 0.56$ V, $\Delta E_p = 110$ mV) and + 0.96 V ($E_{pa} + 1.01$ V, $\Delta E_p = 90$ mV). For each of these oxidations the ratio of oxidation current ($i_{pa}$) to reduction current ($i_{pc}$) has a value of $i_{pa}/i_{pc} \sim 1$ indicating that all three oxidations are fully reversible processes. Similarly the dimeric superaromatic thiophene 40 (Figure 4-20, red)
also shows three fully reversible single electron oxidations with $E_{1/2} + 0.32$ V ($E_{pa} + 0.39$ V, $\Delta E_p = 110$ mV), $+ 0.57$ ($E_{pa} + 0.61$ V, $\Delta E_p = 80$ mV) and $+ 1.00$ V ($E_{pa} + 1.04$ V, $\Delta E_p = 90$ mV).

![Figure 4-20: The cyclic voltammograms of 39 (blue) and 40 (red) vs. Fc/Fc $^+$ (Chloroform 10 mM, supporting electrolyte: Bu$_4$NPF$_6$ 0.1 M).](image)

Comparing these oxidations to those of the analogous all-carbon tetrakis-tert-butyl hexabenzocoronene$^{25}$ in which only two reversible oxidations were observed at $E_{1/2} + 0.45$ and $+ 0.88$ V (reported as $+ 0.99$ V and $+ 1.42$ V vs. Ag/Ag$^+$), the effect of the sulfur substitution on the superaromatic thiophene systems can be seen. The first oxidation of both 39 and 40 occurs at the same potential ($+ 0.32$ V), indicating that this is due to the aromatic phenyl-based platforms and as such it is unaffected upon dimerisation. This oxidation is slightly easier and appears at a slightly lower oxidation potential than that seen for the less electron-rich all-carbon graphene platform; as a result of the increase in electron density due to the presence of sulfur in the thiophene graphenes. The second and third reversible oxidations (one of which is missing from the all carbon HBC) are more influenced by the fused thiophene unit. These two peaks are affected upon dimerisation and are indicative of the additional 5,5’ carbon-carbon bond fusion between the two thiophene units in 40. The result is the shifting of these two oxidation peaks in 40 to slightly higher potentials compared to those of 39. The partially fused di-thiophene-containing systems 29, 30, and 31 have electrochemical behaviour which is distinct from
that of the superaromatic thiophenes 39 and 40, with no oxidation seen within the potential window in either chloroform or acetonitrile.

The processes involved in the chemical oxidations of the di-thienyl polyphenylenes 26, 27, 28 and 33 were studied by examining their oxidation via cyclic voltammograms in chloroform (10 mM, Figure 4-21).

![Cyclic Voltammograms](image)

**Figure 4-21**: The cyclic voltammograms of 26 (black), 27 (green), 28 (blue) and 33 (red) vs. Fc/Fc$^+$ (Chloroform 10 mM, supporting electrolyte: Bu$_4$NPF$_6$ 0.1 M).

Each di-thienyl polyphenylene shows a single quasi-irreversible oxidation with the formation of a cationic species in solution. The lowest oxidation potential is observed for the 3,3’ symmetric species 27, where all four of the 2- and 5- positions on the thiophene rings are unsubstituted and therefore available for oxidation. In fact the correlation between the availability of the 2- and 5- positions on the thiophene units in the polyphenylenes and the magnitude of the oxidation potentials is striking, in 28 there are three such positions and in 26 only two (Table 4-6).
Table 4-6: Irreversible oxidation potentials of 26, 27, 28 and 33 (Chloroform, 10 mM) vs. Fc/Fc⁺.

<table>
<thead>
<tr>
<th>Polyphenylene precursor</th>
<th>Oxidation (V)</th>
<th>Available sites for electrochemical Oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>27</td>
<td>+1.34</td>
<td>2,2’ intra, 5,5’ inter</td>
</tr>
<tr>
<td>28</td>
<td>+1.44</td>
<td>2,3’ or 2,4’ intra, 5,5’ inter</td>
</tr>
<tr>
<td>26</td>
<td>+1.52</td>
<td>3,3’ intra, 5,5’ inter</td>
</tr>
<tr>
<td>33</td>
<td>+1.56</td>
<td>3,3’ intra</td>
</tr>
</tbody>
</table>

This trend implies that oxidative carbon-carbon bond formation is occurring preferentially at the 2- and 5- positions on each thiophene. These intramolecular oxidations are as predicted by standard thiophene electrochemical reactivities and are as a result of the preference for 2- and 5- oxidations over 3- and 4- ones (a higher voltage is required in cases where the 3- and 4- positions are involved in the oxidation). This data mirrors that of the chemically obtained products where intramolecular 2,2’ bond formation occurs ahead of intramolecular 2,3’ fusion (where a choice is available) and none of the partially fused compounds (29, 30 and 31) were found to undergo further chemical oxidation, even under forcing conditions. Interestingly no indication of the formation of polymeric thiophene species upon the electrochemical oxidation of the di-thienyl polyphenyl precursors was observed. We can exclude such possibilities as the formation of thiophene polymers generally occurs at much lower oxidation potentials. For example the bisthiophene based systems developed by Leriche show polymeric oxidation at potentials between + 0.66 and + 0.84 V vs. Fc/Fc⁺ (reported as + 1.2 and + 1.38 V vs. Ag/Ag⁺ in dichloromethane).²¹
In the di-thienyl polyphenylene systems here, the presence of the phenyl substituent on the thiophenes acts to preclude the electrochemical polymerisation and to prevent further chemical oxidation of the compounds. This is a result of both sterics and the effect of substitution on the electron density at the relevant oxidation positions on the thiophenes.\(^{26}\)

To further examine the effect of dimerisation on the polyphenylene precursors the oxidations of the 2,2’ di-thienyl polyphenylene \(^26\) and its chemically oxidised dimeric product \(^29\) along with the similarly substituted but 5,5’ methyl blocked polyphenyl precursor \(^33\) and its partially fused monomeric oxidation product \(^34\) were examined in acetonitrile (Figure 4-22). By changing the solvent from chloroform to acetonitrile the window of the cyclic voltammogram was widened (from – 1.0 to + 1.8 V in chloroform to – 0.5 to + 2.5 V in acetonitrile vs. Fc/Fc\(^+\)),\(^{27}\) allowing for a better examination of the oxidations at higher potentials. As a result a significant decrease in the oxidation potential required is observed due to the radical stabilising effect of the solvent.

![Figure 4-22: The cyclic voltammograms of 26 (black), 29 (green), 33 (red) and 34 (blue) vs. Fc/Fc\(^+\) (Acetonitrile, 10 mM, supporting electrolyte: Bu\(_4\)NPF\(_6\) 0.1 M).](image-url)

No oxidation is seen for the partially fused dimer \(^29\), and only a weak reversible oxidation at + 1.20 V is seen for the blocked monomer \(^34\). The oxidation of \(^34\) has been
attributed to reversible cation formation on the new fused thienyl unit and is consistent with published reports.\textsuperscript{12} The formation of new intramolecular 3,3' carbon-carbon bonds in both 29 and 34 has resulted in the irreversible oxidation of the thiophenes becoming negligible. As such this is further evidence for the preferential formation of intramolecular bonds in thiophenes containing polyphenylene units under electrochemical oxidation conditions.

\textbf{4.4.2 Spectroelectrochemistry of thienyl phenylenes}

Oxidations of the thienyl polyphenylene precursor compounds were investigated further by recording their UV/Vis spectra in chloroform upon oxidation by an open potential of +1.6 V \textit{vs.} Fc/Fc\textsuperscript{+} (higher than the oxidation potential seen for the compounds). In order to do this a spectroelectrochemical cell, allowing for the oxidation of the species while the cell is in a UV/Vis spectrometer was employed. All samples were oxidised at a concentration of 10\textsuperscript{-4} M to allow enough sample for oxidation while not causing saturation of the absorbance being observed by the spectrometer.

The availability of thienyl 2- and 5- positions for oxidative carbon-carbon bond formation in the precursors 26, 27 and 28 controls the products formed electrochemically. In the case of the mixed 2,3' di-thiophene precursor 28, in which the available sites for intramolecular bond formation are 2-3', 5-5' oxidative intermolecular bond formation is still possible (Table 4-3). In the UV/Vis (Figure 4-23) the formation of weak absorptions at $\lambda_{\text{max}}$ 396 and 419 nm occurs after 25 – 30 minutes at open potential. These bands are similar to those seen in the dimeric product 31 at $\lambda_{\text{max}}$ 379, 399 and 421 nm (Table 4-1).
The formation of absorption bands (similar to those seen in the dimeric compounds) is even more pronounced in the case of the 3,3’ di-thienyl polyphenylene 27 than in 28. For 27 absorptions are observed at \( \lambda_{\text{max}} \) 416 and 444 nm after 25 minutes at open potential (Figure 4-24), similar to those seen in the dimeric product 30 at \( \lambda_{\text{max}} \) 394, 415 and 443 nm (Table 4-1). It is also worth noting that in 28 the thiophenes can undergo an oxidative 2-2’ intramolecular bond formation along with a 5-5’ intermolecular one. Assuming both of these occur upon electrochemical oxidation there are still unoxidised 5- positions on the thiophene which could undergo further oxidative bond formation. This could explain the appearance of extra absorption bands (~ 350 nm) after 60 minutes in the same region as reported for thienyl polymers, \(^{28}\) which are not seen in any of the other species.
For the 2,2’ di-thienyl polyphenylene 26 electrochemical oxidation results in no change in the UV/Vis spectrum. This is surprising as 26 is the most chemically reactive species towards iron trichloride and it has an oxidation potential of + 1.52 V (in chloroform) which lies below the open potential applied. If the available oxidation sites on the thiophenes (Table 4-2) are as predicted then in order to form an intramolecular carbon-carbon bond, 26 requires oxidations exclusively at the 3-position on the thiophene rings. As electrochemical oxidation has been reported to drastically favour involving at least one 2- or 5- position on the thiophene rings it can be assumed that under electrochemical conditions the 5-5’ intermolecular oxidation of 26 occurs preferentially over the 3-3’ intramolecular one. This would result in the formation of compound 41 which does not contain the intramolecular conjugation required to give the new absorptions in the UV/Vis spectrum.

Similarly in the case of the blocked di-thienyl polyphenylene 33 no observable change in the UV/Vis spectrum is seen under spectroelectrochemical examination even after 75 min in an open potential. In this case all of the 2- and 5- positions on the thiophenes are blocked, either by conjugation to the phenylene core or by a methyl group. As a result any electrochemical oxidation of this species would be difficult, as observed in the relative decrease in the intensity of the oxidation compared to 26 (Figure 4-22).
4.4.3 Luminescence of electrochemically synthesised dimeric species

The UV/Vis absorption spectra from the electrochemical oxidation of 27 and 28 indicated the formation of species with similar absorption bands to the products of chemical oxidation (30 and 31). As the starting polyphenylenes do not fluoresce strongly in the same regions as the partially fused dimeric products, the emissions of the electrochemically synthesised products (chloroform, 10^{-4} M) were compared to those of the equivalent chemically synthesised compounds. In both cases a dramatic increase in the fluorescence intensity is observed upon electrochemical oxidation (constant potential of + 1.6 V vs. Fc/Fc^+, 40 min).

For 28 a new structured fluorescence with maxima at \( \lambda_{\text{max}} \) 432 and 460 nm similar to that of 31 is observed (Figure 4-25).

![Figure 4-25:](image)

The similarities between the chemically and electrochemically synthesised products can be easily observed in their emission spectra. The small differences can be attributed to the presence of the supporting electrolyte (0.1 M Bu_4NPF_6) along with some unreacted starting material in the electrochemical sample.
For **27** a fluorescence emission similar to that of **30** is observed after electrochemical oxidation (constant potential of + 1.6 V vs. Fc/Fc⁺, 40 min) with vibrationally structured maxima at λ 462 and 489 nm (Figure 4-26).

**Figure 4-26:** The fluorescence emission of the electrochemical oxidation of **27** before (green) and after (red) + 1.6 V is applied for 40 min (Chloroform, 10⁻⁴ M, λₐₓc 421 nm) vs. Fc/Fc⁺; along with the relevant chemically oxidised product **30** (blue). (The spectra have been normalised, the emission before oxidation is normalised relative to the emission after oxidation).

For **26** and **33** no observable change in the fluorescence was detected, this is not surprising as in these compounds the 2-positions on each thiophene are not involved in oxidative intramolecular bond formation.

It is also worth noting that where new absorptions are observed they are at relatively low intensity compared to the starting material present in the sample. It is only due to the growth of peaks in **27** and **28** in a region (340-500 nm) in which the precursor does not strongly absorb that they are observed. Indeed the fact that the precursors weakly fluoresce relative to the dimers, allows for the observation of the fluorescent species formed. This explains why the electrochemical oxidation of the monomeric superaromatic thiophene **39** results in no disconcernable change in the spectrum. It is probable that some 5,5’ oxidation of **39** to **40** is taking place; however as both **39** and **40** absorb and fluoresce at similar wavelengths at low concentration, it is not possible to directly observe the formation of **40** under spectroelectrochemical conditions.
4.5 Conclusions

The photochemical and electrochemical properties of the di-thienyl polyphenylene and their partially fused chemical oxidation products prepared in part 3 have been investigated. In addition a mono-thienyl polyphenylene and its two superaromatic thienyl graphene-like oxidation products were examined.

The superaromatic thiophene precursor 38 and the superaromatic thiophenes 39 and 40 show photochemical and electrochemical properties similar to those reported in the literature for their hexa-alkyl substituted coronene equivalents.

The dimeric mono and di-thienyl species 29, 30, 31 and 40, show optical properties that vary with concentration as a result of the possible conformations of the systems about the newly formed carbon-carbon dimer bond. The twisted conformation of these systems is favoured at low concentrations with an increase in the planar conformation observed as the concentration is increased. The percentage of the planar conformation appears dependent on the ease with which the dimers can rotate in solution or in the solid state.

The methyl “blocked” species 34 does not show the same optical properties as the dimers, instead its luminescence is dependent on temperature, indicating further that the photophysical properties observed are exclusive to the dimers.

Electrochemical examination of the oxidation of the thienyl polyphenylene precursors shows a preference for oxidative carbon-carbon bond formation, either inter- or intramolecularly, at the more reactive 2- and 5- positions on the thiophene rings.

This oxidation has been monitored spectroelectrochemically for the polyphenylenes. It was found that upon electrochemical oxidation, the species 27 and 28 where both inter and intramolecular oxidation is possible a fully fused thienyl unit is produced. Hence this results in the formation of species with comparable fluorescence properties to those of the chemically formed dimers 30 and 31.
4. References

Part 5: Synthesis, reactivity and electrochemistry of multi-thiophene systems
5.1 Introduction

A number of systems involving multiple thiophene units substituted around a benzene core have been reported in the literature. In the work of Brusso tetra-substituted thienyl benzenes have been prepared via a Stille coupling. The reactivity of these systems towards oxidative carbon-carbon bond formation along with the electrochemical and photochemical properties of the species formed has been examined.

![Figure 5-1: Tetra-thienyl compounds studied by Brusso.](image)

Oxidation of these systems with iron trichloride results in the formation of polymeric materials. This has been attributed to the increased stability of the radical cation at the 2-position on the thiophene rings due to the electron density of the sulfur atom, which in turn leads to oxidative intermolecular bond formations. Through protection of these positions with alkyl groups a series of substituted fused aromatic systems (Figure 5-2) have been made; overall yields for these fused systems is less than 5% (over four steps). They show properties such as room temperature processability, allowing for deposition of the compounds on surfaces and high charge carrier mobility which makes them excellent targets for organic light-emitting diodes (OLEDs) and organic field-effect transistors (OFETs).

![Figure 5-2: Fused tetra-thienyl compounds studied by Brusso.](image)
Electrochemical investigations of these systems show that, as was seen for the di-thienyl species (§4.4.1), the location of the available oxidation positions on the thiophene ring affects the reactivity. Where 2- or 5- positions are available for intermolecular bond formation electrochemical oxidation results in the formation of polymers on the surface of the electrode. When no intermolecular oxidations are possible but 2-, 3- or 5-positions on the thiophene are available for intramolecular oxidations, irreversible bond formation is observed. After multiple scans this disappears leaving only reversible oxidations on the molecular core. If no inter- or intramolecular bond formations are possible reversible cation and dication formation is observed; when the central ring is attached to the thiophenes at the 2-position (Figure 5-2, a) two reversible oxidations are seen, but when they are 3-substituted (Figure 5-2, b) only one reversible oxidation is observed.

Similar behaviour has been observed by Tovar for the electrochemical reactivity of a series of di-thienyl substituted fused and unfused systems (Figure 5-3).\(^6\)

![Figure 5-3: Fused and unfused di-thienyl compounds studied by Tovar.](image)

Irreversible electrochemical oxidation is observed for both a and c in dichloromethane with \(E_{pa}\) at +0.28 V vs. Fc/Fc\(^+\), in both cases, these oxidations have been attributed to the formation of cationic species which undergo oxidative intermolecular bond formations to form the fused products b and d. With repeated cyclic voltammetry scans the irreversible oxidations disappear leaving weaker reversible oxidations which overlap with those seen in fused species b and d. When the thiophenes are substituted at the 2-position (a and b) two reversible oxidations are observed at \(E_{1/2} = +0.31\) V (\(E_{pa} = +0.35\) V, \(\Delta E_p = 88\) mV) and \(E_{1/2} = +0.77\) V (\(E_{pa} = +0.84\) V, \(\Delta E_p = 162\) mV); in the case of the 3-thienyl substituted systems (c and d) only one reversible oxidation is observed at \(E_{1/2} = +0.28\) V.
(E\textsubscript{pa} = + 0.33 V, ΔE\textsubscript{p} = 130 mV).\textsuperscript{1} (Values were reported \textit{vs}. Ag/Ag\textsuperscript{+} and have been adjusted \textit{vs}. Fc/Fc\textsuperscript{+}).

Guthrie and co-workers devised a tetra-thienyl system (Figure 5-4) in which no intramolecular bond formations were possible and studied the electrochemical oxidations observed.\textsuperscript{7}

![Figure 5-4](image)

\textbf{Figure 5-4:} The tetra-thienyl system examined by Guthrie.\textsuperscript{7}

In these systems when the positions at which polymerisation can occur are accessible (Fig 5-4, R\textsubscript{1} = R\textsubscript{2} = H) an irreversible oxidation leading to polymer formation is observed. When polymerisation is not possible (Fig 5-4, R\textsubscript{1} = Me/Ph, R\textsubscript{2} = Br/I) a single reversible oxidation for the formation of a cationic species on the thiophene is seen.

In the work of Yoshida\textsuperscript{8-9} rhodium catalysts have been used to successfully trimerise bis(2-thienyl)acetylene 18 to produce hexa(2-thienyl)benzene in a 49% yield (Figure 5-5). This “starburst” type hexa-thienyl compound in which six thiophene substituents are substituted on a central benzene ring has been found to form an electroactive film on the surface of the electrode upon repeated cyclic voltammetry scans between 0.2 and 0.8 V. When the 5-position of each thiophene was substituted with a methyl or acetyl group electrochemical analysis showed no film formation on the surface due to the lack of available sites on the thiophene for polymerisation.
Building on this work Geng et al.\textsuperscript{10} have prepared a series of substituted hexa(2-thienyl)benzenes in which the 5-positions on the thiophenes are substituted with long chain hydrocarbons. These compounds were found to form liquid crystal mesophases which were stable over larger temperature ranges than their all carbon analogues.

This chapter describes the synthesis of a series of four and six thienyl-substituted benzene systems; electrochemical oxidation of these new compounds has been carried out in order to understand the nature of their reactivity. Upon chemical oxidation the poly-thienyl benzenes give highly insoluble polymeric materials which have been examined by powder diffraction and thermal gravimetric analysis.

5.2 \textbf{Synthesis of hexa-thienyl systems}

A series of hexa-thienyl substituted benzenes \textbf{42-45} were synthesised via a \([2 + 2 + 2]\) cyclotrimerisation of the relevant thienyl acetylene using dicobalt octacarbonyl as the catalyst as described in part 2 (§2.2.3).

\[
\text{Th} \equiv \text{Th} \quad \xrightarrow{(i)} \quad \text{Th} \quad \text{Th} \quad \text{Th} \quad \text{Th} \quad \text{Th} \\
(i) \text{Co}_2(\text{CO})_8, \text{Dioxane, 115°C.}
\]

\textbf{Scheme 5-1:} Cobalt catalysed trimerisation of di-thienyl acetylenes.
Hexa(2-thienyl)benzene 42 was prepared from bis(2-thienyl)acetylene 18 in 24 hours to give after workup via column chromatography (hexane: diethyl ether, 9: 1) the compound as a white solid in a 30% yield. Due to the C₆ symmetry of the compound the ¹H NMR spectrum of 42 shows only three thiophene signals at δ 7.11, 6.70 and 6.61 ppm each integrating for six protons (Figure 5-6). Splitting patterns are as expected for a 2-substituted thiophene with ³J₃,₄ = 3.5 Hz, ⁴J₃,₅ = 1.0 Hz and ³J₄,₅ = 5.0 Hz, in agreement with the NMR values for 42 reported by Yoshida.

Again the effect of interaction with other aromatic groups substituted on the central benzene ring is seen with the protons at the 3- and 4-thiophene positions shielded relative to the proton at the 5-position, as was seen in the di-thienyl analogues. The ¹³C NMR spectrum shows the four carbons for the thiophene at δ 133.7, 128.7, 125.8 and 125.3 ppm and the carbon on the central benzene ring at δ 141.9 ppm. Electrospray mass spectral analysis of 42 shows [M+H]⁺ at m/z 570.9829 m.u. (calculated value is 570.9811 m.u.).
The cobalt cyclised trimerisation of bis(3-thienyl)acetylene 19 proceeded in 3 hours to give hexa(3-thienyl)benzene 43 in a 72% yield upon crystallisation from a mixture of dichloromethane and methanol. This yield was higher than that obtained for the 2-thiophene species which is to be expected as there is less steric repulsion in the trimerisation intermediates for 3-substituted thiophene systems. Again as with 42 the C₆ symmetry of 43 results in only three signals in the ¹H NMR spectrum (Figure 5-7).

These signals are as expected for a 3-substituted thiophene with splitting of ⁴J₂₄ = 3.0 Hz, ⁴J₂₅ = 1.0 Hz and ³J₄₅ = 5.0 Hz. The peaks are seen at δ 6.94, 6.60 and 6.52 ppm. In the ¹³C NMR spectrum the four thiophene carbons are seen at δ 136.5, 129.7, 124.1 and 123.3 ppm while the carbon for the central benzene ring is at δ 140.3 ppm (Figure 5-8).

Electrospray mass spectral analysis for 43 shows [M+H]⁺ at m/z 570.9827 m.u. (calculated value is 570.9811 m.u.).
Part 5: Synthesis, reactivity and electrochemistry of multi-thiophene systems.

Cyclotrimerisation of the methyl substituted thienyl acetylene 32 for 24 hours gave hexa(5-methyl-2-thienyl)benzene 44 in a 59% yield after workup via column chromatography (dichloromethane: hexane, 1: 1). The $^1$H NMR spectrum of 44 (Figure 5-9) shows a peak integrating for a total of 12 protons at $\delta$ 6.36 ppm. This appears as a singlet however both HMBC and HMQC experiments shows it to be two overlapping peaks for the thienyl 3- and 4-postions. A signal integrating for 18 protons is observed at $\delta$ 2.33 ppm for the methyl group.

![Figure 5-9: The $^1$H NMR spectrum of 44 (400 MHz, CDCl$_3$, 25°C).](image)

The $^{13}$C NMR spectrum of 44 shows four thienyl carbons at $\delta$ 138.4, 136.5, 128.3 and 123.4 ppm, the benzyl carbon is seen at $\delta$ 139.8 ppm and the methyl carbon is at $\delta$ 14.8 ppm (Figure 5-10).

![Figure 5-10: The $^{13}$C NMR spectrum of 44 with an expansion of the aromatic region (bottom spectrum) (100.6 MHz, CDCl$_3$, 25°C).](image)
Electrospray mass spectral analysis for 44 shows \([M+Na]^+\) at m/z 677.0579 m.u. (calculated value is 677.0570 m.u.).

Cyclotrimerisation of the antisymmetric 2-thienyl-3-thienyl acetylene 21 resulted in the formation of two isomers of the hexa-thienyl product 45s and 45a as was the case for the antisymmetric acetylenes in part 2 (§2.2.3). This gives a much more complicated \(^1\)H NMR spectrum for 45 than was seen for the other hexa-thienyl benzenes due to the presence of both isomers in solution (Figure 5-11).

TOCSY NMR examination of 45 shows the presence of a total of four thiophene environments (Figure 5-11; w, x, y and z) with three thiophene signals observed for each. All of these signals consist of two overlapping protons as a result of the overlap of signals from protons in similar thiophene environments (Figure 5-12). The ratio of the two isomers is as expected with a three times excess of the antisymmetric isomer 45a, this leads to equal ratios of the four thiophene environments in the \(^1\)H NMR spectrum, resulting from the C\(_3\) symmetry in 45s. From the J splitting values observed it can be seen that w and z show the splitting patterns of 3-substituted thiophenes while x and y are 2-thiophenes.
Part 5: Synthesis, reactivity and electrochemistry of multi-thiophene systems.

Figure 5-12: The four thiophene environments seen in the $^1$H NMR spectrum of 45.

The DEPT $135^\circ$ NMR spectrum of 45 shows a total of twenty four thienyl environments in which a carbon with hydrogen attached is present. Each signal overlaps with that of the corresponding carbon of the thiophene in a similar environment, as was seen in the $^1$H NMR spectrum; leading to a total of twelve sets of two overlapping signals. Using a HMQC-NMR experiment these were grouped with their respective proton signals w, x, y and z (Figure 5-13).

Figure 5-13: The DEPT $135^\circ$ NMR spectrum of 45 (100.6 MHz, CDCl$_3$, 25°C).

Electrospray mass spectral analysis of 45 shows m/z for [M+Na]$^+$ at m/z 569.9721 m.u. (calculated value is 569.9733 m.u.).

Cyclodehydrogenation of the hexa-thienyl benzenes 42, 43 and 44, even with a small excess of iron trichloride results in the formation of dark polymeric solids which are
insoluble in all organic solvents. This lack of solubility appears to indicate the formation of cross linked thienyl polymers upon chemical oxidation. Due to their insolvency examination of these polymers by NMR and Mass spectra was not possible. Powder X-Ray diffraction was carried out on the three samples (Figure 5-14a); however only weak background signals at 16° and 23° are observed, indicating the polymers are amorphous in nature.

Thermal gravimetric analysis (Figure 5-14b) shows that all three polymers are stable up to 330°C with the loss of some solvent trapped within the polymer observed for both the polymers of 43 and 44. This loss of solvent is more pronounced in the polymer of 44, in the polymers of 42 and 43 there are three possible sites on each thiophene ring for oxidative bond formation leading to the possibility of each thiophene in the polymer forming three bonds upon oxidation. In 44 only two sites for bond formation are available on each thiophene due to the presence of the methyl substituents. This leads to a decrease in carbon-carbon bonds within the polymer and hence a greater ability for the polymer to retain solvent; along with this the steric results from the methyl groups result in a more open polymer. All three polymers begin to degrade at temperatures above 350°C with a single decomposition pathway observed for polymers of 42 and 43. For the polymer of 44 a fast decomposition begins at 340°C this slows upon reaching 430°C in a manner not seen for polymers of 42 and 43, again this change in decomposition pattern can be attributed to differences in the polymeric structure that come from the methyl substituents in 44.
5.3 Electrochemistry of hexa-thienyl systems

As with the di-thienyl benzenes, electrochemical examination of the oxidations of the hexa-thienyl benzenes gives information about their reactivity. The cyclic voltammograms of the four hexa-thienyl benzenes 42, 43, 44 and 45 show the same pattern in the oxidation potentials as seen in the di-thienyl systems (Figure 5-15).

![Figure 5-15: The cyclic voltammograms of 42, 43, 44 and 45 vs. Fc/Fc⁺ (Dichloromethane, 10 mM except 45 (due to solubility 0.25 mM - rescaled by concentration) supporting electrolyte: Bu₄NPF₆ 0.1 M).](image_url)

In the case of the di-thienyl species the irreversible oxidation potential ($E_{pa}$) was found to decrease with an increase in the availability of 2- and 5- positions on the thiophene. This dependence is again seen for the unsubstituted hexa-thienyl analogues 42, 43 and 45. The lowest $E_{pa}$ (+ 0.88 V) is seen for hexa(3-thienyl)benzene 43 in which two positions for electrochemical oxidative bond formation are available on each of the six thiophene rings. For 42 in which only one position for oxidative bond formation on each thiophene is available $E_{pa}$ is greater, occurring at + 1.12 V. Both 42 and 43 have high symmetry with a $C_6$ axis of rotation present in the molecule; however in 45 no such symmetry is present, as such more than one oxidation is observed with $E_{pa}$ values of + 1.04 and + 1.18 V. These values are much higher than those observed by Tovar,⁶ however Tovar has
incorporated methoxy substituents in his monomers in order to minimise the oxidation potentials required (Figure 5-3).

The weakest oxidation is observed for 44, in this compound all of the 2- and 5- positions on the thiophene at which intermolecular bond formation can occur are blocked, as such no polymer formation is observed (Figure 5-16).

Looking at the cyclic voltammogram of 44 in more detail (Figure 5-16, black line); initially two oxidations are observed, an irreversible oxidation at $E_{pa} + 0.86$ V and a quasi-reversible oxidation with $E_{1/2} + 0.97$ V ($E_{pa} + 1.06$ V, $\Delta E_p = 180$ mV); however a reduction peak is also seen at $E_{pc} + 0.37$ V. When repetitive scans are run (Figure 5-16) the irreversible oxidation is seen to decay while another quasi-reversible oxidation appears at $E_{1/2} + 0.43$ V ($E_{pa} + 0.48$ V, $\Delta E_p = 110$ mV). This behaviour is similar to that seen in the systems of Brusso; when the reactive sites for electropolymerisation are blocked, two reversible oxidations are observed indicating the sequential formation of a radical cation and dication on the fused thienyl system. The dication is reduced back to the cation at high potential ($E_{pc} + 0.88$ V) while the cation formed is relatively stable.
meaning that its reduction back to the starting material occurs at lower potential ($E_{pc} + 0.38 \text{ V}$). Formation of these cationic species results in some irreversible intramolecular oxidative bond formations between the thiophene units on the compound.

In 44 the only possible irreversible electrochemical oxidations are 3,3’ intramolecular bond formations which result in the formation of four possible products 46a-d (Scheme 5-2).

![Scheme 5-2: The four irreversible oxidation products 46a-d of the electrochemical oxidation of 44.](image)

MALDI-TOF Mass spectral analysis of the electrochemical solution after oxidation shows [M]$^+$ at m/z 650.0349 m.u. indicating the formation of two intramolecular bonds to give 46b or 46c (calculated as 650.0359 m.u.). For 46b a further 3,3’ irreversible intramolecular oxidation would be possible; however no such oxidation is seen in the cyclic voltammogram of the product formed even at higher potentials. Because of this 46b cannot be the product observed and as such 46c must be the electrochemical product. The preferential formation of this can be explained by the large amount of sulfur-sulfur lone pair repulsion that would be present in both 46b and 46d preventing their formation.

In order to see if the formation of 46c could be observed spectroscopically the UV/Vis spectrum of 44 after 40 cyclic voltammetry scans (Figure 5-16, green line) was recorded. Due to the concentrations involved ($10^{-2} \text{ M}$ for electrochemistry and $10^{-4} \text{ M}$ for spectrometry) the electrochemical sample was diluted by a factor of 100 before the UV/Vis scan was recorded (Figure 5-17).
Part 5: Synthesis, reactivity and electrochemistry of multi-thiophene systems.

Figure 5-17: The UV/Vis spectrum of 44 after multiple cyclic voltammetry scans (Dichloromethane, $10^{-4}$ M).

Although no significant changes in the absorption spectrum can be seen the sample colour had changed from colourless to light orange so a concentrated sample of 44 after 60 cyclic voltammetry scans was examined (Figure 5-18). This showed a set of weak absorption bands between 395 and 455 nm due to the formation of 46c.

Figure 5-18: The UV/Vis spectrum of 44 after 60 cyclic voltammetry scans showing the formation of bands due to 46c in solution (Dichloromethane, $10^{-2}$ M).
As the starting material 44 showed no luminescence in solution it was possible to examine the luminescence of the new bands due to 46c (Figure 5-19).

![Luminescence spectrum](image)

**Figure 5-19:** The luminescence of 44 after 60 cyclic voltammetry scans showing the fluorescence due to 46c in solution (Dichloromethane, $10^{-2}$ M).

Excitation of 46c at 410 nm gave structured emission bands with $\lambda_{\text{max}} = 451$ and 472 nm. The emission spectra of 46c shows bands at $\lambda_{\text{max}} = 410$ and 437 nm. This luminescence is similar to that of other fused thiényl units as described in part 4 and is due to the formation of 3-3’ thiophene-thiophene intramolecular bonds upon the oxidation of 44 to 46c.

For 42, 43 and 45, electrochemical oxidation results in both inter- and intramolecular carbon-carbon bond formation. Hexa(2-thienyl)benzene 42 has been published in the course of this work by Yoshida and co-workers, an electroactive film was found to form on the surface of the electrode between + 0.2 and + 0.8 V. Repeating this experiment a series of 20 repetitive cyclic voltammetry scans were run on 42, 43 and 45 leading to the formation of an electrochemically active polymer on the surface of the electrode in each case.

The potentials at which the polymers are observed to have redox properties varies depending on the hexa(thienyl) precursor being oxidised. The polymers becoming redox
active at potentials 0.9 V lower than the irreversible oxidation seen for the respective starting materials (Figure 5-20).

![Cyclic voltammograms](image)

**Figure 5-20:** The cyclic voltammograms of a) 42, b) 43 and c) 45 vs. Fc/Fc⁺ after 20 repetitive cycles 42 and 43 10 mM, 45 0.25 mM – rescaled by concentration (Dichloromethane, supporting electrolyte: Bu₄NPF₆ 0.1 M).

For 42 the polymer is redox active between + 0.2 and + 0.8 V (Eₚₐ was + 1.12 V), for 43 the polymer appears between 0.0 and + 0.7 V (Eₚₐ of + 0.88 V) while for 45 the polymer appears between + 0.25 and + 0.85 V (Eₚₐ of + 1.04 and 1.18 V). If the cycles are continued the redox activity decreases with the formation of an electrochemically inactive polymer on the surface of the electrode. For 43 after 50 scans no electrochemical activity remains (Figure 5-21).
Figure 5-21: The cyclic voltammogram 43 vs. Fc/Fc⁺ after 50 repetitive cycles (Dichloromethane, 10 mM, supporting electrolyte: Bu₄NPF₆ 0.1 M).

Similar behaviour can be observed when a constant potential of + 1.1 V (vs. Fc/Fc⁺) is applied to each of 42, 43 and 45 for 240 seconds; in all three cases a dark solid, similar to the one observed from chemical oxidation, was formed on the surface of the electrode. Cyclic voltammograms of these newly formed species were run and for all three samples no oxidation or reduction peaks were observed within the potential window even though the polymer could be seen on the electrode surface.

In the case of both the open potential and after 50 repetitive scans all of the available thienyl inter- and intramolecular oxidation positions have been electrochemically oxidised, leading to the formation of a fully oxidised inactive polymer. After 20 cyclic voltammetry cycles not enough time has passed to allow for the complete oxidation of the polymer, as such only some of the thienyl sites have been oxidised. This results in the formation of a polymer which contains some positions at which redox processes, similar to those seen for the blocked compound 44 can occur at lower potential. When these redox active polymers are further oxidised at higher potentials the unreacted sites undergo electrochemically driven carbon-carbon bond formation to give the unreactive final polymer.
5.4 Synthesis of tetra-thienyl systems

The synthesis of tetra-thienyl substituted benzenes via Stille couplings between the relevant tetra-bromo benzene and a tin substituted thiophene has been reported by Brusso;\(^1\) however this method always gives the same thiophene substituent at all four positions on the central ring.

![Scheme 5-3: Synthetic route of Brusso for the formation of tetra-thienyl benzenes.](image)

In order to allow for more variation in the thienyl substituents on the central benzene ring, along with the synthesis of systems in which other substituents are present on the central benzene ring; the synthesis of a thienyl substituted cyclopentadienone which could undergo a Diels-Alder reaction was attempted. To do this 1,2,-di(3-thienyl)-ethane-1,2-dione 47 was proposed as a starting material.

![47](image)

The synthesis of 47 was first attempted using a variation of the method of Sadhukhan,\(^{11}\) 3-bromothiophene was lithiated using butyl lithium and then reacted with 1,4-dimethylpiperazine-2,3-dione (DMPD); however this reaction upon workup gave only starting materials. Instead 47 was prepared from bis(3-thienyl)acetylene 19, by oxidation with potassium permanganate in acetone, to give the diketone as a yellow solid in a 53% yield.
The $^1$H NMR spectrum of 47 (Figure 5-22) shows the splitting expected for a 3-substituted thiophene with three coupled doublet of doublets at $\delta$ 8.37, 7.72 and 7.41 ppm.

**Figure 5-22:** The $^1$H NMR spectrum of 47 (400 MHz, CDCl$_3$, 25°C).

The presence of the carbonyl groups can be seen in both the $^{13}$C NMR spectrum as a signal at $\delta$ 185.3 ppm and in the IR spectrum with the $\nu$(C=O) observed at 1647 cm$^{-1}$. The electrospray mass spectrum of 47 shows [M+H]$^+$ at m/z 222.9889 m.u. (calculated value is 222.9887 m.u.).

In the di-thienyl species (§3.3) intermolecular thiophene-thiophene bond formation occurs preferentially over intramolecular bond formation between the thiophene and the phenyl substituents on the central benzene ring. To overcome this it was decided to incorporate 3,5-dimethoxybenzyl groups into the cyclopentadienone to increase the reactivity of the phenyl rings. This was done using the monoketone 1,3-bis(3,5-dimethoxbenzyl)propane-2-one 48 made by a variation of the procedure of Ogliaruso, to prepare 2,5-di(3,5-dimethoxybenzyl)-3,4-di(3-thienyl)cyclopentadienone 49.
49 was prepared by dissolving 47 and 48 in refluxing ethanol and then adding potassium hydroxide, after 20 minutes the reaction was cooled and filtered to give a red solid from which 49 was isolated via column chromatography (dichloromethane: methanol, 50: 1) in a 65% yield. The $^1$H NMR spectrum of 49 (Figure 5-23) shows three thienyl signals with coupling constants indicative of a 3-substituted thiophene each integrating for two protons at $\delta$ 7.25, 6.91 and 6.80 ppm. Also present are the two phenyl signals, a doublet integrating for four protons at $\delta$ 6.47 ppm and a triplet integrating for two protons at $\delta$ 6.41 ppm, these are coupled to each other with $^4J_{8,10} = 2.0$ Hz. The signal for the methoxy groups on the phenyl ring can be seen at $\delta$ 3.69 ppm integrating for twelve protons.

The carbonyl group can be seen in both the $^{13}$C NMR spectrum at $\delta$ 182.3 ppm and in the IR spectrum, where the $\nu$ (C=O) is present at 1707 cm$^{-1}$. Electrospray mass spectral analysis of 49 shows [M+Na]$^+$ at m/z 539.0961 m.u. (calculated value is 539.0963 m.u.).

The [2+4] cycloaddition of bis(3-thienyl)acetylene 19 with 49 in benzophenone gave the tetra(3-thienyl) polyphenylene compound 1,2,4,5-tetra(3-thienyl)-3,6-di(3,5-dimethoxybenzyl)benzene 50 as a brown solid in a 41% yield upon crystallisation from methanol (Scheme 5-4). In this compound all four thienyl groups are 3-substituted allowing for easier initial investigations of the $^1$H NMR spectrum due to the high level of symmetry (Figure 5-24).
Three thiophene signals each integrating for four protons are seen for 50, one at $\delta$ 6.90 ppm for the 5-position on the thiophene ring and two for the 2- and 4-positions which are shielded due to interactions with the methoxy-substituted phenyl ring. These are seen at $\delta$ 6.61 and 6.53 ppm and have been assigned based upon their coupling constants. The two signals for the methoxy-substituted phenyl ring are present at $\delta$ 6.14 and 6.07 ppm, these signals are also shifted compared to the cyclopentadienone, due to the interaction with thiophenes substituted ortho to the phenyl group on the central benzene ring. The methoxy groups are seen at $\delta$ 3.52 ppm integrating for twelve protons. Electrospray mass spectral analysis of 50 shows $[\text{M+Na}]^+$ at m/z 701.0922 m.u. (calculated value is 701.0925 m.u.).
In order to prepare the mixed tetra-thienyl substituted benzene 1,2-di(2-thienyl)-4,5-di(3-thienyl)-3,5-di(3,5-dimethoxybenzyl)benzene 51, 49 was reacted with bis(2-thienyl) acetylene 18 in benzophenone. This gave 51 in a 51% yield upon crystallisation from methanol. The $^1$H NMR spectrum of 51 (Figure 5-25) shows two thiophene environments in the molecule each consisting of three hydrogen positions which integrate for two protons; these have been identified using 2D NMR correlation spectroscopy. The peaks at δ 7.06, 6.67 and 6.52 ppm are for the 2-substituted thiophenes and the peaks at δ 6.91, 6.61 and 6.52 ppm are for the 3-substituted thiophenes and have been fully assigned using their coupling constants. Also seen is a multiplet at δ 6.15 ppm integrating for 6 protons, HMQC NMR correlation spectroscopy shows that these are the signals for the two proton positions on the methoxy-substituted phenyl ring overlapping with each other. A peak is also observed at δ 3.54 ppm integrating for twelve protons for the methyl substituents. Electrospray mass spectral analysis of 51 shows [M+Na]$^+$ at m/z 701.0922 m.u. (calculated value is 701.0925 m.u.).

In order to prepare the tetra(2-thienyl) derivative the diketone 1,2-di(2-thienyl)-ethane-1,2-dione 52 was required; the synthesis of this species has been reported within the group$^{13}$ using the method of Sadhukhan,$^{11}$ however this reaction gave the dione in only
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9% yield due to the formation of two side products 53 and 54 (Scheme 5-5) (yields 53 - 18%; 54 – 15%).

![Scheme 5-5: The synthesis of 52 and its two side products 53 and 54.](image)

It was found that none of these diketones could undergo a Knoevenagel condensation using the standard conditions of potassium hydroxide in ethanol. In the work of Kawase it has been reported that as a result of the lability of 2-thienyl units under basic conditions the synthesis of cyclopentadienones containing 2-thienyl substituents requires catalytic conditions. Therefore the condensation of 52 with 1,3-bis(3,5-dimethoxybenzyl)propane-2-one 48 was carried out via the Kawase method (Scheme 5-6). This gave a bright purple solution believed to be 2,5-di(3,5-dimethoxybenzyl)-3,4-di(2-thienyl)cyclopentadienone 55; however upon cooling to room temperature (5 min) the solution decomposed back to the starting materials.

![Scheme 5-6: The synthesis of 55 which decomposes to give starting materials.](image)
Oxidation of the two tetra-thienyl substituted polyphenylene systems 50 and 51 was carried out by addition of an excess of iron trichloride in nitromethane to a solution of the polyphenylene in dichloromethane. After 30 minutes the solutions were quenched with methanol and filtered to give green solids. NMR analysis of these products showed the formation of a large number of polymeric materials. This is due to the large number of possible inter and intramolecular carbon-carbon bond formations that can occur at the chemically reactive positions on both sides of the molecules.

5.5 Electrochemistry of tetra-thienyl systems

Looking at the electrochemical reactivity of the tetra-thienyl substituted benzenes gives information about the reactivity of the species as well as the polymers formed through the oxidation. For the tetra(3-thienyl) substituted compound 50 cyclic voltammetry shows a single irreversible oxidation at $E_{pa} + 0.84$ V (Figure 5-26). This is at a lower potential than observed for both the di(3-thienyl) and hexa(3-thienyl) polyphenylenes. The decrease in oxidation potential is due to the presence of methoxy groups on the phenyl substituents which increases the electron density on the thiophenes lowering the potential at which they can be oxidised.

![Figure 5-26](image)

**Figure 5-26:** The cyclic voltammograms of 50 vs. Fc/Fc' after multiple repetitive cycles (Dichloromethane, 10 mM, supporting electrolyte: Bu4NPF6 0.1 M).
Repertative cyclic voltammetry scans on 50 leads to the rapid decay of the irreversible oxidation, with the formation of two broad quasi-reversible oxidations at $E_{1/2} - 0.08$ V ($E_{pa} = 0.00$ V, $\Delta E_p = 160$ mV) and $+0.11$ V ($E_{pa} = +1.16$ V, $\Delta E_p = 100$ mV) (Figure 5-26). Similarly when the compound is placed in a constant potential of $+0.95$ V (vs. Fc/Fc$^+$) the formation of an electroactive polymer on the surface of the electrode is observed after 120 seconds with $E_{1/2} - 0.13$ V ($E_{pa} = -0.07$ V, $\Delta E_p = 120$ mV) and $E_{1/2} + 0.11$ V ($E_{pa} = +0.16$ V, $\Delta E_p = 110$ mV). The polymers which have formed (Figure 5-27) show two reversible oxidations that are similar to those observed in electroactive thienyl polymers, indicating the formation of new intramolecular carbon-carbon bonds.$^{15-17}$

![Figure 5-27: The cyclic voltammograms of the electrochemical oxidation products of 50 vs. Fc/Fc$^+$ after 20 repetitive cycles (red) and application of an open potential of $+0.95$ V for 120 seconds (blue) (Dichloromethane, 10 mM, supporting electrolyte: Bu$_4$NPF$_6$ 0.1 M).](image)

All four thiophenes in 50 contain two 2-/5- positions that can undergo intermolecular and intramolecular bond formation along with one 4- position at which intramolecular oxidation can occur. A large number of electrochemical bond formations are possible between the adjacent 3-substituted thiophenes in 50 as the thiophenes are free to rotate around the central benzene ring. The enhanced reactivity of the phenyl substituents also allows for other potential oxidations (Figure 5-28).
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![Diagrams of molecular structures](image)

**Figure 5-28:** The available inter and intramolecular electrochemical bond formations for the three possible orientations of the thiophene groups of 50.

In each of these orientations an intramolecular bond formation between two thiophenes to give a new carbon-carbon bond is possible. These fused systems are known to be redox active towards the formation of radical cations and dication at low potential and as such the polymer formed from the oxidation of 50 is redox active.

For the mixed tetra-thienyl substituted benzene 51 cyclic voltammetry shows a broad irreversible oxidation at a potential greater than + 1.26 V, this oxidation is higher than that of 50 and was outside the window provided by dichloromethane.

![Graph of voltammetry](image)

**Figure 5-29:** The cyclic voltammograms of 51 vs. Fc/Fc⁺ after multiple repetitive cycles (Dichloromethane, 10 mM, supporting electrolyte: Bu₄NPF₆ 0.1 M).

Repetitive cyclic voltammetry cycles of a 10 mmol solution of 51 results in the formation of a redox active polymer after 12 cycles, with a reversible oxidation at $E_{1/2} = + 0.17$ V ($E_{pa} = + 0.26$ V, $\Delta E_p = 180$ mV) and an irreversible oxidation at $E_{pa} = + 0.56$ V. Unlike in 50 these peaks begin to decay after 20 cycles. When a constant potential of + 0.95 V (vs. Fc/Fc⁺)
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Fc/Fc\(^+\)) is applied for 120 seconds an electrochemically unreactive polymer forms on the surface of the electrode.

In \textbf{51} there are two pairs of adjacent thiophenes at which irreversible oxidative bond formation can occur. The two 3-substituted thiophenes will undergo oxidative bond formation with the same reactivity patterns observed for \textbf{50} and in the formation of similar redox active products. Looking at the two adjacent 2-thienyl substituents on \textbf{51} a large number of potential oxidative bond formations are present (Figure 5-30).

![Figure 5-30: The possible inter and intramolecular electrochemical bond formations for the three orientations of the 2-thienyl groups in 51.](image)

Comparing the possible oxidations of the 2-thienyl system in \textbf{51} to the 3-thienyl ones in \textbf{50} it can be observed that in only one of the three orientations does a thiophene-thiophene intramolecular bond form. Along with this the possibility of intermolecular 2,3’ bond formations between 2-thienyl and 3-thienyl thiophenes exists for \textbf{51}. For \textbf{50} all of the possible oxidations result in the formation of a well defined redox active system at low potential while for \textbf{51} the percentage of oxidations which result in a redox active system is much less. After 12 cyclic voltammetry scans redox active peaks are observed at an \(E_{1/2}\) of + 0.17 V; however as the polymer is further oxidised a broad redox active polymer, similar to that seen for the hexa(thienyl) oxidations forms between 0.0 and + 0.6 V.

When electrochemical analysis was carried out on the chemically oxidised polymers of \textbf{50} and \textbf{51} no electrochemical activity was observed, this was to be expected as unlike electrochemically, iron trichloride oxidation will result in the formation of new carbon-carbon bonds at all available sites on the thiophene ring.
5.6 Conclusion

A series of tetra- and hexa-thienyl benzene derivatives have been successfully prepared and characterised.

By varying the position of thienyl substitution around the central benzene ring along with the substituent groups on the thiophene rings a series of hexa-thienyl polyphenylene compounds have been prepared via cobalt catalysed cyclotrimerisation reactions. These compounds 42, 43, 44 and 45 have been fully characterised via NMR spectroscopy and mass spectral analysis.

Chemical oxidation of these compounds results in the formation of insoluble chemically and electrochemically inert fused thienyl polymers, which due to their insolubility could only be examined via powder diffraction and thermal gravimetric analysis. Electrochemical examination of 42–45 shows that they readily oxidise at the electrochemically reactive 2- and 5- positions on the thiophenes to give redox active polymers which can themselves undergo further oxidation. This eventually results in the formation of insoluble, unreactive polymers similar to those formed via chemical oxidations. The one exception is 44 which cannot form polymers electrochemically due to the substitution of the thiophene at the reactive positions. Instead it undergoes two intramolecular oxidative bond formations to give 46c which has been identified using mass spectrometry, UV/Vis spectroscopy and luminescence.

Using the di(3-thienyl) substituted cyclopentadienone 49 two tetra-thienyl polyphenylene compounds 50 and 51 have been prepared and fully characterised via a series of $^1$H and $^{13}$C NMR experiments along with mass spectral analysis. Chemical oxidation of these systems results in the formation of complex thienyl polymers due to the many possible inter and intramolecular oxidation sites available on the thiophene rings.

Electrochemical oxidation of 50 and 51 leads to the formation of electrochemically active polymers which oxidise at potentials similar those observed for other thienyl polymeric
systems. In the case of 50 this polymer shows clear redox oxidations while for 51 the redox activity is broad, similar to that observed for the hexa(thienyl) compounds.

These results indicate that electrochemically, intermolecular oxidative bond formation can only occur at the 2- and 5- positions on the thiophene rings, while intramolecular oxidative bond formation can be observed at all available positions on the thiophene rings. In the case of chemical oxidation all available sites on the thiophene are undergoing both inter and intramolecular carbon-carbon bond formation forming highly insoluble cross-linked thienyl polymers.

5.7 References

Part 6: Toward the application of thiophene-containing polyphenylenes
Part 6: Toward the application of thiophene-containing polyphenylenes.

6.1 Introduction

This chapter describes initial investigations into the development of new thiophene containing systems in order to exploit the reactivity observed in earlier chapters.

The use of thiophene in the synthesis of polymeric systems is well known and has been reported extensively in the literature.\textsuperscript{1-4} As a result of the changes in reactivity observed upon substitution of multiple thiophene subunits onto a polyphenylene core a number of possible applications for these systems have been described.

Three examples of the use of such thienyl substituents in novel compounds are discussed in this chapter. (i) The development of di-thienyl based molecular switches which allow for the reversible photo-induced ring opening/closure of the thiophene subunits. (ii) The preparation of tetrazine systems containing thiophene substituents which allow for the potential development of thienyl linked dimeric tetrazines for metal coordination studies. (iii) The incorporation of pre-fused thiophene units into precursors for polyphenylene synthesis in order to allow for the preparation of thienyl polyphenylenes. By synthesis of a thienyl equivalent to the nitrogen containing diketone 1,10-phenanthroline-5,6-dione,\textsuperscript{5-6} in which the thiophene units are already pre-fused thus increasing the control over the products formed.

Along with this some potential future work into thiophene containing polyphenylene systems is discussed in this chapter.

6.2 Thiophene based molecular switches

In 1998 Irie and Uchida reported the stability of diarylethenes substituted with heterocyclic aryl groups towards light induced molecular switching.\textsuperscript{7} In these systems
(Figure 6-1) a light driven transformation between the two isomers is observed which, by varying the frequency of light applied can be reversed.

Figure 6-1: The general form of thiophene based molecular switches.\(^7\)

Differences between the two isomers are apparent from their absorption spectra, geometrical structures, redox potentials, refractive indexes and dielectric constants. This makes them excellent frameworks for the preparation of molecules such as polymers, guest-host molecules, molecular wires or liquid crystals, the functions of which can be switched via photoirradiation.\(^8-10\) By varying the substitution at the 5-position on the thiophenes (R\(_1\) and R\(_2\)) the thermal stability of the closed-ring isomer can be tuned. An increase in electronic donation at the 5-position results in an increase in the stability of the photogenerated carbon-carbon bond.\(^11\)

The performance of a molecular switch is measured by observing its fatigue resistance. This is done by applying light of an appropriate frequency (Figure 6-1, h\(\nu_1\)) to generate the closed-ring isomer in a solution of the sample in degassed benzene. When the absorbance due to the open-ring isomer falls to 10% of the stationary state, application of this frequency of light is stopped. The solution is then bleached by the application of a second light of the correct frequency (Figure 6-1, h\(\nu_2\)) to reverse the photochemical fusion and return the sample to its more stable open-ring isomer. The operation is repeated while the absorbance intensity is monitored until the intensity after bleaching falls to 80% of that of the initial sample. The number of cycles required to reach this point is the fatigue value of the molecular switch.
Table 6-1: Examples of thiophene based molecular switches along with their fatigue value.\textsuperscript{12-16}

<table>
<thead>
<tr>
<th>Structure</th>
<th>Fatigue value</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Structure 1" /></td>
<td>70</td>
</tr>
<tr>
<td><img src="image2.png" alt="Structure 2" /></td>
<td>(3.7 \times 10^3)</td>
</tr>
<tr>
<td><img src="image3.png" alt="Structure 3" /></td>
<td>(1.3 \times 10^4)</td>
</tr>
</tbody>
</table>

In order to incorporate these systems into the thienyl frameworks which have been discussed in Part 3 (§3.3) the thiophene containing acetylene bis(2,5-dimethyl-3-thienyl)acetylene 56 was proposed as a starting material.

![Structure 56](image56.png)

To do this 3-bromo-2,5-dimethylthiophene 57 was prepared from commercially available 2,5-methylthiophene via the method of Lim using n-bromosuccinimide in glacial acetic acid and chloroform in a 76% yield (Scheme 6-1).\textsuperscript{17}
Part 6: Toward the application of thiophene-containing polyphenylenes.

Scheme 6-1: The synthesis of 3-bromo-2,5-dimethylthiophene 57.\textsuperscript{17}

(i) Glacial acetic acid: Chloroform 1:1, n-bromosuccinimide, 70°C, 30 min.

The $^1$H NMR spectrum of 57 is as reported by Lim\textsuperscript{17} with one signal for the unsubstituted thienyl 4-position integrating for one proton at $\delta$ 6.59 ppm and two methyl signals, each integrating for three protons at $\delta$ 2.44 and 2.37 ppm. The bromo substitution can be seen in the $^{13}$C NMR spectrum where resonance of the bromo-substituted carbon is observed at $\delta$ 108.2 ppm. Electron impact mass spectral analysis of 57 shows m/z 189.9455 m.u. for [M]$^+$ which compares to the calculated value of 189.9452 m.u.

Figure 6-2: The $^1$H NMR spectrum of 57 (400 MHz, CDCl$_3$, 25°C).

Initially a method similar to the one used for the synthesis of the bis(thienyl) acetylenes 18 and 19 was attempted (Scheme 6-2). The decreased reactivity of the bromothiophene due to the methyl substituents on 57 meant that only starting materials could be obtained from the reaction mixture.
To increase the reactivity of the 2,5-dimethyl thiophene, 3-iodo-2,5-dimethylthiophene \( \text{58} \) was prepared from 2,5-dimethylthiophene using the method of Barker (Scheme 6-3).\(^1\)\(^8\)

The thiophene was iodised via the dropwise addition of a 1:1 mixture of water and nitric acid to a dichloromethane solution containing the thiophene and resublimed iodine. Quenching with sodium hydroxide and purification via column chromatography (using hexane as the eluent) gave the iodothiophene in 70% yield.

\[ \text{(i) Iodine, 1:1 water: nitric acid, dichloromethane, 38°C, 2 hours.} \]

**Scheme 6-3:** The synthesis of 3-iodo-2,5-dimethylthiophene \( \text{58} \).
Part 6: Toward the application of thiophene-containing polyphenylenes.

Next \textbf{58} was used as the starting material for the Sonogashira reaction (Scheme 6-2) to give on workup (via column chromatography using hexane: dichloromethane 3: 2 as the eluent) the acetylene \textbf{56} in 46\% yield.

The $^1$H NMR spectrum of \textbf{56} shows one thiophene signal, integrating for two protons at $\delta$ 6.68 ppm along with two methyl signals each integrating for six protons at $\delta$ 2.52 and 2.42 ppm. The $^{13}$C NMR spectrum shows the acetylene carbon at $\delta$ 85.5 ppm and the C=C stretch appears in the IR spectrum at 2177 cm$^{-1}$. Electrospray mass spectral analysis of \textbf{56} shows m/z 247.0612 m.u. for [M+H]$^+$ which compares to the calculated value of 247.0615 m.u.

Using bis(2,5-dimethyl-3-thienyl)acetylene \textbf{56} in a Diels-Alder [2+4] cycloaddition with 2,3,4,5-tetrakis-(4-tert-butylphenyl)cyclopentadienone \textbf{25}, the di-substituted
polyphenylene system with the features of a potential molecular switch, 1,2-di(2,5-dimethyl-3-thienyl)-3,4,5,6-tetra-(4-tert-butylphenyl)benzene \(59\) was prepared. The product was purified by flash chromatography using dichloromethane: hexane, 1:2 as the eluent to give a brown solid which was recrystallised from methanol to give the product in 51% yield.

\[
\text{Scheme 6-4: The synthesis of 1,2-di(2,5-dimethyl-3-thienyl)-3,4,5,6-tetra-(4-tert-butylphenyl)benzene 59.}
\]

The \(^1\)H NMR spectrum of \(59\) shows four peaks for the methyl groups on the thiophenes at \(\delta\) 2.16, 2.14, 1.92 and 1.88 ppm. TOCSY NMR examination of the thiophene signal at \(\delta\) 6.04 ppm shows that it contains two overlapping singlets. This indicates that there are two thiophene environments present in the molecule with two methyl and one thiophene signal observed for each thiophene ring.

\[
\text{Figure 6-5: The aromatic and methyl regions of the \(^1\)H NMR spectrum of 59 (400 MHz, CDCl}_3, 25^\circ\text{C).}
\]
In the $^1$H NMR spectrum two tertiary-butyl signals are seen at $\delta$ 1.18 and 1.13 ppm each integrating for eighteen protons along with the phenyl signals between $\delta$ 6.95 and 6.56 ppm integrating for sixteen protons. This indicates that only two phenyl environments are observed for 59, possibly due to overlap of the signals.

These observations are consistent with NMR data reported for other thiophene based molecular switches in which the two thiophene groups are substituents on a hexa-substituted phenyl ring.\textsuperscript{19-20} In such cases the methyl groups on the thiophene substituents result in restricted rotation of the two thiophene groups around each other. This leads to the formation of two atropisomers from the Diels-Alder reaction (Figure 6-6).

![Figure 6-6: The two atropisomers possible for 59 with the methyl groups preventing the rotation of the thiophenes (tertiary-butyl groups have been removed for clarity).](image)

As such the thiophene $^1$H NMR signals appear different depending on the atropisomer involved, while the phenyl signals appear equivalent between the two atropisomers. If the two related thiophene signals on the two atropisomers are taken together then the integration in the $^1$H NMR spectrum is as expected with sixteen protons for the phenyl groups and an integration of two for the thienyl protons. Two methyl signals integrating for six protons each and two tertiary-butyl groups integrating for eighteen protons are also seen. Electrospray mass spectral analysis of 59 shows m/z 826.4589 m.u. for [M]$^+$ which compares to the calculated value of 826.4606 m.u.

In order to examine if 59 acted as a molecular switch, a sample of the solid was sent to Prof. Franco Scandola at the University of Ferrera, Italy. The sample was observed to undergo a photoreaction to give the closed-ring isomer upon irradiation at $\lambda_{\text{max}} = 270$ nm. This reaction was found to be clean (isosbestic points) and led to a red-shifted absorption.
The photo-reversion to the open-ring isomer by irradiation into the red shifted absorption was unsuccessful. This is possibly due to the polyaromatic platform stabilising the closed-ring isomer to such an extent that reversal of the bond formation is not possible. As such the synthesis of thiophene based molecular switches incorporating this particular polyphenylene framework require further investigations.

6.3 Thiophene containing tetrazine derivatives

6.3.1 Synthesis of thiophene containing dihydropyridazines

Tetrazines are six membered aromatic rings containing four nitrogens located at the 1, 2, 4 and 5 positions on the ring. The study of tetrazines in which the 3 and 6 positions on the ring are substituted has become popular in both supramolecular and coordination chemistry.

![Figure 6-7: The general form of 1,2,4,5-tetrazine.](image)

The four nitrogens present on the central ring result in an increase in the electron accepting character of the ring, as a result of this their coordination properties differ from those of other nitrogen-substituted systems, such as bipyridine. A tetrazine ligand is a poor $\sigma$-donor but an excellent $\pi$-acceptor and the properties of its complexes are more dependent on the metal as a result. Tetrazines have been used to prepare mono coordinated, di coordinated and bridging metal systems as well as coordination networks.\(^{21-24}\)

The reactivity of tetrazines towards reverse electron demand Diels-Alder reactions resulting in the formation of pyridazines has been studied by Carboni and Lindsey.\(^{25}\) The
low lying tetrazine LUMO results in an increase in reactivity when electron withdrawing substituents are at the 3- and 6- positions on the tetrazine or when electron donating substituents are present on the dienophile with which the tetrazine is reacting. The use of aromatic substituents for such reactions is therefore difficult; however by carefully controlling the reaction conditions a number of pyridazine products have been reported within the group (Figure 6-8).\textsuperscript{26-27}

![Pyridazines prepared from tetrazine by Cooke.\textsuperscript{26}](image)

In such Diels-Alder reactions it has been found that alkenes require much less harsh conditions than alkynes; the former giving the dihydropyridazine and requiring a further oxidation step (Scheme 6-5).

![Scheme 6-5: Diels-Alder reaction of tetrazine with alkynes and alkenes.](image)
Recently within our group investigations have been carried out into the synthesis of supramolecular architectures in which two or three pyridazine groups are placed on the periphery of the molecule. This has been achieved via the Diels-Alder reaction of tetrazine with a series of systems containing two and three alkynes (Scheme 6-6).

Based on this supramolecular architecture and using the dimerisation patterns of di-thienyl substituted benzenes as observed in Part 3, it was proposed to prepare 3,6-di(2-pyridyl)-4,5-di(2-thienyl)pyridazine 60 and its expected oxidation product 61.
Firstly 3,6-di(2-pyridyl)-1,2,4,5,-tetrazine 62 was prepared according to the synthesis of Geldard and Lyons,\textsuperscript{28} in this 2-cyanopyridine was condensed with hydrazine hydrate at 90°C to give a hydrazone. This condenses in air to give 3,6-di(2-pyridyl)-1,2,4,5,-dihydrotetrazine as a yellow solid in a 41% yield. This was then oxidised via the method of Boger\textsuperscript{29} in which nitrous oxide gases were prepared from hydrochloric acid and sodium nitrite. These oxidising gases were then passed through a solution of the dihydrotetrazine in dichloromethane. Recrystallisation from toluene gave 62 as a pink crystalline solid in an 81% yield.

Scheme 6-7: The synthesis of 3,6-di(2-pyridyl)-1,2,4,5,-tetrazine 62.

This was then reacted with bis(2-thienyl)acetylene 18 in a sealed pressure tube for three days at 180°C; however upon examination of the reaction mixture by tlc only starting materials were observed. In order to counter the electronic effects on the tetrazine ring which were preventing the Diels-Alder reaction with the alkyne, the alkene 1,2-di(2-thienyl)ethene 63 was prepared using the method of Roberts and Pincock.\textsuperscript{30} First 2-bromo-3-thienylmethyltriphenylphosphonium bromide was prepared by reflux of commercially available 2-thienylethanol in the presence of triphenylphosphonium bromide at 65°C. This was then reacted with 2-thiophene carboxaldehyde via a Wittig coupling in tetrahydrofuran using potassium tert-butoxide as a base to give 62 as a white solid in a 69% yield after 2 days.
Part 6: Toward the application of thiophene-containing polyphenylenes.

Scheme 6-8: The synthesis of 1,2-di(2-thienyl)ethene 63.

(i) triphenylphosphinium bromide, chloroform, 65°C, 6 hours;
(ii) 2-thiophenecarboxaldehyde, tetrahydrofuran, KOtBu, 0°C, 1 hour, 60°C, 2 days

The $^1$H NMR spectrum of 63 shows three thienyl peaks each integrating for two protons at $\delta$ 7.20, 7.06 and 7.02 ppm having splitting $^3J_{3-4} = 3.5$ Hz, $^4J_{3-5} = 1.0$ Hz and $^3J_{4-5} = 5.0$ Hz as expected for a 2-substituted thiophene. The alkene hydrogens are observed as a singlet integrating for two protons at $\delta$ 7.08 ppm while the carbons of the alkene are seen in the $^{13}$C NMR spectrum at $\delta$ 121.5 ppm.

The IR spectrum of 63 shows the weak C=C stretch at 1790 cm$^{-1}$ and electrospray mass spectral analysis gives a m/z value of 193.0416 m.u. for [M+H]$^+$ (calculated value of 193.0416 m.u.).

Single crystals of 63 suitable for X-ray crystallographic analysis were obtained from the slow evaporation of a saturated solution of the compound in a 1:1 mixture of methanol: dichloromethane. In the solid state 63 crystallises in the monoclinic space group P21/c with two molecules in the unit cell.
1,2-di(2-thienyl)ethene 63 was dissolved in toluene and reacted with 3,6-di(2-pyridyl)-1,2,4,5-tetrazine 62 for 24 hours at 180°C in a sealed pressure tube. Upon workup using a silica column with ethyl acetate as the eluent a yellow solid was isolated ($R_f = 0.7$). This was found to be 3,6-di(2-pyridyl)-4,5-di(2-thienyl)-1,4-dihydropyridazine 64 and was formed in a 68% yield.

Single crystals of 64 suitable for X-ray crystallographic analysis were obtained from the slow evaporation of a saturated solution of the compound in a 1:1 mixture of methanol: dichloromethane. In the solid state 64 crystallises in the triclinic space group P-1 with two molecules in the unit cell. The sulfur atoms of 64 showed some disorder, with one of the thiophenes having two possible orientations; as such a partial occupancy exists between the sulfur 1-position (S2/S2A) and the carbon 5-position (C70/C70A) on this thiophene ring. This results in the large errors seen for the bond angles around the sulfur atoms.
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Figure 6-12: Crystal packing along the a) c axis and b) a axis of 64.

Figure 6-13: The aromatic region of the $^1$H NMR spectrum of 64 (600 MHz, CDCl$_3$, 25°C).

Looking at the $^1$H NMR spectrum of 64 a total of twenty signals are observed while only sixteen are expected from the X-Ray structure. A series of two dimensional experiments including HMBC, HMQC and TOCSY NMR along with a series of nOe and N-H correlation studies have been carried out on 64. From these it can be seen that in solution one of the pyridyl groups can take up two possible orientations, possibly due to hydrogen bonding between multiple molecules of 64. As such the signals for this pyridyl group appear twice (1 - 4 and 1’- 4’), while the signals for the other pyridyl group and the two thiophenes only appear once. The signals for the hydrogens on the central ring are seen at δ 9.38 and 6.05 ppm. The pyridyl group alpha to the protonated nitrogen on the central ring (12-15) appears at δ 8.68, 7.24 and as two overlapping signals at 7.54 ppm. The
thiophenes are seen at $\delta$ 7.14, 6.99 and 6.91 ppm and at $\delta$ 7.14, 7.13 and 6.93 ppm. The sets of signals for the pyridyl group which appears twice are observed at $\delta$ 8.65, 8.17, 7.68 and 7.21 ppm (1-4) and $\delta$ 8.60, 8.08, 7.77 and 7.36 ppm (1'-4'). Electrospray mass spectral analysis of 64 gives a m/z value of 401.0914 m.u. for [M+H]$^+$ (calculated value of 401.0895 m.u.).

The reaction of 1,2-di(2-thienyl)ethene 63 with 3,6-di(2-pyridyl)-1,2,4,5-tetrazine 62 was repeated with an increase in both the concentration of the reactants by a factor of five and an increase in the reaction time from one to three days. From this 2-(3,6-di(2-pyridyl)-5-(2-thienyl)-2,5-dihydropyridazinyl)-4,7-di(2-pyridyl)thieno[2,3-d]pyridazine 65 was crystallised in a 44% yield by addition of methanol.

The synthesis of 65 can be explained by a Diels-Alder reaction between one of the thiophenes on 64 and another molecule of 3,6-di(2-pyridyl)-1,2,4,5-tetrazine 62 to give a compound in which there are two dihydropyrazine groups present. This then oxidises in air to reform a stable aromatic thiophene ring now fused to one of the pyridazines to give a thienopyridazine (Scheme 6-9).
Electrospray mass spectral analysis of 65 gives a m/z value of 607.1495 m.u. for [M+H]+ (calculated value of 607.1487 m.u.).

Single crystals of 65 suitable for X-ray crystallographic analysis were obtained from the slow evaporation of a saturated solution of the compound in a 1:1 mixture of methanol:dichloromethane. In the solid state 65 crystallises in the triclinic space group P1 with two molecules in the unit cell.

As a result of the oxidation which has occurred, the thiophene and pyridazine which have been fused together have become flattened due to the formation of stable aromatic rings. The molecules of 65 pack in the solid state as dimers due to each molecule showing...
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hydrogen bonding to another with a N-H intermolecular bond distance of 2.203 Å (Figure 6-15).

![Figure 6-15: The intermolecular H to N hydrogen bonding observed between two molecules of 65. H-N intermolecular bond distance (Å).](image)

This hydrogen bonding between two pyridazines has not been observed in other dihydropyridazines\textsuperscript{31-32} it results from the increased bulk of the substituents on the pyridazine which is apparent in the crystal packing where no π-π interactions are observed (Figure 6-16).

![Figure 6-16: Crystal packing along the a axis of 65.](image)
6.3.2 *Photochemistry of thiophene containing dihydropyridazines*

The UV/Vis spectra of 64 and 65 were examined in chloroform (10^{-4} M, Figure 6-17). For 64 two broad absorptions are seen with λ_{max} of 303 and 375 nm.

![UV/Vis spectra graph](image)

These bands are consistent with absorption data for dihydropyrazines observed within the group and those reported in the work of Carboni and Lindsey.\textsuperscript{25} The UV/Vis spectrum of a number of substituted dihydropyrazines in benzene have been reported, all of which show broad absorption bands with λ_{max} between 260 and 326 nm. For 65 the expected dihydropyrazine absorption is seen at λ_{max} 298 nm along with a new lower-energy band at 423 nm, this new band is possibly due to the formation of the fused thienopyridazine in 65. Although the UV/Vis spectra of thienopyridazine have not been reported in the literature, its carbon analogue benzothiophene has been reported by Evans to have an absorption with λ_{max} 417 nm (reported as 23,970 cm^{-1}).\textsuperscript{33}

The luminescence of 64 and 65 were examined in chloroform (10^{-4} M, Figure 6-18) and each showed a broad emission with λ_{max} 506 nm for 64 and λ_{max} 519 for 65. This emission is seen for both 64 and 65 and as such is likely to be due to the dihydropyridazines portion in both compounds.
The emission values are consistent with those observed in the group for other dihydropyridazines which were found to have broad emissions with $\lambda_{\text{max}}$ between 490 and 522 nm. The excitation spectra of the two compounds are similar with an extra band appearing at 424 nm in 65. Again as was seen in the absorption spectra this band is due to the fused thienopyridazine present in 65.

6.3.3 Oxidation of thiophene containing dihydropyridazines

In order to oxidise 3,6-di(2-pyridyl)-4,5-di(2-thienyl)-1,4-dihydropyridazine 64 to form 3,6-di(2-pyridyl)-4,5-di(2-thienyl)pyridazine 60, the method of Boger\textsuperscript{29} was attempted. 64 was dissolved in dichloromethane and nitrous gases, prepared from the dropwise addition of aqueous 6 M sodium nitrite to concentrated hydrochloric acid, were bubbled through the solution for 20 min. The reaction was quenched with aqueous sodium hydrogen carbonate to give a pink solid which was purified by column chromatography using dichloromethane as the eluent ($R_f = 0.9$). Examination of the $^1$H NMR spectrum of the product shows that more than one oxidation product has formed. Using two dimensional NMR spectroscopy and focusing on the $^1$H NMR spectrum of the product formed in the highest concentration (Figure 6-19, coloured peaks) information relating to the nature of the products formed can be obtained.
The dihydropyridazine protons should be lost if the expected oxidation had taken place, yet are still present at δ 9.41 and 6.00 ppm. (Figure 6-19, purple). Also observed are two sets of 2-pyridyl peaks at δ 8.65, 7.61, 7.55 and 7.30 ppm (red) and δ 8.54, 8.01, 7.55 and 7.04 ppm (orange). Interestingly a set of three signals for one of the thiophenes is observed at δ 7.03, 6.99 and 6.80 ppm (green) while only two signals at δ 7.56 and 6.67 ppm (blue) are seen for the other thiophene. This indicates that the oxidation of 64 has occurred intermolecularly between two of the thiophene substituents rather than on the dihydropyridazine ring, leading to the formation of a dimeric species. Such a reaction could result in the formation of three possible products 66a-c (Scheme 6-10) differing in the position of the thiophene-thiophene bond formed, relative to the dihydropyridazine hydrogens.

Figure 6-19: The $^1$H NMR spectrum of the oxidation products of 64 (600 MHz, CDCl$_3$, 25°C).

Investigations carried out by Hohne and Spane indicate that vinyl substitution of thiophene in the 2-position results in a large increase in the reactivity of the 5-position.
under oxidising conditions.\textsuperscript{34} This indicates that in the dihydropyridazine precursor 60 the thiophene which lies beta (\textsuperscript{*} in Scheme 6-10) to a double bond will be the most reactive. As a result of this 66a is expected to form in the greatest concentration while 66c would be the least favourable isomer. Due to the similarities in the $R_f$ values of 66a-c in all solvents it was not possible to separate them chromatographically.

As a result of the three oxidation products formed it was not possible to form 3,6-di(2-pyridyl)-4,5-di(2-thienyl)pyridazine 60 from 64.

6.4 $\eta^1$ thienyl-sulfur coordination to metal centres

As discussed in Part 3 (§3.3) attempts to prepare a di-thienyl acetylene precursor to allow for the synthesis of a monomeric 3,3’ polyphenylene were unsuccessful. Instead the synthesis of diketone 67 which could be used to incorporate the fused 3,3’ di-thienyl unit into the phenylene without using an acetylene was proposed.

In order to prepare 67 the methyl substituted biphenyl compound 5,5’-dimethyl-2,2’-bistiophene 68 was synthesised from commercially available 2,2’-bistiophene (Scheme 6-11). Lithiation of the bistiophene with n-butyllithium gave the di-lithiated intermediate which was reacted with methyl iodide to give 68 in a 40% yield after column chromatography using hexane as the eluent.
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\[ \text{(i) n-butyllithium, tetrahydrofuran, } -40^\circ\text{C, 45 min; (ii) Methyl iodide, } -40^\circ\text{C, 20 min.} \]

**Scheme 6-11**: The synthesis of 68.

\(^1\text{H NMR spectral analysis of 68 shows two thiophene signals each integrating for two protons. The signal for the thienyl hydrogen at the 3-position next to the bisthiophene bond appears as a doublet with } ^3J_{3,4} = 3.5 \text{ Hz at } \delta 6.92 \text{ ppm. The hydrogens at the 4-position appear as a quartet of doublets with } ^3J_{3,4} = 3.5 \text{ Hz and } ^4J_{4,6} = 1.0 \text{ Hz at } \delta 6.68 \text{ ppm. Also seen are the methyl protons integrating for six hydrogens at } \delta 2.51 \text{ ppm and appearing as a doublet due to coupling with the hydrogen at the 4-position.} \]

**Figure 6-20**: The \(^1\text{H NMR spectrum of 68 (400 MHz, CDCl}_3, 25^\circ\text{C).} \]

The two quaternary carbons are seen in the \(^{13}\text{C NMR spectrum, the carbon alpha to the methyl group appears at } \delta 138.0 \text{ ppm whilst the other quaternary carbon is seen at } \delta 135.1 \text{ ppm.} \]

Using a variation on the method of Marsella\(^\text{35}\) \(3,3’\)-dibromo-5,5’-dimethyl-2,2’-bisthiophene 69 was prepared by the addition of n-bromosuccinimide to a solution of 68 in dimethylformamide (Scheme 6-12). This was stirred for 16 hours to give a yellow oil from which the product was precipitated via the addition of a small amount of methanol. This compound was found to slowly decompose at room temperature and therefore was stored at 6°C.
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![Scheme 6-12](image)

(i) n-bromosuccinimide, dimethylformamide, 16 hours.

**Scheme 6-12:** The synthesis of 69 from 68.

The $^1$H NMR spectrum of 69 shows only two signals, the unsubstituted thiophene 4-position integrating for two protons at $\delta$ 6.77 ppm and the methyl groups at $\delta$ 2.51 ppm integrating for six protons (Figure 6-21). As in 68 these signals are coupled to each other with $^4J_{4,6} = 1.0$ Hz.

![Figure 6-21](image)

**Figure 6-21:** The $^{13}$C NMR spectrum and insert $^1$H NMR signals of 69 ($^1$H 400 MHz, $^{13}$C 100.6 MHz, CDCl$_3$, 25°C).

In the $^{13}$C NMR spectrum the bromo substituted thiophene carbons resonate at $\delta$ 111.3 ppm while the two thienyl quaternary carbons are seen at $\delta$ 141.7 and 126.7 ppm. Electron ionisation mass spectral analysis of 68 shows m/z for [M+H]$^+$ at 350.8516 m.u. (compared to a calculated value of 350.8512 m.u.).

Addition of the diketone to 69 in order to give 67 was attempted by a number of methods. Firstly the dibromo compound was lithiated with butyllithium to give a dilithiated transition state (Scheme 6-13, (i)) which could then be reacted with 1,4-dimethylpiperazine-2,3-dione (DMPD); however this reaction upon workup gave only
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starting materials. Next the lithiated species was reacted with oxalyl chloride, again only starting material was obtained. Instead the compound was reacted with dimethylformamide to give 5,5'-dimethyl-2,2'-bithiophene-3,3'-dicarbaldehyde 70 (Scheme 6-13, (ii)).

(i) n-Butyllithium, THF, -78°C, 2 hours; (ii) DMF, THF, 25°C, 16 hours.

Scheme 6-13: The synthesis of 70 from 69.

The $^1$H NMR spectrum of 70 has three signals, one at $\delta$ 9.87 ppm integrating for two protons for the aldehyde hydrogens (Figure 6-22). The thienyl hydrogens appear at $\delta$ 7.29 ppm integrating for two protons. Also seen are the methyl groups which integrate for six protons at $\delta$ 2.55 ppm.

Figure 6-22: The $^1$H NMR spectrum and aromatic region of the $^{13}$C NMR spectrum of 70 ($^1$H 400 MHz, $^{13}$C 100.6 MHz, CDCl$_3$, 25°C).
In the $^{13}$C NMR spectrum the aldehyde carbon is seen at $\delta$ 184.0 ppm while the four thienyl carbons are observed at $\delta$ 142.5, 140.0, 139.5 and 124.3 ppm. Also the carbon signal for the methyl groups is seen at $\delta$ 14.8 ppm. The aldehyde can be observed in the IR spectrum with $\nu$(C=O) at 1664 cm$^{-1}$. Electron ionisation mass spectral analysis of 70 shows m/z for [M+Na]$^+$ at 273.0027 m.u. (compared to a calculated value of 273.0020 m.u.).

The formation of an intermolecular carbon-carbon bond between the two aldehydes in 70 was attempted applying a range of reaction conditions. The classic benzoin condensation using sodium cyanide was unsuccessful so instead the method of Enders and Niemeier\textsuperscript{36} using a thiazolium salt catalyst was attempted (Scheme 6-14).

This reaction gave 67 as a purple solid in a poor yield ($<$ 5%). As 0.2 equivalents of the expensive thiazolium salt are required, work is being carried out in the group to improve the yield of this reaction. In the $^{13}$C NMR spectrum of 67 the C=O carbon signal is seen at $\delta$ 174.5 ppm. The four thiophene ring carbons resonate at $\delta$ 142.8, 140.5, 134.8 and 125.2 ppm while the methyl carbon is observed at $\delta$ 15.3 ppm (Figure 6-23).
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As 67 could only be made in a low yield (less than 10 mg has been prepared) no further reactions with it have yet been carried out.

6.5 Future work

6.5.1 Dehydrogenation of new thiophene containing polyphenylene precursors

Although the reactivity of thienyl polyphenylenes has been discussed in detail in the preceding chapters, there are still possible investigations based upon the observed reactivities which can be carried out. In recent investigations by King et al. into the cyclodehydrogenation of polyphenylene precursors it has been found that by addition of methoxy groups to the periphery of the system the rate of carbon-carbon bond formation can be improved.\(^{37}\) By incorporating such groups into the di-thienyl precursors discussed in part 2 it may be possible to prepare a thienyl precursor 71 which will form a dimeric partially fused di-thiophene containing heterosuperbenzene 72 (Scheme 6-15).

Scheme 6-15: A potential precursor 71 and fused dimeric di-thienyl heterosuperbenzene 72.
In the case of the fully cyclised NHSB stacking was observed in solution at concentrations as low as $10^{-15}$ M.\textsuperscript{38} The proposed thienyl system would have interesting photochemical properties due to the enhanced stacking that would be seen in the system. This would result both from the extended planar $\pi$ system, as seen in N-HSB’s, along with the increased surface area available for $\pi$-$\pi$ interactions due to dimer formation. It may also be possible to prepare a fully fused di-thienyl dimer by using methoxy groups along with two 3-substituted thiophene groups on the precursor. Along with this the incorporation of other heteroatoms into the periphery to allow for increased metal coordination compared to systems containing only sulphur coordination sites (Scheme 6-16).

\textbf{Scheme 6-16:} A precursor 73 and fully fused dimeric di-thienyl heterosuperbenzene 74 with the potential for metal coordination.

If the method of cyclodehydrogenation of such systems can be further understood it may also be possible to develop compounds containing molecular switch units such as 75 in which a partially fused polyaromatic is connected to the molecular switching framework (Figure 6-24).

\textbf{Figure 6-24:} 75 a potential molecular switch containing a partially fused phenylene.
As the electron density will be more delocalised in this system compared to the polyphenylene molecular switch 59, the light induced switching between the closed and open form will be more favourable. The increase in π-delocalisation on 75 will also have an affect on the frequencies of light at which the system can undergo switching. By varying the substituent groups on the polyphenylene it may be possible to tune the switching frequencies of the ring closing and opening.

6.5.2 Development of further thienyl-tetrazine derivatives

The di-thienyl dihydropyrazine 64 was found to undergo dimerisation under oxidising conditions prior to loss of the hydrogens from the dihydropyrazine unit. By preparing the di-3-thienyl precursor 76 it may be possible to avoid this due to the decreased reactivity of the thiophene upon the change in substitution (Figure 6-25). This would allow for the preparation of tetrazine systems containing two thiophene substituents allowing for the preparation of compounds similar to the proposed systems 60 and 61. Another possibility would be to prepare the precursor 77 in which the positions for dimerisation are blocked by methyl groups allowing only for the formation of intramolecular carbon-carbon bonds as was seen in the di-thienyl polyphenylene 33. In both of these systems the possibility of undergoing a second Diels-Alder reaction to give a thienopyridazine as was seen for 65 is decreased as a result of the extra steric present around the double bonds on the thiophenes in the intermediate.

![Figure 6-25](image-url)

Figure 6-25: Two possible dihydropyrazines 76 and 77 in which the dimerisation seen on oxidation for 64 is less likely.
The synthesis of both 76 and 77 would require the preparation of the relevant thienyl-alkenes 78 and 79 (Figure 6-26).

![Figure 6-26: The two alkenes 78 and 79 required for the synthesis of 76 and 77 respectively.](image)

The alkene 78 has been prepared previously by Ngwendson\(^{39}\) while 79 could be prepared via a modification of the method of Rathore and Burns\(^{40}\) used in the synthesis of the 2-thienyl alkene 64. One problem with these reactions is that the thiophene starting materials required are much more expensive than in the 2-thienyl case.

6.5.3 Acid-oxidation of thiényl precursors

In the oxidation reaction of the thiényl-dihydropyrazine 64 it was found that the 2-thienyl group underwent an intermolecular 5-5' dimerisation in the presence of nitrous gases. Using this it may be possible to develop polyphenylene systems which could be dimerised easily by passing nitrous gases through a solution of the precursor. Two such possible systems are shown in Scheme 6-17.

![Scheme 6-17: Two thiophene containing systems that may dimerise in the presence of nitrous gases.](image)
The major advantage in using an acid based oxidation over a metal one is the fact that oxidation will only be observed on the thiophene. This will allow for the formation of dimeric species in solution that can then be further oxidised using reagents such as iron trichloride without the risk of further thiophene reactivity. It also allows for the formation of dimers which can be coordinated to metal centres at both ends of the dimer in order to prepare coordination networks.

6.5.4 *Metal coordination to thienyl polyphenylenes*

Although the diketone 67 containing a fused 3,3’ di-thienyl unit has been synthesised the successful coordination of a metal centre to a thienyl polyphenylene derivative has not yet been achieved; however this coordination could be done in one of two ways.

Firstly the η¹ coordination of thienyl groups to a metal centre through the sulfur atom could be attempted. Studies on the coordination ability of thiophene show that d⁶ metal centres such as Re(I), Ru(II) or Ir(III) are the best candidates for these complexes. Although the bite angle for these complexes will be unfavourable some coordination may be possible using large metal centres (Figure 6-27).

Alternatively the η⁶ coordination of thienyl and phenyl groups to coordinatively unsaturated metal centres such as Cr(CO)₆ and Rh(Pr₃)₂ has been reported. Using these compounds it may be possible to prepare complexes of fused thiophene containing heterosuperbenzenes such as those shown in Figure 6-28.
6.6 Conclusion

A series of compounds have been made in an attempt to exploit the reactivity patterns of the multi-thienyl polyphenylenes established in earlier chapters.

59 a potential molecular switch was prepared from the new acetylene 56. Upon spectral NMR analysis 59 showed the formation of two atropisomers in solution; this is similar to observations reported for other molecular switch compounds. Photochemical examination of the molecular switching properties of 59 indicated it was not usable as a molecular switch. This is due to the high stability of the closed-form of the compound resulting from the effect of the phenyl substituents.

In attempting to prepare the di-thienyl tetrazine 60 the dihydropyridazine 64 was synthesised from the di-thienyl ethene 63. Upon oxidation 64 gave a racemic mixture of dimers that were formed as a result of the intermolecular carbon-carbon bond formation between the thienyl units. This was found to be preferable to the oxidation of the dihydropyridazine to a pyridazine and prevented the synthesis of the desired products.

Synthesis of the fused di-thienyl containing diketone 67 was achieved on a small scale. Due to the low yields obtained attempts to optimise the synthesis of 67 are still ongoing.
6.7 References

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Part 7: Experimental
7.1 General Methods

Unless otherwise stated all reactions were carried out in a nitrogen atmosphere. The solvents were distilled under nitrogen and dried with appropriate drying agents using standard techniques. Flash chromatography was performed using silica gel (Aldrich) as the stationary phase. Separations were undertaken in air. All chemicals were obtained from commercial sources (mostly Aldrich Chemical Co. Ltd.) and were used without further purification unless otherwise stated. The following reagents were prepared according to literature procedures, palladium dichlorodiphenylphosphene,$^1$ DMPD,$^2$ lithium diisopropylamine.$^3$ Compounds 52-54 were prepared by Cécile Ollagnier.

IR spectra were recorded in solid form either neat or mixed with potassium bromide on a PerkinElmer Spectrum 100 FTIR spectrometer fitted with a Universal ATR accessory. Elemental analysis was obtained on a Carlo Erba 1006 automatic analyser at University College Dublin. Melting points are given uncorrected and were measured in capillary tubes using a Griffin melting point apparatus.

Electrospray mass spectra were recorded on a micromass LCT electrospray mass spectrometer, Electron impact mass spectra were measured on a Waters corp. GCT Premier electron impact mass spectrometer and MALDI mass spectra were measured on a MALDI-Q-ToF Premier mass spectrometer. Accurate MS were referenced against leucine enkephalin (555.6 g mol$^{-1}$) or [Glu1]-Fibrinopeptide B (1570.6 g mol$^{-1}$) and were reported within 5 ppm.

Nuclear magnetic resonance spectra were recorded in deuterated chloroform, dichloromethane or 1,1,2,2-tetrachloroethane with (i) a Bruker Avance DPX-400 MHz spectrometer operating at 400.13 MHz for $^1$H, 100.6 MHz for $^{13}$C, and 162.0 MHz for $^{31}$P (ii) a Bruker AV-400 MHz spectrometer operating at 400.23 MHz for $^1$H and 100.6 MHz for $^{13}$C or (iii) a Bruker Avance II 600 NMR spectrometer operating at 600.13 MHz for $^1$H and 150.9 MHz for $^{13}$C. The signals for $^1$H and $^{13}$C were referenced to TMS at δ 0.0 ppm and coupling constants were recorded in Hz. $^{13}$C signals were assigned with the aid
of DEPT 135 and DEPT 90 experiments. 2-D correlation spectra were recorded on the AV-400 MHz spectrometer or the Avance-600 MHz spectrometer and were employed to assign the $^1$H and $^{13}$C peaks. Homonuclear correlation spectroscopy was performed using TOCSY or $^1$H-$^1$H COSY experiments; heteronuclear correlation spectroscopy was performed using HSQC, HMQC and HMBC (long-range) experiments.

All photophysical studies were carried out with solutions contained within 1x1 or 0.1x1 cm$^2$ quartz cells in HPLC grade solvents and were degassed using argon bubbling. UV/Vis absorption spectra were recorded on a Shimadzu UV-2450 UV/Vis recording spectrophotometer. Emission and excitation spectra were obtained on a Fluorolog FL-3-11 spectrofluorimeter, in which lifetime measurements were performed with an IBH Datastation HUB 5000F. All samples were degassed under an argon atmosphere prior to the experiment being carried out.

All electrochemical experiments were performed with a CH Instruments potentiostat model 660B. Cyclic voltammograms were measured on 10 mmol solutions of the compounds in acetonitrile, dichloromethane or chloroform and open potential experiments were carried out on 0.1 mmol solutions of the compounds in chloroform. Tetra-n-butylammonium hexafluorophosphate (Bu$_4$NPF$_6$, 0.1 M) was used as supporting electrolyte, a glassy carbon working electrode, a Pt wire counter electrode and a SCE reference electrode were used. Potentials are quoted versus the ferrocene–ferrocenium couple (0.0 V) and all potentials were referenced to internal ferrocene added at the end of each experiment. All solutions were continuously degassed for ten minutes by nitrogen bubbling before the experiments were performed and a flow of nitrogen was maintained over the solution for the duration of the experiments.

Crystal and structural experimental data are summarised in Tables 1-3 in the Annex. Selected bond lengths and angles are given in the discussion. The remaining angles, distances, atom coordinates as well as anisotropic displacement parameters and hydrogen atom coordinates are on the enclosed CD. The single-crystal analysis was performed by Dr. Christopher Fitchett, Dr Sunil Varghuse and Dr. Longsheng Wang in Trinity College.
with a Brüker SMART APEX CCD diffractometer using graphite monochromated Mo-K$_\alpha$ ($\lambda$=0.71073Å) radiation at the temperatures given in tables. Data reduction was performed using SAINT. Intensities were corrected for Lorentz and polarisation effects and for absorption by SADABS. Space groups were determined from systematic absences and checked for higher symmetry. The structures were solved by direct methods using SHELXS and refined on $F^2$ using all data by full-matrix least-squares procedures with SHELX-97. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.3 times the isotropic equivalent of their carrier carbons. Absolute structure determinations were based on the Flack parameter. The functions minimised were $\Sigma w(F_o^2 - F_c^2)$, with $w=\sigma^2(F_o^2) + (aP) + bP$, where $P=\max(F_o^2 + 2F_c^2)/3$. In all cases, final Fourier syntheses showed no significant residual electron density in chemically sensible positions.

### 7.2 Synthesis and cyclotrimerisations of thiophene acetylenes

**(3-thienyl)phenylacetylene (1)**

![Chemical Structure](attachment:structure.png)

To benzyltriethylammonium chloride (45.5 mg, 0.199 mmol), copper(I) iodide (62 mg, 0.329 mmol), and tetrakis(triphenylphosphine) palladium(0) (200 mg, 0.17 mmol), 3-bromothiophene (0.6 mL, 6.0 mmol) and phenylacetylene (0.66 mL, 6.0 mmol) in benzene (20 mL), was added a 5.5 N solution of aqueous sodium hydroxide (12 mL, 66 mmol), and the mixture was left stirring at 80°C for 3 days. It was cooled to room temperature and a solution of saturated aqueous ammonium chloride (40 mL) was added. The phases were separated and the aqueous layer was extracted with toluene. The organic phases were dried with magnesium sulfate and evaporated. The product was purified by column chromatography using hexane as eluent ($R_f = 0.8$) to give the desired product as a white solid. **Yield:** 0.724 g, 3.93 mmol, 66%. **Melting Point:** 43-44°C (lit. 44°C). **$^1$H-NMR** (400 MHz, CDCl$_3$, 25°C, TMS) $\delta$: 7.63 (dd, 1H, $^J_{H-H} = 1.0$ and 3.0 Hz, H$_2$), 7.61
(m, 2H, H₉), 7.42 (m, 3H, H₁₀ and H₁₁), 7.35 (dd, 1H, ⁴J_H-H = 3.0 and ³J_H-H = 5.0 Hz, H₅),
7.30 (dd, 1H, ⁴J_H-H = 1.0 and ³J_H-H = 5.0 Hz, H₄). ¹³C{¹H}-NMR (100 MHz, CDCl₃,
25°C, TMS) δ: 131.2 (C₉), 129.5 (C₄), 128.3 (C₂), 128.0 (C₁₀), 127.9 (C₁₁), 125.1 (C₃),
122.9 (C₃/₈), 121.9 (C₃/₈), 88.6 (C₆), 84.3 (C₇). IR (neat) cm⁻¹: 3104, 2203 (C≡C), 1957,
1886, 1813, 1760, 1676, 1595, 1519, 1485, 1441, 1355, 1202, 1124, 1070, 1026, 916,
868, 833, 756, 739, 688. ESI-MS: (Acetonitrile) m/z 185.0415 ([M+H]+) (calc. 185.0425).

(4-tert-butylphenyl)(3-thienyl)acetylene (2)

To benzyltriethylammonium chloride (45.5 mg, 0.199 mmol), copper(I) iodide (62 mg,
0.329 mmol), tetrakis(triphenylphosphine) palladium(0) (200 mg, 0.17 mmol), 3-
bromothiophene (0.6 mL, 6.0 mmol) and 4-tert-butylphenylacetylene (1.1 mL, 6.0 mmol)
in benzene (20 mL), was added a 5.5 N solution of aqueous sodium hydroxide (12 mL,
66 mmol) and the mixture was left stirring at 80°C for 3 days. It was cooled to room
temperature and a solution of saturated aqueous ammonium chloride (40 mL) was added.
The phases were separated and the aqueous layer was extracted with toluene. The organic
phases were dried with magnesium sulfate and evaporated. The product was purified by
column chromatography using hexane as eluent (Rf = 0.8) to give the desired product as a
white solid. **Yield**: 1.04 g, 4.33 mmol, 72%. **Melting Point**: 48-49°C. ¹H-NMR (400
MHz, CDCl₃, 25°C, TMS) δ: 7.55 (d, 1H, ⁴J_H-H = 2.0 Hz, H₂), 7.52 (d, 2H, ³J_H-H = 8.0 Hz,
H₉/₁₀), 7.42 (d, 2H, ³J_H-H = 8.0 Hz, H₉/₁₀), 7.33 (dd, 1H, ⁴J_H-H = 3.0 Hz and ³J_H-H = 5.0 Hz,
H₅), 7.26 (d, 1H, ³J_H-H = 5.0 Hz, H₄) 1.38 (s, 9H, H₁₃). ¹³C{¹H}-NMR (100 MHz, CDCl₃,
25°C, TMS) δ: 151.0 (C₁₁), 131.2 (C₉/₁₀), 129.5 (C₄), 127.9 (C₂), 124.9 (C₉/₁₀), 122.1
(C₃/₈), 119.8 (C₃/₈), 88.6 (C₇), 83.5 (C₆), 34.4 (C₁₂), 30.8 (C₁₃). IR (neat) cm⁻¹: 3100,
2959, 2865, 2200 (C≡C), 1916, 1805, 1728, 1657, 1596, 1524, 1464, 1423, 1362, 1267,
1214, 1097, 1070, 1037, 915, 833, 759, 707. **EI-MS**: (Chloroform) m/z 241.1058 ([M+H]+) (calc. 241.1051).
4-(3-thienyl)ethylphenylferrocene (3)

Benzyltriethylammonium chloride (7.1 mg, 0.03 mmol), copper (I) iodide (10 mg, 0.053 mmol), tetrakis(triphenylphosphine) palladium(0) (20 mg, 0.017 mmol), 3-bromothiophene (0.5 mL, 5 mmol, excess) and 4-ethynylphenylferrocene (7) (0.2 g, 0.66 mmol) were dissolved in benzene (10 mL). To this was added a 5.5 N solution of aqueous sodium hydroxide (0.8 mL, 4.4 mmol), and the mixture was left stirring at 80°C for 3 days. It was cooled to room temperature and saturated aqueous ammonium chloride (40 mL) was added and the solution stirred for 1 hour. The phases were separated and the aqueous layer was extracted with toluene. The organic phases were dried with magnesium sulfate and solvent was evaporated. The product was purified by column chromatography using hexane: dichloromethane (3:1) as eluent (Rf = 0.6) to give the desired product as an orange solid. **Yield:** 207 mg, 0.56 mmol, 85%. **Melting Point:** 81°C. **1H-NMR** (400 MHz, CDCl$_3$, 25°C, TMS) δ: 7.55 (d, 1H, $^4$J$_{H-H}$ = 2.5 Hz, H$_2$), 7.47 (m, 4H, H$_0$ and H$_{10}$), 7.33 (dd, 1H, $^4$J$_{H-H}$ = 2.5 Hz and $^3$J$_{H-H}$ = 4.6 Hz, H$_5$), 7.24 (d, 1H, $^3$J$_{H-H}$ = 5.0 Hz, H$_4$), 4.69 (s, 2H, H$_{13/14}$), 4.38 (s, 2H, H$_{13/14}$), 4.07 (s, 5H, H$_{15}$). **13C{1H}-NMR** (100 MHz, CDCl$_3$, 25°C, TMS) δ: 139.4 (C$_3$), 131.1 (C$_{9/10}$), 129.4 (C$_4$), 127.9 (C$_2$), 125.4 (C$_{9/10}$), 124.9 (C$_5$), 122.0 (C$_{8/11}$), 119.8 (C$_{8/11}$), 88.8 (C$_{12}$), 84.1 (C$_7$), 83.8 (C$_6$), 69.2 (C$_{15}$), 68.9 (C$_{13/14}$), 66.1 (C$_{13/14}$). **IR (neat)** cm$^{-1}$: 3103, 2208 (C≡C), 1916, 1640, 1601, 1529, 1414, 1283, 1217, 1104, 1035, 1001, 888, 820, 708. **MALDI-MS:** (Chloroform) m/z 368.0326 ([M]+) (calc. 368.0322).

(2-thienyl)phenylacetylene (4)
To benzyltriethylammonium chloride (45.5 mg, 0.199 mmol), copper(I) iodide (62 mg, 0.329 mmol) and tetrakis(triphenylphosphine) palladium(0) (200 mg, 0.17 mmol), 2-bromothiophene (0.6 mL, 6.0 mmol) and phenylacetylene (0.66 mL, 6.0 mmol) in benzene (20 mL), was added a 5.5 N solution of aqueous sodium hydroxide (12 mL, 66 mmol), and the mixture was left stirring at 80°C for 3 days. It was cooled to room temperature and a solution of saturated aqueous ammonium chloride (40 mL) was added. The phases were separated and the aqueous layer was extracted with toluene. The organic phases were dried with magnesium sulfate and evaporated. The product was purified by column chromatography using hexane as eluent ($R_f = 0.8$) to give the desired product as a white solid. **Yield:** 0.659 g, 3.48 mmol, 58%. **Melting Point:** 46-47°C (lit. 49°C). $^1$H-NMR (400 MHz, CDCl$_3$, 25°C, TMS) $\delta$: 7.66 (dt, 2H, $^4$J$_{H-H} = 1.0$ Hz and $^3$J$_{H-H} = 3.5$ Hz, H$_9$), 7.43 (m, 3H, H$_{10}$ and H$_{11}$), 7.37 (dd, 1H, $^4$J$_{H-H} = 1.0$ Hz and $^3$J$_{H-H} = 3.5$ Hz, H$_3$), 7.35 (dd, 1H, $^4$J$_{H-H} = 1.0$ Hz and $^3$J$_{H-H} = 5.3$ Hz, H$_5$), 7.10 (dd, 1H, $^3$J$_{H-H} = 3.8$ and 5.3 Hz, H$_4$). $^{13}$C($^1$H)-NMR (100 MHz, CDCl$_3$, 25°C, TMS) $\delta$: 132.1 (C$_3$), 131.5 (C$_9$), 128.6 (C$_{11}$), 128.5 (C$_{10}$), 127.5 (C$_5$), 127.3 (C$_4$), 123.4 (C$_8$ or C$_2$), 123.1 (C$_8$ or C$_2$), 93.3 (C$_6$), 82.9 (C$_7$). **IR** (neat) cm$^{-1}$: 2200 (C≡C), 1595, 1485, 1424, 1276, 1213, 1111, 1069, 1024, 918, 851, 753, 687. **ESI-MS:** (Acetonitrile) m/z 185.0426 ([M+H]$^+$) (calc. 185.0425).

(4-tert-butylphenyl)(2-thienyl)acetylene (5)

![Chemical Structure](https://example.com/structure.png)

To benzyltriethylammonium chloride (45.5 mg, 0.199 mmol), copper(I) iodide (62 mg, 0.329 mmol) and tetrakis(triphenylphosphine) palladium(0) (200 mg, 0.17 mmol), 2-bromothiophene (0.6 mL, 6.0 mmol) and 4-tert-butylphenylacetylene (1.1 mL, 6.0 mmol) in benzene (20 mL) was added a 5.5 N solution of aqueous sodium hydroxide (12 mL, 66 mmol) and the mixture was left stirring at 80°C for 3 days. It was cooled to room temperature and a solution of saturated aqueous ammonium chloride (40 mL) was added. The phases were separated and the aqueous layer was extracted with toluene. The organic phases were dried with magnesium sulfate and evaporated. The product was purified by
column chromatography using hexane as eluent ($R_f = 0.7$), to give the desired product as a white solid. **Yield:** 0.92 g, 3.83 mmol, 64%. **Melting Point:** 39-40°C. **$^1$H-NMR** (400 MHz, CDCl$_3$, 25°C, TMS) $\delta$: 7.48 (d, 2H, $^3$J$_{H-H} = 6.5$ Hz, H$_{9/10}$), 7.39 (d, 2H, $^3$J$_{H-H} = 7.0$ Hz, H$_{9/10}$), 7.30 (m, 2H, H$_3$ and H$_5$), 7.04 (dd, 1H, $^3$J$_{H-H} = 4.0$ and 5.0 Hz, H$_4$), 1.36 (s, 9H, H$_{13}$). **$^{13}$C{$^1$H}-NMR** (100 MHz, CDCl$_3$, 25°C, TMS) $\delta$: 151.3 (C$_{11}$), 130.2 (C$_{3/5}$), 130.7 (C$_{9/10}$), 127.9 (C$_{8/11}$), 126.6 (C$_{3/5}$ and C$_4$), 125.0 (C$_{9/10}$), 119.4 (C$_2$), 92.8 (C$_6$), 81.5 (C$_7$), 34.4 (C$_{12}$), 30.7 (C$_{13}$). **IR (neat)** cm$^{-1}$: 2200 (C≡C) 1524, 1423, 1363, 1214, 1097, 1037, 832, 706. **EI-MS:** (Acetonitrile) m/z 241.1054 ([M+H]$^+$) (calc. 241.1051).

### 4-(2-thienyl)ethylphenylferrocene (6)

Benzyltriethylammonium chloride (7.1 mg, 0.03 mmol), copper (I) iodide (10 mg, 0.053 mmol), tetrakis(triphenylphosphine) palladium(0) (20 mg, 0.017 mmol), 2-bromothiophene (0.5 mL, 5 mmol) and 4-ethynylphenylferrocene (7) (0.2 g, 0.66 mmol) were dissolved in benzene (10 mL). To this was added a 5.5 N solution of aqueous sodium hydroxide (0.8 mL, 4.4 mmol) and the mixture was left stirring at 80°C for 3 days. It was cooled to room temperature, saturated ammonium chloride (40 mL) was added and the solution stirred for 1 hour. The phases were separated and the aqueous layer was extracted with toluene. The organic phases were dried with magnesium sulfate and solvent was evaporated. The product was purified by column chromatography using hexane: dichloromethane (3: 1) as eluent ($R_f = 0.5$), to give the desired product as an orange solid. **Yield:** 196 mg, 0.53 mmol, 80%. **Melting Point:** 112-113°C. **$^1$H-NMR** (400 MHz, CDCl$_3$, 25°C, TMS) $\delta$: 7.49 (m, 4H, H$_9$ and H$_{10}$), 7.33 (s, 1H, H$_3$), 7.32 (dd, 1H, $^3$J$_{H-H} = 1.0$ Hz and $^3$J$_{H-H} = 3.0$ Hz, H$_3$), 7.06 (dd, 1H, $^3$J$_{H-H} = 3.0$ and 5.0 Hz, H$_4$), 4.71 (t, 2H, $^3$J$_{H-H} = 1.8$ Hz, H$_{13/14}$), 4.39 (t, 2H, $^3$J$_{H-H} = 1.7$ Hz, H$_{13/14}$), 4.08 (s, 5H, H$_{15}$). **$^{13}$C{$^1$H}-NMR** (100 MHz, CDCl$_3$, 25°C, TMS) $\delta$: 140.1 (C$_3$), 131.7 (C$_2$), 131.5 (C$_{9/10}$), 127.1 (2C, C$_3$ and C$_4$), 125.9 (C$_{9/10}$), 123.6 (C$_{8/11}$), 120.0 (C$_{8/11}$), 93.5 (C$_{12}$), 84.2 (C$_7$), 82.7 (C$_6$), 69.8 (C$_{15}$), 69.5 (C$_{13/14}$), 66.8 (C$_{13/14}$). **IR (neat)** cm$^{-1}$: 3917, 3101, 2923, 2853,
2456, 2216 (C≡C), 2050, 1917, 1734, 1667, 1602, 1526, 1455, 1408, 1281, 1205, 1103, 1029, 938, 884, 814, 773, 696. **MALDI-MS**: (Chloroform) m/z 368.0326 ([M]+) (calc. 368.0322).

4-ethynylphenylferrocene (7)

4-acetylphenylferrocene

Ferrocene (15.2 g, 81.6 mmol) was added to sulfuric acid (100 mL) and the resulting deep blue ferrocenium solution was stirred at room temperature for 2 hours. The solution was then poured into ice/water (400 mL) and allowed to warm to room temperature. A solution of sodium nitrite (3.64 g, 52.8 mmol) in water (20 mL) at 0°C was added dropwise to a stirred solution of 4-aminoacetphenone (6.48 g, 480 mmol) in 1:1 water: hydrochloric acid (40 mL) at 0°C and stirred at this temperature for 30 minutes to ensure full diazotization. Copper powder (4.0 g, 63.04 mmol) was added to the ferrocenium solution and the diazonium solution was added dropwise with vigorous stirring. After 24 hours stirring at room temperature, effervescence due to liberated nitrogen had ceased and ascorbic acid (20 g, 0.11 mol) was added to the dark mixture to reduce any remaining ferrocenium to ferrocene. Dichloromethane (400 mL) was added and the organic layer separated. The aqueous layer was extracted with further dichloromethane (4 x 150 mL), and the combined organic extracts were filtered through celite before removal of the solvent to give a dark solid. This was subjected to column chromatography using gradient elution. The first yellow fraction, eluted with hexane, yielded unchanged ferrocene. The second orange-red fraction, eluted with 4:1 (dichloromethane:hexane) gave upon evaporation of solvents the desired product as an orange crystalline solid. **Yield**: 4.90 g, 16.11 mmol, 34%. **H NMR** (400 MHz, CDCl₃, 25°C, TMS) δ: 7.90 (d, 2H, J₆₋₇ = 8.0 Hz, H₆/₇), 7.55 (d, 2H, J₆₋₇ = 8.0 Hz, H₆/₇), 4.74 (t, 2H, J₂₋₃ = 1.8 Hz, H₂/₃), 4.42 (t, 2H, J₂₋₃ = 1.8 Hz, H₂/₃), 4.06 (s, 5H, H₁), 2.62 (s, 3H, H₁₀).
α-chloro-β-formyl-p-ferrocenylstyrene

A solution of phosphorous oxychloride (1.4 mL, 14 mmol) in dimethylformamide (10 mL) at 0°C, was added dropwise to a solution of 4-acetylphenylferrocene (1.2 g, 4 mmol) in dimethylformamide (15 mL) at 0°C. The reaction was allowed to proceed for 15 minutes at 0°C and then for 4 hours at room temperature, then transferred into a 20% w/v solution of sodium acetate in water (40 mL) and allowed to stir for 90 minutes. The solution was extracted several times with dichloromethane and the combined organic extract was washed several times with water, dried over magnesium sulfate and the solvents were removed under reduced pressure. The residue was columned with dichloromethane: hexane (2: 1) as the eluent (Rf = 0.6) to yield a purple solid. **Yield:** 0.7 g, 2.0 mmol, 50%. **1H NMR** (400 MHz, CDCl3, 25°C, TMS) δ: 10.25 (d, 1H, 3JH-H = 6.8 Hz, H11), 7.70 (d, 2H, 3JH-H = 8.0 Hz, H6/7), 7.53 (d, 2H, 3JH-H = 8.0 Hz, H6/7), 6.72 (d, 1H, 3JH-H = 6.8 Hz, H10), 4.77 (s, 2H, H2/3), 4.47 (s, 2H, H2/3), 4.11 (s, 5H, H1).

4-ethynylphenylferrocene

α-chloro-β-formyl-p-ferrocenylstyrene (0.65 g, 1.85 mmol) was dissolved in dioxane (20 mL) and the solution was heated to reflux at 115°C. To this was added rapidly 0.5 M aqueous sodium hydroxide (15 mL, 7.5 mmol). The reaction was allowed to continue for 5 minutes at reflux and the solution was then poured into deionised water (100 mL). After acidification with 10% aqueous hydrochloric acid (40 mL), the solution was extracted exhaustively with diethyl ether and the combined ether extracts were combined and washed to neutrality before being dried over magnesium sulfate. The solvent was then...
removed and the residue was recrystallised from hexane to yield the desired product as an orange solid. **Yield:** 0.49 g, 1.71 mmol, 93%. **Melting Point:** 84-85°C. **$^1$H NMR** (400 MHz, CD$_2$Cl$_2$, 25°C, TMS) $\delta$: 7.48 (d, 2H, $^3$J$_{H-H}$ = 8.5 Hz, H$_{6/7}$), 7.43 (d, 2H, $^3$J$_{H-H}$ = 8.5 Hz, H$_{6/7}$), 4.71 (s, 2H, H$_{2/3}$), 4.40 (s, 2H, H$_{2/3}$), 4.07 (s, 5H, H$_1$), 3.19 (s, 1H, H$_{10}$). **$^{13}$C{$^1$H}-NMR** (100 MHz, CD$_2$Cl$_2$, 25°C, TMS) $\delta$: 140.2 (C$_5$), 131.6 (C$_{6/7}$), 125.3 (C$_{6/7}$), 118.5 (C$_8$), 83.4 (C$_{9/10}$), 83.3 (C$_{9/10}$), 76.4 (C$_4$), 69.2 (C$_1$), 69.0 (C$_{2/3}$), 66.1 (C$_{2/3}$). **IR (neat)** cm$^{-1}$: 3283, 2105 (C≡C), 1604, 1260, 1106, 1026, 818. **ESI-MS** (Toluene) m/z 286.0452 ([M]$^+$) (calculated 286.0445).

**Cyclotrimerisation of thienyl acetylenes - Synthesis of 8-13**

In dioxane (10 mL), the acetylene being trimerised 1-6 (0.50 mmol) and dicobalt octacarbonyl (26.22 mg, 0.075 mmol, 0.15 eq.) were stirred at 115°C (1, 4 and 5 for 1 day; 2, 3 and 6 for 3 days). The solution was cooled to room temperature and solvent was removed to give a brown solid. The products were purified by column chromatography using dichloromethane: hexane, 1: 1 as the eluent. **$^1$H** and **$^{13}$C** NMR data of 8-13 are discussed in the main text.

**1,3,5–tri(3-thienyl)-2,4,6-tri(4-phenylferrocene)benzene/1,3,4–tri(3-thienyl)-2,5,6-tri(4-phenylferrocene)benzene (8)**

![Structural formula of 8s and 8a](image)

**Yield:** 86.2 mg, 0.078 mmol, 47% of a orange solid ($R_f$ = 0.6). **Melting Point:** > 330°C. **IR (neat)** cm$^{-1}$: 3093, 2923, 2330, 2179, 2060, 1412, 1261, 1106, 1002, 817. **MALDI-MS:** (Chloroform) m/z 1104.0970 ([M]$^+$) (calc. 1104.0966).
1,3,5–tri(3-thienyl)-2,4,6-triphenylbenzene/1,3,4–tri(3-thienyl)-2,5,6-
triphenylbenzene (9)

**Yield:** 55.3 mg, 0.10 mmol, 61% of a white solid (R<sub>f</sub> = 0.6). **Melting Point:** > 330°C. **IR (neat) cm<sup>-1</sup>:** 1600, 1493, 1425, 1349, 1072, 1023, 917, 841, 823, 758, 697. **ESI-MS:** (Acetonitrile) m/z 553.1119 ([M+H]<sup>+</sup>) (calc. 553.1118).

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1,3,5–tri(3-thienyl)-2,4,6-tri(4-tert-butylphenyl)benzene/1,3,4–tri(3-thienyl)-2,5,6-
tri(4-tert-butylphenyl)benzene (10)

**Yield:** 67.1 mg, 0.093 mmol, 56% of a white solid (R<sub>f</sub> = 0.5). **Melting Point:** 292-293°C. **IR (neat) cm<sup>-1</sup>:** 1512, 1461, 1393, 1362, 1269, 1203, 1104, 1020, 942, 848, 777, 712. **ESI-MS:** (Acetonitrile) m/z 743.2831 ([M+Na]<sup>+</sup>) (calc. 743.2816).
1,3,5-tri(2-thienyl)-2,4,6-tri(4-phenylferrocene)benzene/1,3,4-tri(2-thienyl)-2,5,6-tri(4-phenylferrocene)benzene (11)

![Structures 11s and 11a](image11.png)

**Yield:** 75.2 mg, 0.068 mmol, 41% of an orange solid ($R_f = 0.7$). **Melting Point:** > 330°C.

**IR (KBr) cm$^{-1}$:** 3086, 2926, 2483, 1729, 1610, 1412, 1380, 1261, 1106, 1019, 807. **ESI-MS:** (Chloroform) m/z 1104.0989 ([M+H]$^+$) (calc. 1104.0966).

1,3,5-tri(2-thienyl)-2,4,6-triphenylbenzene/1,3,4-tri(2-thienyl)-2,5,6-triphenylbenzene (12)

![Structures 12s and 12a](image12.png)

**Yield:** 51.4 mg, 0.093 mmol, 56% of a white solid ($R_f = 0.6$). **Melting Point:** > 330°C.

**IR (neat) cm$^{-1}$:** 1600, 1441, 1383, 1260, 1217, 1026, 799, 690. **ESI-MS:** (Acetonitrile) m/z 553.1117 ([M+H]$^+$) (calc. 553.1118).

1,3,5-tri(2-thienyl)-2,4,6-tri(4-tert-butylphenyl)benzene/1,3,4-tri(2-thienyl)-2,5,6-tri(4-tert-butylphenyl)benzene (13)

![Structures 13s and 13a](image13.png)
**Yield:** 57.7 mg, 0.08 mmol, 48% of a white solid ($R_f = 0.6$). **Melting Point:** 290-291°C. **IR (neat) cm$^{-1}$:** 1508, 1461, 1391, 1362, 1268, 1221, 1116, 1020, 823, 688. **ESI-MS:** (Acetonitrile) m/z 743.2816 ([M+Na$^+$]) (calc. 743.2816).

**2-ethynylthiophene (15)**

2-(2,2-dibromovinyl)thiophene

![Diagram of 2-(2,2-dibromovinyl)thiophene](image)

Triphenylphosphine (10.48 g, 39.95 mmol) and carbon tetrabromide (6.64 g, 20.26 mmol) were dissolved in dichloromethane (50 mL) and stirred at 0°C for 5 min. To this 2-thiophenecarboxaldehyde (1.5 mL, 16.05 mmol) was added and the solution warmed to room temperature and stirred for 1 hour to give a yellow solution. Solvent was removed and the residue washed twice with acetone (100 mL) and recrystallised from acetone to give the product as a white solid. **Yield:** 3.91 g, 14.7 mmol, 91%. **$^1$H NMR** (400 MHz, CDCl$_3$, 25°C, TMS) $\delta$: 7.69 (s, 1H, H$_6$), 7.42 (dd, 1H, $^3J_{H-H} = 0.5$ Hz and $^4J_{H-H} = 5.3$ Hz, H$_3$), 7.28 (dd, 1H, $^4J_{H-H} = 0.5$ Hz and $^3J_{H-H} = 3.8$ Hz, H$_3$), 7.07 (dd, 1H, $^3J_{H-H} = 3.8$ and 5.3 Hz, H$_4$).

**2-ethynylthiophene**

![Diagram of 2-ethynylthiophene](image)

2-(2,2-dibromovinyl)thiophene (2.0 g, 7.46 mmol) was dissolved in diethyl ether (100 mL) and cooled to -78°C. To this 2.5 M n-butyllithium (6.57 mL, 16.41 mmol) was added dropwise and the solution stirred at -78°C for 1 hour and then warmed to room temperature over 1 hour. The solution was poured into water (150 mL) and extracted with diethyl ether. The solution was dried over magnesium sulfate and solvent removed to give a yellow oil. The product was purified by column chromatography using hexane as
eluent (R_t = 0.8), to give a yellow viscous liquid. Yield: 0.516 g, 4.77 mmol, 64%. \(^{1}H\)-NMR (400 MHz, CDCl\(_3\), 25°C, TMS) \(\delta\): 7.33 (dd, 1H, \(^{4}J_{HH} = 1.0\) Hz and \(^{3}J_{HH} = 3.5\) Hz, H\(_{3}\)), 7.29 (dd, 1H, \(^{4}J_{HH} = 1.0\) Hz and \(^{3}J_{HH} = 5.0\) Hz, H\(_{5}\)), 7.01 (dd, 1H, \(^{3}J_{HH} = 3.5\) and 5.0 Hz, H\(_{4}\)), 3.40 (s, 1H, H\(_{7}\)). \(^{13}C\)\(^{1}H\)-NMR (100 MHz, CDCl\(_3\), 25°C, TMS) \(\delta\): 132.7 (C\(_{3}\)), 127.2 (C\(_{5}\)), 126.5 (C\(_{4}\)), 121.6 (C\(_{2}\)), 81.0 (C\(_{7}\)), 76.6 (C\(_{6}\)).

\(\text{EI-MS: (Chloroform) m/z 108.0036 ([M]+)}\) (calcd. 108.0034).

1,2,4–tri(3-thienyl)benzene (16)

3-ethynlthiophene (14) (0.5 mL, 5.08 mmol) was dissolved in dioxane (10 mL). To this dicobalt octacarbonyl (260.6 mg, 0.76 mmol) was added and the mixture was refluxed at 115°C for 3 days. The mixture was cooled to room temperature and solvent was removed to give a brown residue from which a white solid was precipitated by the addition of methanol (1 mL). Yield: 347 mg, 1.07 mmol, 63%. Melting Point: 122-123°C. \(^{1}H\)-NMR (400 MHz, CDCl\(_3\), 25°C, TMS) \(\delta\): 7.72 (d, 1H, \(^{4}J_{HH} = 1.7\) Hz, H\(_{3}\)), 7.61, (dd, 1H, \(^{4}J_{HH} = 1.7\) Hz and \(^{3}J_{HH} = 8.1\) Hz, H\(_{5}\)), 7.55 (m, 2H, H\(_{6}\) and H\(_{d5}\)), 7.47 (dd, 1H, \(^{4}J_{HH} = 1.2\) Hz and \(^{3}J_{HH} = 4.8\) Hz, H\(_{d4}\)), 7.45 (dd, 1H, \(^{4}J_{HH} = 1.2\) and 2.8 Hz, H\(_{d2}\)), 7.25 (dd, 1H, \(^{4}J_{HH} = 2.9\) Hz and \(^{3}J_{HH} = 4.9\) Hz, H\(_{b5}\)), 7.24 (dd, 1H, \(^{4}J_{HH} = 3.0\) Hz and \(^{3}J_{HH} = 4.8\) Hz, H\(_{a5}\)), 7.17 (dd, 1H, \(^{4}J_{HH} = 1.2\) and 2.9 Hz, H\(_{b2}\)), 7.12 (dd, 1H, \(^{4}J_{HH} = 1.1\) and 2.7 Hz, H\(_{a2}\)), 6.88 (dd, 1H, \(^{4}J_{HH} = 1.0\) Hz and \(^{3}J_{HH} = 5.0\) Hz, H\(_{b4}\)), 6.84 (dd, 1H, \(^{4}J_{HH} = 1.0\) Hz and \(^{3}J_{HH} = 5.0\) Hz, H\(_{a4}\)). \(^{13}C\)\(^{1}H\)-NMR (150.9 MHz, CDCl\(_3\), 25°C, TMS) \(\delta\): 141.9 (C\(_{b3}\)), 141.5 (2C, C\(_{a3}\) and C\(_{d3}\)), 135.7 (C\(_{2}\)), 134.9 (C\(_{4}\)), 134.1 (C\(_{1}\)), 130.5 (C\(_{6}\)), 128.8 (C\(_{b4}\)), 128.7 (C\(_{a4}\)), 128.2 (C\(_{3}\)), 126.2 (C\(_{d4}\)), 126.1 (C\(_{d2}\)), 125.4 (C\(_{5}\)), 124.7 (C\(_{b5}\)), 124.6 (C\(_{a5}\)), 122.9 (C\(_{b2}\)), 122.7 (C\(_{a2}\)), 120.4 (C\(_{d5}\)). IR (neat) cm\(^{-1}\): 3099, 2165, 1783, 1669, 1603, 1561, 1474, 1410, 1364, 1220, 1179, 1131, 1082, 1025, 933, 859, 831, 775, 666. MALDI-MS: (Acetonitrile) 324.0103 ([M]+) (calculated 324.0101).
1,2,4–tri(2-thienyl)benzene (17)

2-ethynlthiophene (15) (0.5 mL, 5.08 mmol) was dissolved in dioxane (10 mL). To this dicobalt octacarbonyl (260.6 mg, 0.76 mmol) was added and the mixture was refluxed at 115°C for 3 days. The mixture was cooled to room temperature and solvent was removed to give a brown solid, this was purified by column chromatography using hexane: diethyl ether (9: 1) as eluent to give a white solid which was recrystallised from dichloromethane and methanol (1 mL of each). **Yield:** 126 mg, 0.39 mmol, 23%. **Melting Point:** 179-180°C. **$^1$H-NMR** (400 MHz, CDCl$_3$, 25°C, TMS) δ: 7.77 (s, 1H, H$_3$), 7.63 (d, 1H, $^3$J$_{H-H}$ = 5.3 Hz, H$_5$), 7.56 (d, 1H, $^3$J$_{H-H}$ = 5.3 Hz, H$_6$), 7.41 (d, 1H, $^3$J$_{H-H}$ = 3.5 Hz, H$_{d3}$), 7.33 (m, 2H, H$_{d5}$ and H$_{b5}$), 7.30 (d, 1H, $^3$J$_{H-H}$ = 4.9 Hz, H$_{a5}$), 7.12 (dd, 1H, $^3$J$_{H-H}$ = 3.5 and 5.0 Hz, H$_{d4}$), 7.03 (dd, 1H, $^3$J$_{H-H}$ = 3.5 and 5.0 Hz, H$_{b4}$), 6.99 (m, 2H, H$_{a4}$ and H$_{b3}$), 6.93, (d, 1H, $^3$J$_{HH}$ = 2.6 Hz, H$_{a3}$). **$^{13}$C($^1$H)-NMR** (100 MHz, CDCl$_3$, 25°C, TMS) δ: 143.1 (C$_{d2}$), 142.1 (2C, C$_{a2}$ and C$_{b2}$), 134.0 (C$_2$), 133.8 (C$_4$), 132.8 (C$_1$), 130.9 (C$_6$), 128.1 (C$_3$), 127.7 (C$_{d4}$), 127.0 (C$_{b3}$), 126.7 (C$_{a3}$), 126.6 (2C, C$_{b4}$ and C$_{a4}$), 125.8 (C$_{h5}$), 125.6 (C$_{a5}$), 124.9 (2C, C$_{d5}$ and C$_5$), 123.2 (C$_{d3}$). **IR (neat)** cm$^{-1}$: 3100, 2963, 2160, 1796, 1667, 1599, 1537, 1478, 1395, 1351, 1261, 1181, 1127, 1080, 1041, 957, 892, 814, 780, 697. **MALDI-MS:** (Dichloromethane) m/z 324.0096 ([M]+) (calc.324.0101).

7.3 Synthesis and oxidation of di-thienyl polyphenylene derivatives

**Bis(2-thienyl)acetylene (18)**$^9$-$^{10}$
To 2-bromothiophene (2.0 mL, 20 mmol), 2-methyl-3-butyne-2-ol (2.0 mL, 20 mmol), benzyltriethylammonium chloride (71 mg, 0.31 mmol), copper(I) iodide (100 mg, 0.53 mmol) and tetrakis(triphenylphosphine)palladium(0) (200 mg, 0.17 mmol) in benzene (10 mL), was added a 5.5 N solution of aqueous sodium hydroxide (8 mL, 66 mmol) and the mixture was left stirring for 3 days. Then 2-bromothiophene (2.0 mL, 20 mmol) in benzene (8 mL) was added and the solution was heated to 80°C and left stirring at this temperature for a further 3 days. It was cooled to room temperature and a solution of saturated aqueous ammonium chloride (40 mL) was added and the solution stirred for 1 hour. The phases were separated and the aqueous layer was extracted with toluene. The organic phases were dried with magnesium sulfate and solvent was evaporated. The product was purified by column chromatography using hexane as eluent (Rf = 0.8) to give the desired product as a white solid. **Yield:** 0.51 g, 2.68 mmol, 14%. **Melting Point:** 73-74°C (lit. 68-70°C).**\(^{11}\)**

\[^{1}H\text{-NMR}\ (400 \text{ MHz, } \text{CDCl}_3, 25°C, \text{TMS}) \delta:\] 7.33 (dd, 2H, \(^4J_{HH} = 1.0 \text{ Hz and } \(^3J_{HH} = 5.0 \text{ Hz, } H_3\)), 7.30 (dd, 2H, \(^4J_{HH} = 1.0 \text{ Hz and } \(^3J_{HH} = 3.5 \text{ Hz, } H_3\)), 7.03 (dd, 2H, \(^3J_{HH} = 3.5 \text{ and } 5.0 \text{ Hz, } H_4\)).**\(^{13}C\{^{1}H\}-\text{NMR}\ (100 \text{ MHz, } \text{CDCl}_3, 25°C, \text{TMS}) \delta:\] 131.7 (C\(_3\)), 127.2 (C\(_4\)), 126.7 (C\(_4\)), 122.4 (C\(_2\)), 85.7 (C\(_1\)).**\(^{1}R\ (\text{neat}) \text{ cm}^{-1}:\] 2901, 2186 (C≡C), 1433, 1407, 1199, 1041, 1028, 850, 825, 694. **ESI-MS:** (Acetonitrile) m/z 189.9919 ([M+] (calc. 189.9911)).

**Bis(3-thienyl)acetylene (19)**\(^{10}\)

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\downarrow \quad \downarrow \\
\text{C} \quad \text{C} \\
\text{S} \quad \text{S} \\
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\]

To 3-bromothiophene (2.0 mL, 20 mmol), 2-methyl-3-butyne-2-ol (2.0 mL, 20 mmol), benzyltriethylammonium chloride (71 mg, 0.31 mmol), copper(I) iodide (100 mg, 0.53 mmol) and tetrakis(triphenylphosphine)palladium(0) (200 mg, 0.17 mmol) in benzene (10 mL), was added a 5.5 N solution of aqueous sodium hydroxide (8.0 mL, 66 mmol) and the mixture was left stirring for 3 days. Then 3-bromothiophene (2.0 mL) in benzene (8.0 mL) was added and the solution was heated to 80°C and left stirring at this temperature for a further 3 days. It was cooled to room temperature and a solution of aqueous saturated ammonium chloride (40 mL) was added and the solution stirred for 1
hour. The phases were separated and the aqueous layer was extracted with toluene. The organic phases were dried with magnesium sulfate and evaporated. The product was purified by column chromatography using hexane: dichloromethane (3: 2) as eluent, to give the desired product as a white solid. **Yield:** 1.52 g, 7.99 mmol, 40%. **Melting Point:** 76-77 °C. **\(^1\)H-NMR** (400 MHz, CDCl\(_3\), 25°C, TMS) \(\delta\): 7.54 (dd, 2H, \(^4\)J\(_{H-H} = 1.5 \text{ and } 3.0\) Hz, H\(_2\)), 7.32 (dd, 2H, \(^4\)J\(_{H-H} = 3.0 \text{ Hz and } 3\)J\(_{H-H} = 5.0 \text{ Hz, H}_3\)), 7.21 (dd, 2H, \(^4\)J\(_{H-H} = 1.5 \text{ Hz and } 3\)J\(_{H-H} = 4.5 \text{ Hz, H}_4\)). **\(^{13}\)C\(^{\{1\}H\}\)-NMR** (100 MHz, CDCl\(_3\), 25°C, TMS) \(\delta\): 129.4 (C\(_5\)), 128.1 (C\(_2\)), 124.9 (C\(_4\)), 121.7 (C\(_3\)), 85.7 (C\(_1\)). **IR (neat)** cm\(^{-1}\): 3099, 2161 (C≡C), 1352, 1076, 968, 828, 774, 693. **ESI-MS:** (Acetonitrile) m/z 189.9916 ([M]+) (calc. 189.9911).

4-(3-thienyl)-2-methyl-3-butyn-2-ol (20)

To 3-bromothiophene (2 ml, 20.64 mmol) in diethyl amine (30 mL), palladium dichlorodiphenylphosphene (289.9 mg, 0.41 mmol, 2 mol %) and copper iodide (196 mg, 1.03 mmol, 5 mol%) were added. To this 2-methyl-3-butyn-2-ol (2 mL, 20 mmol) was added and the solution was stirred for 20 hours. A solution of saturated aqueous ammonium chloride (40 mL) was added and the solution stirred for 1 hour, then extracted with chloroform. The organic phases were dried with magnesium sulfate and evaporated. This was purified by column chromatography using dichloromethane: methanol (50: 1) as eluent to give the product (R\(_f\) = 0.4) as an off yellow solid which was recrystallised from petroleum ether. **Yield:** 850 mg, 5.1 mmol, 25%. **Melting Point:** 39-40°C. **\(^1\)H-NMR:** (400 MHz, CDCl\(_3\), 25°C, TMS) \(\delta\): 7.44 (dd, 1H, \(^4\)J\(_{H-H} = 1.0 \text{ and } 3.0\) Hz, H\(_2\)), 7.27 (dd, 1H, \(^4\)J\(_{H-H} = 3.0 \text{ Hz and } 3\)J\(_{H-H} = 5.0 \text{ Hz, H}_3\)), 7.11 (dd, 1H, \(^4\)J\(_{H-H} = 1.0 \text{ Hz and } 3\)J\(_{H-H} = 5.0 \text{ Hz, H}_4\)), 2.04 (s, 1H, H\(_{10}\)), 1.63 (s, 6H, H\(_9\)). **\(^{13}\)C\(^{\{1\}H\}\)-NMR** (100 MHz, CDCl\(_3\), 25°C, TMS) \(\delta\): 129.4 (C\(_4\)), 128.2 (C\(_2\)), 124.8 (C\(_5\)), 121.5 (C\(_3\)), 92.9 (C\(_6/7\)), 76.9 (C\(_6/7\)), 65.2 (C\(_8\)), 31.0 (C\(_9\)). **IR (neat)** cm\(^{-1}\): 3206 (O-H), 2980, 2221 (C≡C), 1356, 1260, 1153, 943, 783. **ESI-MS:** (Acetonitrile) m/z 167.0531 ([M+H]+) (calc. 167.0531).
2-thienyl-3-thienyl acetylene (21)

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To benzyltriethylammonium chloride (25 mg, 0.11 mmol), copper(I) iodide (34 mg, 0.13 mmol) and tetrakis(triphenylphosphine) palladium(0) (110 mg, 0.091 mmol), 2-bromothiophene (0.31 mL, 3.15 mmol) and 4-(3-thienyl)-2-methyl-3-butyn-2-ol (20) (0.59 g, 3.3 mmol) in benzene (10 mL), was added a 5.5 N solution of aqueous sodium hydroxide (8 mL, 66 mmol) and the mixture was left stirring at 80°C for 3 days. It was cooled to room temperature and a solution of saturated aqueous ammonium chloride (40 mL) was added and the solution stirred for 1 hour. The phases were separated and the aqueous layer was extracted with toluene. The organic phases were dried with magnesium sulfate and evaporated. The product was purified by column chromatography using hexane as eluent to give the desired product (R_f = 0.8) as a white solid. **Yield:** 0.47 g, 2.43 mmol, 77%. **Melting Point:** 75-76°C. **^1H-NMR** (400 MHz, CDCl_3, 25°C, TMS) δ: 7.55 (dd, 1H, J_H-H = 1.0 and 3.0 Hz, H2'), 7.33 (dd, 1H, J_H-H = 3.0 Hz and J_H-H = 5.0 Hz, H5'), 7.30 (m, 2H, H3 and H5), 7.22 (dd, 1H, J_H-H = 1.0 Hz and J_H-H = 5.0 Hz, H4'), 7.03 (dd, 1H, J_H-H = 3.0 and 5.0 Hz, H3). **^13C{^1H}-NMR** (100 MHz, CDCl_3, 25°C, TMS) δ: 131.4 (C3/5), 129.3 (C4'), 128.4 (C2'), 126.8 (C3/5), 126.7 (C4), 125.1 (C5'), 122.8 (C2/3'), 121.5 (C2/3'), 87.8 (C1/1'), 81.7 (C1/1'). **IR (neat)** cm⁻¹: 2163 (C≡C), 1213, 1118, 866, 849, 824, 774, 699, 689, 619. **EI-MS:** (Acetonitrile) m/z 189.9919 ([M]+) (calc. 189.9911).

**Synthesis of (1,2-di(3-thienyl)-3,4,5,6-tetraphenyl)benzene (22)**

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\]
Bis(3-thienyl)acetylene (19) (60 mg, 0.315 mmol), 2,3,4,5-cyclopentadiene-1-one (110 mg, 0.246 mmol) and benzophenone (0.6 g) were heated at 300°C for 1 hour while attached to an air condenser giving a brown mixture. After cooling to room temperature the product as a white solid, was precipitated by addition of dichloromethane and methanol (2 mL of each). **Yield:** 77 mg, 0.14 mmol, 57%. **Melting Point:** > 330°C. **H-NMR** (400 MHz, CDCl₃, 25°C, TMS) δ: 6.96 - 6.92 (m, 6H, H₁₅ and H₁₃/₁₄), 6.89 - 6.85 (m, 12H, H₅, H₈/₉, H₁₀ and H₁₃/₁₄), 6.83 - 6.81 (m, 4H, H₈/₉), 6.56 (dd, 2H, J_H-H = 1.0 and 3.0 Hz, H₂), 6.51 (dd, 2H, J_H-H = 1.0 Hz and J_H-H = 5.0 Hz, H₄). **C{H}-NMR** (100 MHz, CDCl₃, 25°C, TMS) δ: 140.8 (C_quat), 140.7 (C_quat), 140.6 (C_quat), 140.5 (C_quat), 140.4 (C_quat), 135.8 (C₃), 131.4 (C₈/₉), 131.0 (C₁₃/₁₄), 130.2 (C₄), 126.8 (C₁₃/₁₄), 126.6 (C₁₃/₁₄), 125.4 (C₁₀), 125.3 (C₁₅), 124.4 (C₂), 123.0 (C₅). **IR (neat)** cm⁻¹: 1495, 1441, 1072, 1017, 760, 696, 682. **ESI-MS:** (Acetonitrile) m/z 569.1369 ([M+Na]⁺) (calc. 569.1374).

1,2-bis(4-tert-butylphenyl)ethane-1,2-dione (23)

To 1-bromo-4-tert-butylbenzene (3.8 mL, 21.2 mmol) in dry tetrahydrofuran (50 mL) at -78°C, 2.5 M n-butyllithium (9.2 mL, 23 mmol) was added dropwise and the mixture was left stirring for two hours at -78°C. It was then transferred into a suspension of DMPD (1.50 g, 10.6 mmol) in dry tetrahydrofuran (30 mL) at -78°C and the mixture was left stirring while warming to room temperature overnight. It was then poured into 10% aqueous hydrochloric acid (150 mL) and extracted with dichloromethane. The organic layer was dried over magnesium sulfate and evaporated to give a yellow oil. The product was recrystallised from hexane to give yellow crystals. **Yield:** 2.42 g, 7.5 mmol, 54%. **Melting Point:** 60-61°C. **H-NMR** (400 MHz, CDCl₃, 25°C, TMS) δ: 7.93 (d, 4H, J_H-H = 8.5 Hz, H₃/₄), 7.54 (d, 4H, J_H-H = 8.5 Hz, H₃/₄), 1.36 (s, 18H, H₇). **C{H}-NMR** (100
MHz, CDCl$_3$, 25°C, TMS) $\delta$: 194.1 (C$_1$), 158.4 (C$_{2/5}$), 130.1 (C$_{2/5}$), 129.4 (C$_{3/4}$), 125.6 (C$_{3/4}$), 35.0 (C$_6$), 30.5 (C$_7$). **IR (neat)** cm$^{-1}$: 2961, 1676 (C=O), 1661, 1601, 1410, 1223, 1178, 1108, 895, 851, 769, 684. **Elemental Anal:** Calculated for C$_{22}$H$_{26}$O$_2$: C, 81.95; H 8.13. Found: C, 81.99; H 8.11. **ESI-MS:** (Acetonitrile) m/z 345.1830. ([M+Na]$^+$) (calc. 345.1831).

**1,3-bis(4-tert-butylphenyl)propane-2-one (24)**

![Structure of 1,3-bis(4-tert-butylphenyl)propane-2-one (24)]

To a mixture of 1: 1 dichloromethane: water (160 mL), calcium hydroxide (2.60 g, 3.52 mmol) and tetrabutylammonium hydrogen sulfate (1.50 g, 4.4 mmol) were added. To this (4-tert-butyl)benzyl bromide (3.33 mL, 18.12 mmol) and iron pentacarbonyl (1.16 mL, 88 mmol) were added and the solution was stirred for 5 hours and then oxidised by bubbling with a stream of air for one hour. 10% aqueous hydrochloric acid (60 mL) was added, the organic layer was extracted, dried over magnesium sulfate and solvent was removed. The residue was recrystallised from hexane to give the product as white needles. **Yield:** 1.20 g, 3.72 mmol, 42%. **Melting Point:** 69-70°C. **$^1$H-NMR** (400 MHz, CDCl$_3$, 25°C, TMS) $\delta$: 7.38 (d, 4H, $^3$J$_{H-H}$ = 2.0 Hz, H$_{4/5}$), 7.14 (d, 2H, $^3$J$_{H-H}$ = 2.0 Hz, H$_{4/5}$), 3.74 (s, 4H, H$_2$), 1.36 (s, 18H, H$_8$). **$^{13}$C($^1$H)-NMR** (100 MHz, CDCl$_3$, 25°C, TMS) $\delta$: 205.6 (C$_1$), 149.4 (C$_{3/6}$), 103.6 (C$_{3/6}$), 128.7 (C$_{4/5}$), 125.2 (C$_{4/5}$), 48.1 (C$_2$), 34.0 (C$_7$), 30.9 (C$_8$). **IR (neat)** cm$^{-1}$: 2954, 2903, 1703 (C=O), 1510, 1365, 1267, 1231, 1192, 1070, 1020, 839, 818, 713. **Elemental Anal:** Calculated for C$_{23}$H$_{30}$O: C, 85.66; H, 9.38. Found: C, 85.36; H 9.24. **ESI-MS:** (Acetonitrile) m/z 345.2209 ([M+Na]$^+$) (calc. 345.2194).
2,3,4,5-tetrakis-(4-tert-butylphenyl)cyclopentadienone (25)

\[
\begin{align*}
&\text{1,3-bis(4-tert-butylphenyl)propane-2-one (24) (200 mg, 0.62 mmol) and 1,2-bis(4-tert-butylphenyl)ethane-1,2-dione (23) (200 mg, 0.62 mmol) were dissolved in ethanol (1.5 mL) and heated to reflux (78°C). To this potassium hydroxide (35 mg, 0.62 mmol) in ethanol (3 mL) was added dropwise through the condenser and the solution was stirred for 20 min. The solution was columned with silica using 1:1 hexane: dichloromethane as the eluent giving the product (R_f = 0.5) as a purple solid. **Yield:** 0.24 g, 1.18 mmol, 42%. **Melting Point:** 213-214°C.} \\
&\text{**1H-NMR** (400 MHz, CDCl}_3, 25°C, TMS) \delta: 7.27 (d, 4H, \text{3J_H-H = 8.9 Hz, H_4/5}), 7.22 (d, 4H, \text{3J_H-H = 8.9 Hz, H_4/5}), 7.16 (d, 4H, \text{3J_H-H = 8.2 Hz, H_11/12}), 6.85 (d, 4H, \text{3J_H-H = 8.2 Hz, H_11/12}), 1.31 (s, 18H, H_8/15), 1.30 (s, 18H, H_8/15).} \\
&\text{**13C{\text{1H}}-NMR** (100 MHz, CDCl}_3, 25°C, TMS) \delta: 200.9 (C_1), 154.3 (C_9), 151.4 (C_{6/13}), 150.0 (C_{6/13}), 130.5 (C_{10/3}), 129.7 (C_{4/5/11/12}), 129.1 (C_{4/5/11/12}), 128.1 (C_{10/3}), 124.9 (C_{4/5/11/12}), 124.6 (C_{4/5/11/12}), 124.3 (C_2), 34.7 (C_{7/14}), 34.6 (C_{7/14}), 31.3 (C_{8/15}), 31.2 (C_{8/15}).} \\
&\text{**IR (neat) cm}^{-1}: 2960, 1709 (C=O), 1607, 1501, 1474, 1461, 1362, 1269, 1113, 1095, 1017, 849, 838, 777. **Elemental Anal:** Calculated for C_{46}H_{53}O: C, 88.76; H 8.61. Found: C, 88.56; H 8.61. **ESI-MS:** (Acetonitrile) m/z 609.4070. ([M+H]^+) (calc. 609.4096). \\
\end{align*}
\]

1,2-di(2-thienyl)-3,4,5,6-tetra-(4-tert-butylphenyl)benzene (26)

\[
\begin{align*}
&\text{1,2-di(2-thienyl)-3,4,5,6-tetra-(4-tert-butylphenyl)benzene (26)} \\
&\text{**IR (neat) cm}^{-1}: 2960, 1709 (C=O), 1607, 1501, 1474, 1461, 1362, 1269, 1113, 1095, 1017, 849, 838, 777. **Elemental Anal:** Calculated for C_{46}H_{53}O: C, 88.76; H 8.61. Found: C, 88.56; H 8.61. **ESI-MS:** (Acetonitrile) m/z 609.4070. ([M+H]^+) (calc. 609.4096).
Bis(2-thienyl)acetylene (18) (104.25 mg, 0.55 mmol), 2,3,4,5-tetrakis-(4-tert-butylphenyl)cyclopentadienone (25) (300 mg, 0.49 mmol) and benzophenone (1.0 g) were mixed in a round bottom flask and attached to an air condenser. The mixture was heated to 300°C for 90 min giving a brown mixture. After cooling to room temperature this was purified by column chromatography using hexane: diethyl ether (9: 1) as the eluent to give the product (R_f = 0.8) as a yellow solid. This was recrystallised from a mixture of chloroform and methanol (2 mL each). **Yield:** 248 mg, 0.32 mmol, 65%.

**Melting Point:** 270-271°C. **1H-NMR** (400 MHz, CDCl₃, 25°C, TMS) δ: 7.02 (dd, 2H, 3_jH-H = 1.0 Hz and 3_jH-H = 5.0 Hz, H₅), 6.92 (d, 4H, 3_jH-H = 8.0 Hz, H₁₁), 6.83 (d, 4H, 3_jH-H = 8.0 Hz, H₁₆), 6.63 (dd, 2H, 3_jH-H = 3.5 Hz and 5.0 Hz, H₄), 6.51 (dd, 2H, 3_jH-H = 1.0 Hz and 3_jH-H = 3.5 Hz, H₃), 1.16 (s, 18H, H₁₄), 1.11 (s, 18H, H₂₀). **13C{¹H}-NMR** (100 MHz, CDCl₃, 25°C, TMS) δ: 147.6 (C₁₂), 147.2 (C₁₈), 141.6 (C₈), 141.4 (C₆/₇), 141.4 (C₆/₇), 137.1 (C₉), 137.0 (C₁₅), 133.4 (C₄), 130.4 (C₁₆), 130.0 (C₁₀), 128.6 (C₃), 125.1 (C₅), 125.0 (C₂), 122.9 (C₁₁), 122.7 (C₁₇), 33.7 (C₁₉), 33.6 (C₁₃), 30.8 (C₁₄), 30.7 (C₂₀). **IR (neat)** cm⁻¹: 3031, 2958 (C-H, CH₃), 2901, 2866, 1510, 1461, 1390, 1362, 1269, 1019, 827, 699. **Elemental Anal:** Calculated for C₅₄H₅₈S₂: C, 84.10; H, 7.58. Found: C, 84.10; H 7.62. **ESI-MS:** (Acetonitrile) m/z 771.4058 ([M+H]^+) (calc. 771.4058).

1,2-di(3-thienyl)-3,4,5,6-tetra-(4-tert-butylphenyl)benzene (27)

Bis(3-thienyl)acetylene (19) (60 mg, 0.315 mmol), 2,3,4,5-tetrakis-(4-tert-butylphenyl)cyclopentadienone (25) (150 mg, 0.246 mmol) and benzophenone (0.6 g) were heated for 1 hour to 300°C while attached to an air condenser giving a brown mixture. After cooling to room temperature the product was purified by column chromatography using hexane: diethyl ether as eluent to give the product (R_f = 0.8).
as a white solid. **Yield:** 125 mg, 0.16 mmol, 65%. **Melting Point:** 253-254°C. **$^1$H-NMR** (400 MHz, CDCl$_3$, 25°C, TMS) δ: 6.90 (d, 4H, $^3$J$_{H-H} = 8.5$ Hz, H$_{11}$), 6.85-6.82 (m, 6H, H$_5$ and H$_{17}$), 6.74 (d, 4H, $^3$J$_{H-H} = 8.0$ Hz, H$_{10}$), 6.65 (d, 4H, $^3$J$_{H-H} = 8.0$ Hz, H$_{16}$), 6.56 (dd, 2H, $^4$J$_{H-H} = 1.5$ and 3.0 Hz, H$_2$), 6.51 (dd, 2H, $^4$J$_{H-H} = 1.0$ and $^5$J$_{H-H} = 5.0$ Hz, H$_4$), 1.16 (s, 18H, H$_{14}$), 1.11 (s, 18H, H$_{20}$). **$^{13}$C{$^1$H}-NMR** (100 MHz, CDCl$_3$, 25°C, TMS) δ: 147.4 (C$_{12/18}$), 147.1 (C$_{12/18}$), 140.6 (C$_{6/7/8}$), 140.4 (C$_{6/7/8}$), 140.3 (C$_{9/15}$), 137.3 (C$_{9/15}$), 137.2 (C$_{9/15}$), 134.9 (C$_3$), 130.5 (C$_{10}$), 130.2 (C$_{16}$), 130.0 (C$_4$), 123.9 (C$_2$), 122.9 (C$_{11}$), 122.6 (C$_{17}$), 122.1 (C$_5$), 33.7 (C$_{13/19}$), 33.6 (C$_{13/19}$) 30.8 (C$_{14/20}$), 30.7 (C$_{14/20}$). **IR (neat) cm$^{-1}$:** 1511, 1461, 1392, 1362, 1269, 1202, 1119, 1018, 853, 803, 763. **Elemental Anal:** Calculated for C$_{54}$H$_{58}$S$_2$: C, 84.10; H, 7.58. Found: C, 84.29; H, 7.53. **ESI-MS:** (Acetonitrile) m/z 771.4048. ([M+H]$^+$) (calc. 771.4058)

**1-(2-thienyl)-2-(3-thienyl)-3,4,5,6-tetra-(4-tert-butylphenyl)benzene (28)**

![Diagram](image)

2-thienyl-3-thienylacetylene (21) (60 mg, 0.315 mmol), 2,3,4,5-tetrakis-(4-tert-butylphenyl)cyclopentadienone (25) (150 mg, 0.246 mmol) and benzophenone (0.6 g) were heated at 300°C for 90 minutes while attached to an air condenser giving a brown mixture. After cooling to room temperature the product was purified by column chromatography using 9: 1 hexane: diethyl ether as eluent to give the product (R$_f$ = 0.8) as a brown solid, which was washed with cold methanol. **Yield:** 120 mg, 0.16 mmol, 63%. **Melting Point:** 247-248°C. **$^1$H-NMR** (600 MHz, CDCl$_3$, 25°C, TMS) δ: 7.00 (d, 1H, $^3$J$_{H-H} = 5.0$ Hz, H$_5$), 6.91 (m, 4H, 2*H$_{Ar}$), 6.86 (dd, 1H, $^4$J$_{H-H} = 2.9$ Hz and $^3$J$_{H-H} = 5.1$ Hz, H$_5$), 6.81 (m, 6H, 3*H$_{Ar}$), 6.75 (d, 2H, $^3$J$_{H-H} = 8.0$ Hz, H$_{Ar}$), 6.66 (m, 4H, 2*H$_{Ar}$), 6.64 - 6.59 (m, 3H, H$_{Ar}$, H$_{2'}$ and H$_{4'}$), 6.44 (d, 1H, $^3$J$_{H-H} = 3.5$ Hz, H$_3$), 1.16 (s, 18H, CMe$_3$), 1.11 (s, 18H, CMe$_3$). **$^{13}$C{$^1$H}-NMR** (100 MHz, CDCl$_3$, 25°C, TMS) δ: 147.5 (C$_{quat}$), 147.4 (C$_{quat}$), 147.2 (C$_{quat}$), 147.1 (C$_{quat}$), 141.9 (C$_{quat}$), 141.3 (C$_{quat}$), 140.7 (C$_{quat}$), 140.5 (C$_{quat}$), 140.3 (C$_{quat}$), 137.2 (C$_{quat}$), 137.0 (C$_{quat}$), 130.9 (C$_{quat}$), 130.7 (C$_{quat}$), 123.9 (C$_{quat}$), 122.9 (C$_{quat}$), 122.5 (C$_{quat}$), 122.0 (C$_{quat}$), 130.0 (C$_{quat}$), 141.9 (C$_{quat}$).
140.4 (C\textsubscript{quat}), 140.2 (C\textsubscript{quat}), 137.2 (C\textsubscript{quat}), 137.1 (C\textsubscript{quat}), 137.0 (C\textsubscript{quat}), 135.8 (C\textsubscript{quat}), 132.4 (C\textsubscript{quat}), 130.4 (2\textsuperscript{a}C\textsubscript{Ar}), 130.1 (C\textsubscript{Ar}), 130.0 (C\textsubscript{Ar}), 129.9 (C\textsubscript{4}), 128.4 (C\textsubscript{3}), 125.0 (C\textsubscript{3'}), 124.9 (C\textsubscript{5}), 124.0 (C\textsubscript{4'}), 122.9 (C\textsubscript{Ar}), 122.8 (C\textsubscript{Ar}), 122.6 (2\textsuperscript{a}C\textsubscript{Ar}), 122.1 (C\textsubscript{5'}), 33.7 (C\textsubscript{Me\textsubscript{3}}), 33.6 (C\textsubscript{Me\textsubscript{3}}), 30.8 (CH\textsubscript{3}), 30.7 (CH\textsubscript{3}). **IR (neat)** cm\textsuperscript{-1}: 2957, 2863, 1461, 1361, 1270, 1153, 1102, 1019, 828. **ESI-MS**: (Acetonitrile) m/z 771.4050 ([M+H]\textsuperscript{+}) (calc. 771.4058).

**Cyclodehydrogenation of di-thienyl polyphenylenes - Synthesis of 29-31\textsuperscript{15}**

The relevant di-thienyl benzene 22, 26-28 (0.065 mmol) was dissolved in dry dichloromethane (20 mL) and an excess of iron trichloride (0.189 g, 1.12 mmol, 20 eq.) in nitromethane (3 mL) was added dropwise under bubbling nitrogen. The mixture was left stirring for 40 min giving a brown solution. This was quenched with methanol (30 mL), poured into water, extracted into chloroform, dried over magnesium sulfate and solvent evaporated.

**Dehydrogenation of 22** – Addition of methanol (5 mL) gave an insoluble red polymer (29 mg) which could not be characterised due to its insolubility.

**Dehydrogenation of 26 – (29)**

![Dehydrogenation of 26 (29)](image)

Purified via silica preparative plate using dichloromethane: hexane (1: 4) as eluent. **Yield**: 27 mg, 0.018 mmol, 55%. **Melting Point**: > 330°C. **1H-NMR** (600 MHz, CDCl\textsubscript{3}, 25°C, TMS) δ: 7.44 (d, \textsuperscript{3}J\textsubscript{H-H} = 5.5 Hz, 2H, H\textsubscript{4}), 7.41 (s, 2H, H\textsubscript{4'}), 7.35 (d, \textsuperscript{3}J\textsubscript{H-H} = 7.7 Hz, 4H, H\textsubscript{Ar}), 7.32 (d, \textsuperscript{3}J\textsubscript{H-H} = 5.2 Hz, 2H, H\textsubscript{5}), 7.27 (m-with CHCl\textsubscript{3}. peak, 4H, H\textsubscript{Ar}), 7.21 (d, \textsuperscript{3}J\textsubscript{H-H} = 7.9 Hz, 4H, H\textsubscript{Ar}), 7.18 (d, \textsuperscript{3}J\textsubscript{H-H} = 8.0 Hz, 4H, H\textsubscript{Ar}), 6.83 (d, \textsuperscript{3}J\textsubscript{H-H} = 7.9 Hz, 4H,
H$_{Ar}$), 6.81 (d, $^3J_{H-H} = 8.1$ Hz, 4H, H$_{Ar}$), 6.76 (d, $^3J_{H-H} = 8.1$ Hz, 4H, H$_{Ar}$), 6.71 (d, $^3J_{H-H} = 8.1$ Hz, 4H, H$_{Ar}$), 1.42 (s, 18H, CMe$_3$), 1.32 (s, 18H, CMe$_3$), 1.08 (s, 36H, 2*CMe$_3$).

$^{13}$C($^1$H)-NMR (150.9 MHz, CDCl$_3$, 25°C, TMS) $\delta$: 150.9 (C$_{quat}$), 150.8 (C$_{quat}$), 147.4 (C$_{quat}$), 147.3 (C$_{quat}$), 140.3 (C$_{quat}$), 140.0 (C$_{quat}$), 138.3 (C$_{quat}$), 137.4 (C$_{quat}$), 137.2 (C$_{quat}$), 136.8 (C$_{quat}$), 136.7 (C$_{quat}$), 135.7 (C$_{quat}$), 135.2 (C$_{quat}$), 134.9 (C$_{quat}$), 134.2 (C$_{quat}$), 131.9 (C$_{Ar}$), 131.8 (C$_{Ar}$), 130.7 (C$_{Ar}$), 130.6 (C$_{Ar}$), 127.7 (C$_5$), 126.5 (C$_{quat}$), 126.0 (C$_{quat}$), 125.7 (C$_{Ar}$), 125.0 (C$_{Ar}$), 124.7 (C$_{quat}$), 122.7 (C$_{Ar}$), 122.6 (C$_{Ar}$), 120.4 (C$_4$), 118.1 (C$_4$), 117.2 (C$_{quat}$), 34.5 (CMe$_3$), 34.4 (CMe$_3$), 33.9 (CMe$_3$), 33.8 (CMe$_3$), 31.5 (CH$_3$), 31.3 (CH$_3$), 31.0 (2*CH$_3$). MALDI-MS: (Chloroform) m/z 1534.7516 ([M]$^+$) (calc. 1534.7490).

Dehydrogenation of 27 – (30)

Purified via silica preparative plate using dichloromethane: hexane (1: 4) as eluent. **Yield:** 30 mg, 0.20 mmol, 60%. **Melting Point:** > 330°C. $^1$H-NMR (600 MHz, CDCl$_3$, 25°C, TMS) $\delta$: 7.34 (d, 4H, $^3J_{H-H} = 5.2$ Hz, H$_{Ar}$), 7.22 (d, 4H, $^3J_{H-H} = 5.3$ Hz, H$_{Ar}$), 7.11 (d, 4H, $^3J_{H-H} = 5.3$ Hz, H$_{Ar}$), 7.08 (d, 4H, $^3J_{H-H} = 5.3$ Hz, H$_{Ar}$), 6.96 (d, 2H, $^3J_{H-H} = 3.8$ Hz, H$_5$), 6.83 (m, 8H, 2*H$_{Ar}$), 6.67 (m, 8H, 2*H$_{Ar}$), 6.38 (s, 2H, 30a-H$_{4'}$, 30b-H$_{2'}$), 6.31 (d, 2H, $^3J_{H-H} = 3.8$ Hz, H$_5$), 1.44 (s, 18H, CMe$_3$), 1.32 (s, 18H, CMe$_3$), 1.11 (s, 18H, CMe$_3$), 1.10 (s, 18H, CMe$_3$). $^{13}$C($^1$H)-NMR (150.9 MHz, CDCl$_3$, 25°C, TMS) $\delta$: 149.6 (C$_{quat}$), 149.4 (C$_{quat}$), 147.3 (C$_{quat}$), 147.2 (C$_{quat}$), 140.0 (C$_{quat}$), 139.9 (C$_{quat}$), 139.7 (C$_{quat}$), 137.8 (C$_{quat}$), 137.7 (C$_{quat}$), 137.6 (C$_{quat}$), 137.5 (C$_{quat}$), 134.3 (C$_{quat}$), 134.2 (C$_{quat}$), 133.6 (C$_{quat}$), 132.3 (C$_{quat}$), 130.8 (C$_{Ar}$), 130.7 (C$_{Ar}$), 130.6 (C$_{Ar}$), 129.9 (C$_{Ar}$), 128.1 (C$_5$), 127.4 (C$_{quat}$), 127.3 (C$_{quat}$), 127.0 (C$_{quat}$), 126.8 (C$_{quat}$), 125.1 (30a-C$_4'$, 30b-C$_2'$), 124.8 (C$_{Ar}$), 124.6 (C$_{Ar}$), 122.7 (2*C$_{Ar}$), 120.7 (C$_4$), 34.7 (CMe$_3$), 34.4 (CMe$_3$), 34.0 (CMe$_3$), 31.9 (CMe$_3$), 31.7 (CH$_3$), 31.4 (CH$_3$), 31.2 (CH$_3$), 29.7 (CH$_3$). **IR (KBr) cm$^{-1}$:** 3414, 2963, 1638, 1462,
1363, 1261, 1096, 1022, 801, 610. **MALDI-MS:** (Acetonitrile) m/z 1534.7457 ([M]⁺) (calc. 1534.7409).

**Dehydrogenation of 28 – (31)**

Purified via silica preparative plate using dichloromethane: hexane (1: 4) as eluent. **Yield:** 26 mg, 0.017 mmol, 52%. **Melting Point:** > 330°C. **1H-NMR** (600 MHz, [d₂]1,2-dichloroethane, 25°C, TMS) δ: 7.33 (m, 6H, H_Ar and H₄), 7.27 (m, 4H, H_Ar), 7.22 - 7.16 (m, 10H, 2*H_Ar and H₅), 6.82 (m, 8H, 2*H_Ar), 6.70 (m, 8H, 2*H_Ar), 6.44 (s, 2H, 31a-H₄, 31b-H₂), 1.40 (s, 18H, CMe₃), 1.33 (s, 18H, CMe₃), 1.11 (s, 18H, CMe₃), 1.10 (s, 18H, CMe₃). **13C{¹H}-NMR** (150.9 MHz, CDCl₃, 25°C, TMS) δ: 150.8 (C_quat), 149.4 (C_quat), 147.3 (C_quat), 140.2 (C_quat), 140.0 (C_quat), 138.0 (C_quat), 137.7 (C_quat), 137.5 (C_quat), 137.4 (C_quat), 137.2 (C_quat), 136.9 (C_quat), 135.4 (C_quat), 134.9 (C_quat), 134.2 (C_quat), 132.8 (C_quat), 132.6 (C_quat), 131.9 (C₅), 130.8 (C_Ar), 130.6 (2*C_Ar), 128.9 (C_quat), 128.2 (31a-C₄, 31b-C₂), 126.7 (C_quat), 126.0 (C_quat), 125.1 (C_Ar), 124.9 (C_Ar), 124.7 (C_Ar), 122.7 (C_Ar), 122.6 (C_Ar), 120.2 (C₄), 34.5 (CMe₃), 34.4 (CMe₃), 33.9 (2*CMe₃), 31.4 (CH₃), 31.3 (CH₃), 31.0 (2*CH₃). **IR (KBr)** cm⁻¹: 3414, 2963, 1638, 1462, 1363, 1261, 1096, 1022, 801, 610. **MALDI-MS:** (Acetonitrile) m/z 1534.7480 ([M]⁺) (calc. 1534.7490).

**bis(5-methyl-2-thienyl)acetylene (32)**
Reaction was carried out in the dark. To 2-bromo-5-methylthiophene (1.14 mL, 10 mmol), 2-methyl-3-butyn-2-ol (1.0 mL, 10 mmol), benzyltriethylammonium chloride (71 mg, 0.31 mmol), copper(I) iodide (100 mg, 0.53 mmol) and tetrakis(triphenylphosphine)palladium(0) (200 mg, 0.17 mmol) in benzene (10 mL), was added a 5.5 N solution of aqueous sodium hydroxide (8 mL) and the mixture was left stirring for 3 days. Then 2-bromo-5-methylthiophene (1.14 mL, 10 mmol) in benzene (8.0 mL, 44 mmol) was added and the solution was heated to 80°C and left stirring at this temperature for a further three days. It was cooled to room temperature and a solution of saturated aqueous ammonium chloride (40 mL) was added and stirred for 1 hour. The phases were separated and the aqueous layer was extracted with toluene. The organic phases were dried with magnesium sulfate and evaporated. The product was purified by column chromatography using 6: 1 hexane: dichloromethane as eluent to give the desired product ($R_f = 0.5$) as a yellow solid. This compound is light sensitive and had to be stored in the dark. **Yield:** 0.92 g, 4.21 mmol, 42%. **Melting Point:** 55-56°C. $^1$H-NMR (400 MHz, CDCl$_3$, 25°C, TMS) $\delta$: 7.07 (d, 2H, $^3J_{H-H} = 3.5$ Hz, H$_3$), 6.67 (qd, 2H, $^4J_{H-H} = 1.0$ Hz and $^3J_{H-H} = 3.8$ Hz, H$_4$), 2.50 (d, 6H, $^4J_{H-H} = 0.8$ Hz, H$_6$). $^{13}$C$^1$H-NMR (100 MHz, CDCl$_3$, 25°C, TMS) $\delta$: 142.3 (C$_{2/5}$), 132.2 (C$_3$), 125.4 (C$_4$), 120.7 (C$_{2/5}$), 85.8 (C$_1$), 15.5 (C$_6$). **IR (neat) cm$^{-1}$:** 2195, 2190 ($\equiv$C), 1487, 1439, 1200, 1159, 1044, 804, 789, 720. **EI-MS:** (Acetonitrile) m/z 218.0225 ([M]$^+$) (calc. 218.0224).

**1,2-di(5-methyl-2-thienyl)-3,4,5,6-tetra-(4-tert-butylphenyl)benzene (33)**

![Structure of 1,2-di(5-methyl-2-thienyl)-3,4,5,6-tetra-(4-tert-butylphenyl)benzene (33)](image)

Bis(5-methyl-2-thienyl)acetylene (32) (65.8 mg, 0.32 mmol), 2,3,4,5-tetrakis-(4-tert-butylphenyl)cyclopentadienone (150 mg, 0.25 mmol) (25) and benzophenone (0.5 g) were heated at 300°C for 90 minutes while attached to an air condenser giving a brown mixture. After cooling to room temperature the product was purified by column
chromatography using 9:1 hexane: diethyl ether as eluent to give the product ($R_f = 0.6$) as a white solid, which was recrystallised from chloroform and methanol (2 mL of each). **Yield:** 82 mg, 0.10 mmol, 41%. **Melting Point:** 245-246°C. \[^1^H\text{-NMR}\] (400 MHz, CDCl\textsubscript{3}, 25°C, TMS) δ: 6.92 (d, 4H, $^3$J\textsubscript{H-H} = 8.3 Hz, H\textsubscript{9/10/16/17}), 6.80 (m, 4H, H\textsubscript{9/10/16/17} and H\textsubscript{9/10/16/17}), 6.62 (d, 4H, $^3$J\textsubscript{H-H} = 8.6 Hz, H\textsubscript{9/10/16/17}), 6.27 (m, 4H, H\textsubscript{3} and H\textsubscript{4}), 2.26 (s, 6H, H\textsubscript{6}), 1.16 (s, 18H, H\textsubscript{13/20}), 1.10 (s, 18H, H\textsubscript{13/20}). \[^{13}\text{C}\{^1^H\}\text{-NMR}\] (100 MHz, CDCl\textsubscript{3}, 25°C, TMS) δ: 147.9 (C\textsubscript{11/18}), 147.5 (C\textsubscript{11/18}), 141.7 (C\textsubscript{quat}), 141.6 (C\textsubscript{quat}), 139.8 (C\textsubscript{quat}), 139.7 (C\textsubscript{quat}), 137.8 (C\textsubscript{quat}), 137.6 (C\textsubscript{quat}), 134.2 (C\textsubscript{quat}), 130.8 (C\textsubscript{9/10/16/17}), 130.5 (C\textsubscript{9/10/16/17}), 128.8 (C\textsubscript{3/4}), 123.7 (C\textsubscript{3/4}), 123.3 (C\textsubscript{9/10/16/17}), 123.0 (C\textsubscript{9/10/16/17}), 34.2 (C\textsubscript{12/19}), 34.0 (C\textsubscript{12/19}), 31.3 (C\textsubscript{13/20}), 31.2 (C\textsubscript{13/20}), 15.2 (C\textsubscript{6}). \[^{13}\text{C}\{^1^H\}\text{-NMR}\] (100 MHz, CDCl\textsubscript{3}, 25°C, TMS) δ: 147.9 (C\textsubscript{11/18}), 147.5 (C\textsubscript{11/18}), 141.7 (C\textsubscript{quat}), 141.6 (C\textsubscript{quat}), 139.8 (C\textsubscript{quat}), 139.7 (C\textsubscript{quat}), 137.8 (C\textsubscript{quat}), 137.6 (C\textsubscript{quat}), 134.2 (C\textsubscript{quat}), 130.8 (C\textsubscript{9/10/16/17}), 130.5 (C\textsubscript{9/10/16/17}), 128.8 (C\textsubscript{3/4}), 123.7 (C\textsubscript{3/4}), 123.3 (C\textsubscript{9/10/16/17}), 123.0 (C\textsubscript{9/10/16/17}), 34.2 (C\textsubscript{12/19}), 34.0 (C\textsubscript{12/19}), 31.3 (C\textsubscript{13/20}), 31.2 (C\textsubscript{13/20}), 15.2 (C\textsubscript{6}). **IR (neat)** cm\textsuperscript{-1}: 2960, 1511, 1460, 1391, 1361, 1269, 1118, 1019, 830, 797, 571. **ESI-MS:** (Acetone) m/z 821.4197 ([M+Na]\textsuperscript{+}) (calc. 821.4191).

**Dehydrogenation of 33 – (34)**

![Diagram](image)

1,2-di(5-methyl-2-thienyl)-3,4,5,6-tetra-(4-tert-butylphenyl)benzene (33) (40 mg, 0.05 mmol) was dissolved in dry dichloromethane (20 mL) and an excess of iron trichloride (0.16 g, 1.0 mmol, 20 eq.) in nitromethane (3 mL) was added dropwise under bubbling nitrogen. The solution was left stirring for 30 min giving a brown solution. This was quenched with methanol (30 mL) poured into water, extracted into chloroform, dried over magnesium sulfate and solvent was evaporated. The residue was purified by column chromatography with dichloromethane: hexane (1:3) as the eluent to give the product ($R_f = 0.6$) as a yellow solid. **Yield:** 36 mg, 0.045 mmol, 90%. **Melting Point:** > 330°C. \[^1^H\text{-NMR}\] (400 MHz, CDCl\textsubscript{3}, 25°C, TMS) δ: 7.18 (d, 4H, $^3$J\textsubscript{H-H} = 6.5 Hz, H\textsubscript{Ar}), 7.16 (s, 2H, H\textsubscript{4}), 7.09 (d, 4H, $^3$J\textsubscript{H-H} = 8.0 Hz, H\textsubscript{Ar}), 6.72 (d, 4H, $^3$J\textsubscript{H-H} = 8.0 Hz, H\textsubscript{Ar}), 6.63 (d, 4H, $^3$J\textsubscript{H-H} = 8.5 Hz, H\textsubscript{Ar}), 2.36 (s, 6H, H\textsubscript{6}), 1.24 (s, 18H, CH\textsubscript{3}), 1.00 (s, 18H, CH\textsubscript{3}). \[^{13}\text{C}\{^1^H\}\text{-NMR}\]
(100 MHz, CDCl$_3$, 25°C, TMS) δ: 150.3 (C$_{quat}$), 146.8 (C$_{quat}$), 141.2 (C$_{quat}$), 139.1 (C$_{quat}$), 137.3 (C$_{quat}$), 136.8 (C$_{quat}$), 136.5 (C$_{quat}$), 134.6 (C$_{quat}$), 133.8 (C$_{quat}$), 131.5 (C$_{Ar}$), 130.4 (C$_{Ar}$), 125.1 (C$_{quat}$), 124.4 (C$_{Ar}$), 122.3 (C$_{Ar}$), 118.7 (C$_4$), 34.1 (CMe$_3$), 33.6 (CMe$_3$), 31.0 (C(CH$_3$)$_3$), 30.7 (C(CH$_3$)$_3$) 15.0 (C$_6$). IR (neat) cm$^{-1}$: 2957, 1520, 1388, 1361, 853, 789, 696. MALDI-MS: (Acetonitrile) m/z 796.4168 ([M]$^+$) (calc. 796.4136).

### 4-bromo-2-methylthiophene (35)$^{16-17}$

![4-bromo-2-methylthiophene](image)

A solution of 0.82 M lithium diisopropylamine (20 mL, 16.4 mmol) was added to 2-bromo-5-methylthiophene (2 mL, 1.29 g, 0.73 mmol) in tetrahydrofuran (15 mL) at -78°C, dropwise while being stirred over 2 hours. The solution was then quenched with methanol (20 mL), saturated aqueous ammonium chloride (20 mL) was added and the solution extracted with diethyl ether to give a brown solution which was washed with water (40 mL) and then with brine (40 mL). This was purified by column chromatography using hexane as the eluent to give the desired product ($R_f = 0.8$) as a clear solution. Yield: 1.04 g, 0.60 mmol, 82%. $^1$H-NMR (400 MHz, CDCl$_3$, 25°C, TMS) δ: 7.01 (d, 1H, $^4$J$_{H-H} = 1.0$ Hz, H$_5$), 6.71 (d, 1H, $^4$J$_{H-H} = 1.0$ Hz, H$_3$), 2.51 (s, 3H, H$_6$). $^{13}$C($^1$H)-NMR (100 MHz, CDCl$_3$, 25°C, TMS) δ: 141.1 (C$_2$), 127.8 (C$_{3/5}$), 120.3 (C$_{3/5}$), 108.9 (C$_4$), 15.3 (C$_6$).

### 3-(bis(5-methyl-3-thienyl)methylene)-2-methyl-5-(5-methyl-3-thienyl)pent-4-yn-2-ol (37)

![3-(bis(5-methyl-3-thienyl)methylene)-2-methyl-5-(5-methyl-3-thienyl)pent-4-yn-2-ol](image)
In the dark 3-bromo-5-methylthiophene (35) (2.25 mL, 6.9 mmol), 2-methyl-3-butyln-2-ol (0.7 mL, 7 mmol), benzyltriethylammonium chloride (24.4 mg, 0.11 mmol), copper (I) iodide (34.9 mg, 0.18 mmol) and tetrakis(triphenylphosphine) palladium (0) (66.4 mg, 0.058 mmol) were dissolved in benzene (10 mL). Then a 5.5 N solution of aqueous sodium hydroxide (5.5 mL, 0.03 mmol) was added and the mixture was left stirring for 3 days. Then 3-bromo-5-methylthiophene (35) (2.25 mL, 6.9 mmol) in benzene (8.0 mL) was added and the solution was heated to 80°C and left stirring at this temperature for a further 3 days. It was cooled to room temperature and a solution of saturated ammonium chloride (40 mL) was added and the solution stirred for 1 hour. The phases were separated and the aqueous layer was extracted with toluene. The organic phases were dried with magnesium sulfate and evaporated. The product was purified by column chromatography using dichloromethane as eluent, to give the product (R_f = 0.5) as a yellow solid. **Yield:** 0.95 g, 2.39 mmol, 52%. 

**7.4 Photochemistry and electrochemistry of mono- and di-thienyl polyphenylenes**

1-(3-thienyl)-2,3,4,5,6-penta(4-tert-butylphenyl)benzene (38)

(4-tert-butylphenyl)(3-thienyl)acetylene (2) (76 mg, 0.32 mmol), 2,3,4,5-tetrakis-(4-tert-butylphenyl) cyclopentadienone (25) (150 mg, 0.25 mmol) and benzophenone (0.5 g) were heated for 90 minutes at 300°C while attached to an air condenser, giving a brown mixture. After cooling to room temperature the residue was crystallised from dichloromethane and methanol (2 mL) to give the product as a white solid. **Yield:** 182
mg, 0.22 mmol, 87%. **Melting Point:** 320-321°C. $^1$H-NMR (400 MHz, CDCl$_3$, 25°C, TMS) δ: 6.90 (d, 4H, $^3$J$_{H-H}$ = 8.5 Hz, H$_7$), 6.83 (d, 4H, $^3$J$_{H-H}$ = 8.5 Hz, H$_{11}$), 6.82 (d, 4H, $^3$J$_{H-H}$ = 8.5 Hz, H$_9$), 6.77 (m, 5H, H$_5$ and H$_6$), 6.69 (d, 4H, $^3$J$_{H-H}$ = 8.5 Hz, H$_{10}$), 6.68 (d, 4H, $^3$J$_{H-H}$ = 8.5 Hz, H$_8$), 6.50 (dd, 1H, $^4$J$_{H-H}$ = 1.0 and 3.0 Hz, H$_2$), 6.47 (dd, 1H, $^4$J$_{H-H}$ = 1.0 Hz and $^3$J$_{H-H}$ = 5.0 Hz, H$_4$), 1.20 (m, 27H, H$_{13}$ and H$_{14}$), 1.16 (s, 18H, H$_{12}$).

$^{13}$C{$^1$H}-NMR (100 MHz, CDCl$_3$, 25°C, TMS) δ: 147.3 (C$_{quat}$), 147.0 (C$_{quat}$), 146.9 (C$_{quat}$), 140.4 (C$_{quat}$), 140.2 (C$_{quat}$), 140.2 (C$_{quat}$), 140.1 (C$_{quat}$), 137.5 (C$_{quat}$), 137.4 (C$_{quat}$), 134.5 (C$_{quat}$), 130.6 (C$_{Th/quat}$ and 2*C$_{Ar}$), 130.3 (C$_{Th}$), 130.2 (C$_{Ar}$), 124.2 (C$_{Th}$), 122.9 (C$_{Ar}$), 122.6 (C$_{Ar}$), 122.5 (C$_{Ar}$), 121.6 (C$_{Th}$), 33.7 (CMe$_3$), 33.6 (2*CMe$_3$), 30.8 (2*CH$_3$), 30.7 (CH$_3$). **IR (neat)** cm$^{-1}$: 2960, 1509, 1460, 1361, 1269, 830, 764. ESI-MS: (Acetonitrile) m/z 859.4684 ([M+K]$^+$) (calc. 859.4679).

**Dehydrogenation of 38 – (39) and (40)**

To a solution of 1-(3-thienyl)-2,3,4,5,6-penta(4-tert-butylphenyl)benzene (38) (150 mg, 0.182 mmol) in dichloromethane (60 mL) iron trichloride (710 mg, 4.35 mmol, 24 eq.) in nitromethane (3 mL) was added dropwise while nitrogen was bubbled through the solution. The solution was stirred for 5 hours and then quenched with methanol (30 mL). Solvent was reduced to 10 mL and a yellow solid was filtered off. This was purified using column chromatography with hexane: dichloromethane (1: 1) as the eluent to give two products.

(39) $R_f$ = 0.7 **Yield:** 14.2 mg, 0.018 mmol, 28%. **Melting Point:** > 330°C. $^1$H-NMR (600 MHz, CDCl$_3$, 25°C, TMS) δ: 9.33 (s, 1H, H$_{Ar}$), 9.28 (m, 2H, 2*H$_{Ar}$), 9.25 (s, 1H, H$_{Ar}$), 9.22 (s, 1H, H$_{Ar}$), 9.18 (s, 1H, H$_{Ar}$), 9.16 (s, 1H, H$_{Ar}$), 9.09 (s, 1H, H$_{Ar}$), 9.03 (s, 1H, H$_{Ar}$), 8.93 (s, 1H, H$_{Ar}$), 8.21 (s, 1H, H$_{Th}$), 1.89 (s, 9H, CMe$_3$), 1.86 (s, 18H, 2*CMe$_3$), 1.76 (s, 9H, CMe$_3$), 1.72 (s, 9H, CMe$_3$). $^{13}$C{$^1$H}-NMR (150.9 MHz, CDCl$_3$, 25 C, TMS) δ:
149.2 (C_{quat}), 148.9 (C_{quat}), 148.6 (2*C_{quat}), 148.5 (C_{quat}), 148.4 (C_{quat}), 132.1 (C_{quat}), 130.8 (C_{quat}), 130.3 (C_{quat}), 130.2 (3*C_{quat}), 130.1 (4*C_{quat}), 127.9 (C_{quat}), 127.4 (C_{quat}), 127.2 (C_{quat}), 125.4 (C_{quat}), 124.4 (C_{quat}), 123.8 (C_{quat}), 123.7 (C_{quat}), 123.2 (C_{quat}), 122.4 (C_{quat}), 121.4 (C_{Ar}), 120.0 (C_{quat}), 119.4 (C_{quat}), 119.0 (2*C_{Ar}), 118.9 (2*C_{Ar}), 118.8 (C_{Ar}), 118.7 (3*C_{Ar}), 118.3 (C_{Th}), 118.2 (C_{quat}), 118.1 (C_{quat}), 117.7 (C_{Ar}), 35.6 (3*CMe_{3}), 35.4 (2*CMe_{3}), 32.2 (2*CH_{3}), 32.1 (CH_{3}), 32.0 (CH_{3}), 31.9 (CH_{3}). IR (neat) cm\(^{-1}\): 2954, 1604, 1574, 1461, 1362, 1260, 169, 763, 750.

(40) R\(_f\) = 0.4 Yield: 14.9 mg, 0.009 mmol, 28%. Melting Point: > 330°C. \(^1\)H-NMR (600 MHz, CDCl\(_3\), 25°C, TMS) \(\delta\): 9.43 (s, 2H, H_{Ar}), 9.41 (s, 2H, H_{Ar}), 9.38 (s, 4H, 2*H_{Ar}), 9.35 (s, 2H, H_{Ar}), 9.31 (s, 2H, H_{Ar}), 9.12 (s, 2H, H_{Ar}), 8.87 (s, 2H, H_{Ar}), 8.86 (s, 2H, H_{Ar}), 8.75 (s, 2H, H_{Ar}), 1.89 (m, 36H, 2*CMe_{3}), 1.80 (m, 36H, 2*CMe_{3}), 0.58 (s, 18H, CMe_{3}). \(^{13}\)C\((^1\)H\)-NMR (150.9 MHz, CDCl\(_3\), 25°C, TMS) \(\delta\): 149.7 (C_{quat}), 149.5 (C_{quat}), 149.0 (C_{quat}), 148.8 (C_{quat}), 148.7 (C_{quat}), 135.4 (C_{quat}), 134.1 (C_{quat}), 132.0 (C_{quat}), 131.2 (C_{quat}), 130.5 (3*C_{quat}), 130.4 (C_{quat}), 130.3 (3*C_{quat}), 130.2 (C_{quat}), 129.1 (C_{quat}), 128.9 (C_{quat}), 128.2 (C_{quat}), 128.1 (C_{quat}), 127.9 (C_{quat}), 125.2 (C_{quat}), 124.9 (C_{quat}), 124.1 (2*C_{quat}), 123.5 (C_{quat}), 123.2 (C_{quat}), 122.2 (C_{Ar}), 123.5 (C_{quat}), 119.9 (C_{quat}), 119.5 (C_{Ar}), 119.2 (C_{Ar}), 119.1 (C_{Ar}), 119.0 (C_{Ar}), 118.9 (C_{Ar}), 118.7 (C_{Ar}), 118.6 (C_{Ar}), 118.5 (C_{Ar}), 118.2 (C_{Ar}), 35.7 (2*CMe_{3}), 35.5 (CMe_{3}), 35.5 (CMe_{3}), 34.6 (CH_{3}), 32.0 (2*CH_{3}), 31.9 (CH_{3}), 30.4 (CH_{3}). IR (neat) cm\(^{-1}\): 2953, 1604, 1575, 1476, 1471, 1362, 1258, 866, 761.

MALDI-MS: (Acetonitrile) m/z 1614.8081 ([M]+) (calc.1614.8049).

7.5 Synthesis, reactivity and electrochemistry of multi-thiophene systems

Hexa(2-thienyl)benzene (42)
Part 7: Experimental.

Bis(2-thienyl)acetylene (18) (0.20 g, 0.83 mmol) was dissolved in dioxane (20 ml). To this dicobalt octacarbonyl (58 mg, 0.17 mmol) was added and the mixture was refluxed at 115°C for 24 hours. The mixture was cooled to room temperature and solvent was removed to give a brown solid. The product was purified by column chromatography using hexane: diethyl ether 9:1 as eluent to give the product as a white solid. **Yield:** 37 mg, 0.083 mmol, 30%. **Melting Point:** > 330°C. $^1$H-NMR (400 MHz, CDCl$_3$, 25°C, TMS) $\delta$: 7.11 (dd, 6H, $^4$J$_{H-H}$ = 1.0 Hz and $^3$J$_{H-H}$ = 5.0 Hz, H$_5$), 6.70 (dd, 6H, $^3$J$_{H-H}$ = 3.5 Hz, H$_3$), 6.61 (dd, 6H, $^4$J$_{H-H}$ = 1.0 Hz and $^3$J$_{H-H}$ = 3.5 Hz, H$_3$). $^{13}$C{$^1$H}-NMR (100 MHz, CDCl$_3$, 25°C, TMS) $\delta$: 141.9 (C$_1$), 133.7 (C$_2$), 128.7 (C$_3$), 125.8 (C$_4$), 125.3 (C$_5$). IR (neat) cm$^{-1}$: 3100, 2935, 1583, 1451, 1424, 1382, 1267, 1220, 1195, 1157, 1069, 1036, 840, 826, 776. **ESI-MS:** (Acetonitrile) m/z 570.9829 ([M+H]$^+$) (calc. 570.9811).

**Hexa(3-thienyl)benzene (43)**

Bis(3-thienyl)acetylene (19) (0.285 g, 1.50 mmol) was dissolved in dioxane (20 ml). To this dicobalt octacarbonyl (78.6 mg, 0.23 mmol) was added and the mixture was refluxed at 115°C for 3 hours. The mixture was cooled to room temperature and solvent was removed to give a brown solid. This was recrystallised from dichloromethane and methanol (2 ml of each) to give a white precipitate. **Yield:** 205 mg, 0.36 mmol, 72%. **Melting Point:** > 330°C. $^1$H-NMR (400 MHz, CDCl$_3$, 25°C, TMS) $\delta$: 6.94 (dd, 6H, $^4$J$_{H-H}$ = 3.0 Hz and $^3$J$_{H-H}$ = 5.0 Hz, H$_4$), 6.60 (dd, 6H, $^4$J$_{H-H}$ = 1.0 Hz and 3.0 Hz, H$_2$), 6.52 (dd, 6H, $^4$J$_{H-H}$ = 1.5 Hz and $^3$J$_{H-H}$ = 5.0 Hz, H$_3$). $^{13}$C{$^1$H}-NMR (100 MHz, CDCl$_3$, 25°C, TMS) $\delta$: 140.3 (C$_1$), 136.5 (C$_3$), 129.7 (C$_5$), 124.1 (C$_2$), 123.3 (C$_4$). IR (neat) cm$^{-1}$: 1432, 1336, 921, 863, 829, 773, 734, 667. **ESI-MS:** (Acetonitrile) m/z 570.9827 ([M+H]$^+$) (calc. 570.9811).
Hexa(5-methyl-2-thienyl)benzene (44)

Bis(5-methyl-2-thienyl)acetylene (32) (0.12 g, 0.53 mmol) was dissolved in dioxane (10 mL). To this dicobalt octacarbonyl (25 mg, 0.082 mmol, 0.15 eq.) was added and the mixture was refluxed at 115°C for 24 hours. The mixture was cooled to room temperature quenched by addition of methanol (10 mL) and filtered, then solvent was removed to give a brown solid. The product was purified by column chromatography using dichloromethane: hexane (1: 1) as the eluent to give the product (Rf = 0.7) as a brown solid. Yield: 205 mg, 0.31 mmol, 59%. Melting Point: > 330°C. 1H-NMR (400 MHz, CDCl3, 25°C, TMS) δ: 6.36 (m, 12H, H3 and H4), 2.33 (s, 18H, H6). 13C{1H}-NMR (100 MHz, CDCl3, 25°C, TMS) δ: 139.8 (C1), 138.4 (C5), 136.5 (C2), 128.3 (C3), 123.4 (C4), 14.8 (C6). IR (neat) cm⁻¹: 1143, 1218, 1162, 919, 798. ESI-MS: (Chloroform) m/z 677.0579 ([M+Na]⁺) (calc. 677.0570).

1,3,5–tri(2-thienyl)-2,4,6-tri(3-thienyl)benzene/1,3,4–tri(2-thienyl)-2,5,6-tri(3-thienyl)benzene (45)

2-thienyl-3-thienyl acetylene (21) (0.1 g, 0.53 mmol) was dissolved in dioxane (10 mL). To this dicobalt octacarbonyl (28 mg, 0.082 mmol) was added and the mixture was refluxed at 115°C for 3 hours. The mixture was cooled to room temperature and solvent
was removed to give a brown solid. This was recrystallised from dichloromethane: methanol (2 mL of each) to give a white precipitate. The product was purified by column chromatography using 6:1 hexane: dichloromethane as eluent to give the product ($R_f = 0.7$) as a white solid. **Yield:** 73 mg, 0.13 mmol, 72%. **Melting Point:** $>330^\circ$C. **$^1$H and $^{13}$C-NMR** data of 42 is discussed in the main text. **IR (neat) cm$^{-1}$:** 3099, 2922, 1669, 1543, 1414, 1358, 1222, 1075, 1038, 937, 835, 778. **MALDI-MS:** (Acetonitrile) m/z 569.9721 ([M]$^+$(calculated 569.9733)).

**Cyclodehydrogenation of hexa-thienyl polyphenylenes**

The relevant hexa-thienyl benzene 42, 43 and 44 (0.065 mmol) was dissolved in dry dichloromethane (20 mL) and an excess of iron trichloride (38 mg, 0.28 mmol, 5 eq.) in nitromethane (3 mL) was added dropwise under bubbling nitrogen. The mixture was left stirring for 40 min giving a dark solution. This was quenched with methanol (30 mL), and filtered to give a dark solid.

**Dehydrogenation of 42** – Addition of methanol (5 mL) gave an insoluble purple polymer (29 mg) which could not be characterised due to its insolvability.

**Dehydrogenation of 43** – Addition of methanol (5 mL) gave an insoluble brown polymer (26 mg) which could not be characterised due to its insolvency.

**Dehydrogenation of 44** – Addition of methanol (5 mL) gave an insoluble red polymer (32 mg) which could not be characterised due to its insolvency.

**1,2-di(3-thienyl)-ethane-1,2-dione (47)**
Bis(3-thienyl)acetylene (19) (450 mg, 2.36 mmol) was dissolved in acetone (50 mL). To this sodium hydrogen carbonate (70 mg) and magnesium sulfate (700 mg) in water (15 mL) were added. Then potassium permanganate (860 mg, 5.44 mmol) was added and the mixture was stirred for 16 hours, then sodium nitrite (360 mg, 5.22 mmol) and 10% aqueous hydrochloric acid (12 mL) were added to oxidise the manganese. The acetone was evaporated off and the aqueous layer was extracted with diethyl ether, washed with aqueous sodium hydroxide (0.1 M, 30 mL), dried over magnesium sulfate and evaporated to give a yellow oil. The oil was purified by column chromatography using dichloromethane as the eluent to give the product (R_f = 0.8) as a yellow solid. **Yield:** 280 mg, 1.26 mmol, 53%. **Melting Point:** 65-66°C. **^1H-NMR** (400 MHz, CDCl₃, 25°C, TMS) δ: 8.37 (dd, 2H, J_H-H = 1.5 and 3.0 Hz, H₂), 7.72 (dd, 2H, J_H-H = 1.0 Hz and J_H-H = 5.5 Hz, H₄), 7.41 (dd, 2H, J_H-H = 3.0 Hz and J_H-H = 5.0 Hz, H₅). **^13C{^1H}-NMR** (100 MHz, CDCl₃, 25°C, TMS) δ: 185.3 (C₁), 137.2 (C₃), 137.0 (C₂), 127.1 (C₄), 126.5 (C₅). **IR (neat) cm⁻¹:** 1647 (C=O), 1500, 1393, 1227, 1205, 1161, 1105, 1075, 958, 876, 824, 87, 700. **ESI-MS:** (Acetonitrile) m/z 222.9889 ([M+H]+) (calc.222.9887).

1,3-bis(3,5-dimethoxybenzyl)propane-2-one (48)

Calcium hydroxide (1.62 g, 2.2 mmol) and tetrabutylammonium hydrogensulfate (0.94 g, 2.76 mmol) were dissolved in a 1:1 mixture of dichloromethane and water (160 mL). To this 3,5-dimethoxybenzyl bromide (2.0 g, 8.6 mmol) and iron pentacarbonyl (0.75 mL, 5.69 mmol) were added and the solution was stirred under a stream of argon for 16 hours. The reaction mixture was oxidised by a stream of bubbling air for 30 min and then 10% aqueous hydrochloric acid was added (50 mL). The organic layer was extracted into dichloromethane, dried over magnesium sulfate and evaporated. The product was recrystallised from methanol to give a brown solid. **Yield:** 0.95 g, 2.86 mmol, 67%. **Melting Point:** 101-102°C. **^1H-NMR** (400 MHz, CDCl₃, 25°C, TMS) δ: 6.39 (t, 2H, J_H-
$H = 2.0 \text{ Hz, } H_6, 6.32 \text{ (d, } 4H, \; ^4J_{H-H} = 2.0 \text{ Hz, } H_4), 3.78 \text{ (s, } 12H, \; H_7), 3.66 \text{ (s, } 4H, \; H_2).$

$^{13}C\{^1H\text{-}NMR \text{ (100 MHz, CDCl}_3, 25^\circ\text{C, TMS): } \delta: 205.0 \text{ (C}_1), 160.5 \text{ (C}_5), 135.7 \text{ (C}_3), 107.1 \text{ (C}_4), 98.7 \text{ (C}_6), 54.8 \text{ (C}_7), 48.8 \text{ (C}_2). \text{ IR (neat) cm}^{-1}: 1711, 1608, 1588 \text{ (C=O), 1467, 1430, 1306, 1208, 1149, 1064, 1055, 818. Elemental Anal: Calculated for } C_{19}H_{22}O_5: C, 69.01; H, 6.71. \text{ Found: C, 68.89; H, 6.71. ESI-MS (Methanol/Toluene) m/z 353.1374 ([M+Na]^+ (calc. 353.1365).}$

**2,5-di(3,5-dimethoxybenzyl)-3,4-di(3-thienyl)cyclopentadienone (49)**

![Diagram of 2,5-di(3,5-dimethoxybenzyl)-3,4-di(3-thienyl)cyclopentadienone (49)](image)

Reaction carried out in air. 1,2-di(3-thienyl)-ethane-1,2-dione (47) (200 mg, 0.89 mmol) and 1,3-bis(3,5-dimethoxybenzyl)propane-2-one (48) (290 mg, 0.89 mmol) were dissolved in ethanol (5 mL) and the solution was heated under reflux to 80°C. Then to the mixture 0.2 M potassium hydroxide in ethanol (2 mL, 0.4 mmol) was slowly added in two portions through the condenser. The solution was refluxed for 20 minutes giving a dark red mixture. This was purified by column chromatography using dichloromethane: methanol 50: 1 as the eluent to give the product (R$_f$ = 0.6) as a red solid. **Yield:** 300 mg, 0.58 mmol, 65%. **Melting Point:** 182-183°C. $^1H\text{-NMR \text{ (400 MHz, CDCl}_3, 25^\circ\text{C, TMS)} \delta: 7.25 \text{ (dd, } 2H, \; ^4J_{H-H} = 1.5 \text{ Hz and } ^3J_{H-H} = 5.0 \text{ Hz, } H_4), 6.91 \text{ (d, } 2H, \; ^4J_{H-H} = 1.5 \text{ Hz, } H_2), 6.80 \text{ (d, } 2H, \; ^3J_{H-H} = 5.0 \text{ Hz, } H_5), 6.47 \text{ (d, } 4H, \; ^4J_{H-H} = 2.0 \text{ Hz, } H_8), 6.41 \text{ (t, } 2H, \; ^4J_{H-H} = 2.0 \text{ Hz, } H_10), 3.69 \text{ (s, } 12H, \; H_{11}). \text{ IR (neat) cm}^{-1}: 1707 \text{ (C=O), 1585, 1452, 1422, 1306, 1275, 1206, 1150, 1057, 842, 754, 683. ESI-MS: (Acetonitrile) m/z 539.0961 ([M+Na]^+) (calc.539.0963).}
1,2,4,5-tetra(3-thienyl)-3,6-di(3,5-dimethoxybenzyl)benzene (50)

Bis(3-thienyl)acetylene (19) (60 mg, 0.32 mmol), 2,5-di(3,5-dimethoxybenzyl)-3,4-di(3-thienyl)cyclopentadienone (49) (150 mg, 0.29 mmol) and benzophenone (0.5 g) were mixed and attached to an air condenser. The mixture was heated at 300°C for 90 minutes giving a brown solution. After cooling to room temperature the product, as a brown solid, was precipitated by addition of dichloromethane and methanol (2 mL of each). **Yield:** 76 mg, 0.11 mmol, 41%. **Melting Point:** 322-323°C. **¹H-NMR** (400 MHz, CDCl₃, 25°C, TMS) δ: 6.90 (dd, 4H, 4J_H-H = 2.0 Hz and 3J_H-H = 5.0 Hz, H₄), 6.61 (dd, 4H, 4J_H-H = 1.0 and 3.0 Hz, H₂), 6.53 (dd, 4H, 4J_H-H = 1.0 Hz and 3J_H-H = 5.0 Hz, H₃), 6.14 (t, 2H, 4J_H-H = 2.0 Hz, H₁₁), 6.07 (d, 4H, 4J_H-H = 2.0 Hz, H₉), 3.52 (s, 12H, H₁₂). **¹³C{¹H}-NMR** (100 MHz, CDCl₃, 25°C, TMS) δ: 159.1 (C₁₀), 141.9 (C₆/₇/₈), 140.5 (C₆/₇/₈), 139.8 (C₆/₇/₈), 135.5 (C₃), 129.5 (C₅), 123.8 (C₂), 122.7 (C₆), 108.5 (C₉), 98.8 (C₁₁), 54.8 (C₁₂). **IR (neat)** cm⁻¹: 1581, 1423, 1307, 1265, 115, 1038, 937, 854, 775. **ESI-MS:** (Acetonitrile) m/z 701.0922 ([M+Na]⁺) (calc.701.0925).

1,2-di(2-thienyl)-4,5-di(3-thienyl)-3,5-di(3,5-dimethoxybenzyl)benzene (51)
Part 7: Experimental.

Bis(2-thienyl)acetylene (18) (72 mg, 0.38 mmol), 2,5-di(3,5-dimethoxybenzyl)-3,4-di(3-thienyl)cyclopentadienone (49) (180 mg, 0.35 mmol) and benzophenone (0.5 g) were mixed and attached to an air condenser. The mixture was heated at 300°C for 90 minutes giving a brown solution. After cooling to room temperature the product, as a brown solid, was precipitated by addition of methanol (2 mL). **Yield:** 119 mg, 0.18 mmol, 51%.

**Melting Point:** 318-319°C. **1H-NMR** (400 MHz, CDCl₃, 25°C, TMS) δ: 7.06 (dd, 2H, 4J_H-H = 0.8 Hz and 3J_H-H = 5.0 Hz, H₅), 6.91 (dd, 2H, 4J_H-H = 2.8 Hz and 3J_H-H = 4.8 Hz, H₁₆), 6.67 (dd, 2H, 3J_H-H = 2.8 and 4.8 Hz, H₁₄), 6.61 (dd, 2H, 4J_H-H = 2.8 and 3.5 Hz, H₁₃), 6.52 (m, 4H, H₃ and H₁₄), 6.15 (m, 6H, H₈ and H₁₀), 3.54 (s, 12H, H₁₁). **13C{1H}-NMR** (100 MHz, CDCl₃, 25°C, TMS) δ: 159.6 (C₁₀), 142.2 (C_quat), 142.0 (C_quat), 140.0 (C_quat), 136.8 (C_quat), 134.6 (C_quat), 129.9 (C₁₅), 129.1 (C₅), 128.3 (C_quat) 126.0 (C₃), 125.8 (C₄), 124.3 (C₁₃), 123.3 (C₁₆), 108.9 (C₉), 99.3 (C₁₀), 55.3 (C₁₁). **IR (neat)** cm⁻¹: 3102, 2960, 2836, 1701, 1581, 1451, 1412, 1308, 1264, 1194, 1155, 1057, 1015, 936, 794, 782, 695. **ESI-MS:** (Chloroform) m/z 701.0922 ([M+Na]⁺) (calc. 701.0925).

2,5-di(3,5-dimethoxybenzyl)-3,4-di(2-thienyl)cyclopentadienone (55)¹⁸

![Chemical Structure](image)

1,2-di(2-thienyl)-ethane-1,2-dione (52) (1.0 g, 4.5 mmol), 1,3-bis(3,5-dimethoxybenzyl)propane-2-one (48) (2.32 g, 4.5 mmol) and 18-crown-6 (0.26 g, 0.5 mmol) were heated to 95°C in dichlorobenzene (10 mL). To this potassium hydroxide (140 mg, 2.5 mmol) in ethanol (5 mL) was added and the solution stirred at 95°C for 2 minutes giving a purple solution. This decomposed upon cooling to room temperature within 3 minutes to give only starting materials.
7.6 Towards applications of thiophene containing polyphenylenes

**Bis(2,5-dimethyl-3-thienyl)acetylene (56)**

To 3-iodo-2,5-dimethylthiophene 58 and (1 mL, 4.2 mmol), 2-methyl-3-butyn-2-ol (0.5 mL, 5 mmol), benzyltriethylammonium chloride (71 mg, 0.31 mmol), copper(I) iodide (100 mg, 0.53 mmol), and tetrakis(triphenylphosphine) palladium(0) (200 mg, 0.17 mmol) in benzene (10 mL), was added a 5.5 N solution of aqueous sodium hydroxide (2 mL, 16.5 mmol) and the mixture was left stirring for 3 days. Then 3-iodo-2,5-dimethylthiophene (58) (1 mL, 4.2 mmol) in benzene (8.0 mL) was added and the solution was heated to 80°C and left stirring at this temperature for a further 3 days. It was cooled to room temperature and a solution of saturated aqueous ammonium chloride (40 mL) was added and the solution stirred for 1 hour. The phases were separated and the aqueous layer was extracted with toluene. The organic phases were dried with magnesium sulfate and solvent evaporated. The product was purified by column chromatography using hexane: dichloromethane (3: 2) as eluent to give the product (R<sub>f</sub> = 0.5) as a brown solid. **Yield:** 0.48 g, 1.93 mmol, 46%. **Melting Point:** 60-61°C. **<sup>1</sup>H-NMR:** (400 MHz, CDCl<sub>3</sub>, 25°C, TMS) δ: 6.68 (s, 2H, H<sub>4</sub>), 2.52 (s, 6H, H<sub>6/7</sub>), 2.42 (s, 6H, H<sub>6/7</sub>). **<sup>13</sup>C{<sup>1</sup>H}-NMR:** (100 MHz, CDCl<sub>3</sub>, 25°C, TMS) 140.1 (C<sub>2/5</sub>), 135.3 (C<sub>2/5</sub>), 126.8 (C<sub>4</sub>), 119.1 (C<sub>3</sub>), 85.5 (C<sub>1</sub>), 14.7 (C<sub>6/7</sub>), 14.0 (C<sub>6/7</sub>). **IR (neat) cm<sup>-1</sup>:** 2961, 2177 (C≡C), 1437, 1232, 1165, 1140, 828, 820, 813, 588. **ESI-MS:** (Dichloromethane) m/z 247.0612 ([M+H]<sup>+</sup>) (calc. 247.0615).

**3-bromo-2,5-dimethylthiophene (57)**

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In a 1:1 mixture of glacial acetic acid: chloroform (40 mL), 2,5-dimethylthiophene (1 mL, 8.77 mmol) and n-bromosuccinimide (1.87 g, 10.52 mmol) were refluxed for 30 min at 70°C. Water (40 mL) was added and the chloroform layer extracted and washed with 2 N aqueous potassium hydroxide solution (40 mL), dried over magnesium sulfate and solvent evaporated to give a yellow liquid. This was purified by column chromatography using hexane as the eluent to give the product (Rf = 0.9) as a clear liquid. **Yield:** 1.27 g, 6.67 mmol, 76%. **1H-NMR:** (400 MHz, CDCl₃, 25°C, TMS) δ: 6.59 (s, 1H, H₄), 2.44 (s, 3H, H₆/₇), 2.37 (s, 3H, H₆/₇). **13C{¹H}-NMR:** (100 MHz, CDCl₃, 25°C, TMS) δ: 137.3 (C₂/₅), 131.9 (C₂/₅), 127.9 (C₄), 108.2 (C₃), 14.8 (C₆/₇), 14.1(C₆/₇). **EI-MS:** (Chloroform) m/z 189.9455 ([M]+) (calc. 189.9452).

**3-iodo-2,5-dimethylthiophene (58)**

To a stirred solution of 2,5-dimethylthiophene (5 mL, 45 mmol) in dichloromethane (20 mL) was added iodine (5.72 g, 47 mmol). Water and nitric acid (1:1, 4 mL) were added dropwise and the solution was refluxed for 2 hr at 38°C. The organic layer was extracted, washed with water (2 x 30 mL), aqueous sodium hydroxide (0.1 M, 3 x 30 mL) and again with water (30 mL), dried over magnesium sulfate and solvent removed to give a orange liquid. The product was purified by column chromatography using hexane as eluent to give the desired product (Rf = 0.8) as a clear liquid. **Yield:** 7.49 g, 31.5 mmol, 70%. **1H-NMR** (400 MHz, CDCl₃, 25°C, TMS) δ: 6.68 (s, 1H, H₄), 2.48 (s, 3H, H₆/₇), 2.43 (s, 3H, H₆/₇). **13C{¹H}-NMR** (100 MHz, CDCl₃, 25°C, TMS) δ: 138.0 (C₂/₅), 135.6 (C₂/₅), 132.0 (C₄), 78.9 (C₃), 20.2 (C₆/₇), 17.1 (C₆/₇).
Part 7: Experimental.

1,2-di(2,5-dimethyl-3-thienyl)–3,4,5,6-tetra-(4-tert-butyphenyl)benzene (59)

1,2-bis(2,5-dimethyl-3-thienyl)acetylene (56) (115.2 mg, 0.63 mmol), 3,4,5-tetrakis-(4-tert-butyphenyl)cyclopentadienone (25) (300 mg, 0.49 mmol) and benzophenone (0.5 g) were heated for 90 minutes at 300°C while attached to an air condenser giving a brown mixture. This was purified by column chromatography using dichloromethane: hexane (1: 2) as the eluent to give the product (R_f = 0.7) as a brown solid which was further purified by recrystallisation from methanol. **Yield:** 207 mg, 0.25 mmol, 51%. **Melting Point:** 224-225°C. **^1H-NMR** (400 MHz, CDCl_3, 25°C, TMS) δ: 6.95 - 6.56 (m, 16H, 8*H_Ar), 6.04 (s, 2H, 2*H_Th), 2.16 (s, 3H, CH_3), 2.14 (s, 3H, CH_3), 1.92 (s, 3H, CH_3), 1.88 (s, 3H, CH_3), 1.18 (s, 18H, 2*CMe_3), 1.13 (s, 18H, 2*CMe_3). **^13C{^1H}-NMR** (100 MHz, CDCl_3, 25°C, TMS) δ: 147.0 (2*C_quat), 146.9 (C_quat), 146.8 (C_quat), 140.5 (C_quat), 140.4 (C_quat), 140.0 (C_quat), 139.9 (C_quat), 137.6 (2*C_quat), 137.3 (C_quat), 137.2 (C_quat), 136.9 (C_quat), 136.6 (C_quat), 135.6 (2*C_quat), 132.3 (C_quat), 132.1 (C_quat), 132.0 (C_quat), 131.4 (C_quat), 130.8 (C_Ar), 130.7 (C_Ar), 130.6 (C_Ar), 130.1 (C_Ar), 128.5(C_Th), 128.1 (C_Th), 122.5 (4*C_Ar), 31.3 (2*CMe_3), 31.2 (2*CMe_3), 15.0 (CH_3), 14.9 (CH_3), 14.5 (CH_3), 14.4 (CH_3). **IR (neat):** cm⁻¹ 2960, 1685, 1511, 1461, 1362, 1269, 1201, 1117, 10 18, 832. **ESI-MS:** (Acetonitrile) m/z 826.4589 ([M]^+)(calc. 826.4606).

3,6-di(2-pyridyl)-1,2,4,5-tetrazine (62)^20-21

3,6-di(2-pyridyl)-1,2-dihydro-1,2,4,5-tetrazine
2-cyanopyradine (5.29 g, 51.0 mmol) and hydrazine hydrate (5 mL, 103 mmol) were stirred for 3 hours at 90°C. The solid formed was filtered off and recrystallised from ethanol to give the product as a yellow solid. **Yield:** 2.52 g, 10.6 mmol, 42%. **^1H-NMR** (400 MHz, CDCl₃, 25°C, TMS) δ: 8.61 (s, 2H, H₇), 8.59 (d, 2H, J₆₋₇ = 5.3 Hz, H₆), 8.07 (d, 2H, J₆₋₇ = 7.9 Hz, H₃), 7.77 (dd, 2H, J₃₋₄ = 1.5 and 7.8 Hz, H₄), 7.37 (dd, 2H, J₅₋₆ = 5.3 and 7.8 Hz, H₅).

![3,6-di(2-pyridyl)-1,2,4,5-tetrazine](image) **3,6-di(2-pyridyl)-1,2,4,5-tetrazine**

3,6-di(2-pyridyl)-1,2-dihydro-1,2,4,5-tetrazine (2.52 g, 10.6 mmol) was dissolved in dichloromethane (60 mL) and cooled to 0°C. Nitrous gases (prepared via the addition of 6 M aqueous sodium nitrite (100 mL) to concentrated hydrochloric acid (60 mL)) were passed through the solution for 30 minutes. The solution was quenched with aqueous sodium hydrogen carbonate until no further gas evolved (~60 mL). Solvent was removed and the residue dissolved in water (50 mL) extracted with dichloromethane and dried with magnesium sulfate. The solvent was evaporated to give a purple solid which was recrystallised from toluene. **Yield:** 2.12 g, 8.97 mmol, 85%. **Melting Point:** 218-220°C (lit. 219-220°C). **^1H-NMR** (400 MHz, CDCl₃, 25°C, TMS) δ: 9.01 (d, 2H, J₆₋₇ = 4.8 Hz, H₆), 8.77 (d, 2H, J₆₋₇ = 8.2 Hz, H₃), 8.03 (dd, 2H, J₃₋₄ = 2.1 and 8.2 Hz, H₄), 7.60 (m, 2H, H₅). **^13C{^1H}-NMR** (100 MHz, CDCl₃, 25°C, TMS) δ: 163.4 (C₁), 150.6 (C₆), 149.6 (C₂), 137.1 (C₃), 126.2 (C₄), 124.1 (C₅). **IR (neat):** cm⁻¹: 3060, 1581, 1387, 1258, 1128, 1091, 993, 919, 796, 743. **ESI-MS:** (Chloroform) m/z 237.0895 ([M+H]^+) (calc.237.0889).

**1,2-di(2-thienyl)ethene (63)**

![1,2-di(2-thienyl)ethene](image)
2-bromo-3-thienylmethyltriphenylphosphonium bromide

To a solution of 2-thienylethanol (1.6 g, 13.95 mmol) in chloroform (30 mL), triphenylphosphonium bromide (4.86 g, 14.22 mmol) was added and the solution was refluxed at 65°C for 6 hours. Solvent was removed and the solution dissolved in the minimum amount of chloroform, then diethyl ether was added and the solution left overnight to give a white precipitate. **Yield:** 4.43 g, 10.1 mmol, 74%. **Melting Point:** 297-298°C. **¹H-NMR** (400 MHz, CDCl₃, 25°C, TMS) δ: 7.78 - 7.63 (m, 15H, H₉, H₁₀ and H₁₁), 7.14 (m, 2H, H₃ and H₄/₅), 6.86 (m, 1H, H₄/₅), 5.74 (d, 2H, ²J₆-P = 13.0 Hz, H₆).

**¹³C{¹H}-NMR** (100 MHz, CDCl₃, 25°C, TMS) δ: 135.1 (d, ⁴J₃-P = 2.9 Hz, C₁₁), 134.3 (d, ³J₃-P = 9.8 Hz, C₁₀), 131.9 (d, ³J₃-P = 7.8 Hz, C₅), 130.3 (d, ²J₃-P = 12.7 Hz, C₉), 127.5 (d, ⁴J₃-P = 3.9 Hz, C₅), 127.4 (d, ²J₃-P = 9.8 Hz, C₂), 126.9 (d, ⁴J₃-P = 4.9 Hz, C₄), 117.6 (d, ¹J₃-P = 86.0 Hz, C₈), 26.9 (d, ¹J₃-P = 49.9 Hz, C₆). **³¹P-NMR** (162.0 MHz, CDCl₃, 25°C) δ: 21.67 (s, P₇).

**IR (neat)** cm⁻¹: 2858, 1485, 135, 1108, 995, 886, 723, 690. **ESI-MS:** (Acetonitrile) m/z 359.1020 ([M+H]⁺) (calc. 359.1023).

1,2-di(2-thienyl)ethene

In degassed tetrahydrofuran (40 mL) 2-thienyl triphenylphosphonium bromide (6.0 g, 14 mmol) and 2-thiophene carboxaldehyde (1.24 mL, 1.49 g, 14 mmol) were cooled to 0°C. To this potassium tert-butoxide (2.0 g, 17.8 mmol) in tetrahydrofuran (25 mL) was added and the solution stirred at this temperature for 60 min. The solution was then heated to 60°C for 2 days. Then 10% aqueous hydrochloric acid (60 mL) was added followed by water (100 mL) and dichloromethane (200 mL). The organic layer was extracted, dried over magnesium sulfate and solvent was removed. This was purified by column chromatography using hexane as the eluent to give the product (Rᵣ = 0.6) as an air
sensitive white solid which was stored in an inert atmosphere. **Yield:** 1.86 g, 9.7 mmol, 69%. **Melting Point:** 126-128°C (lit. 127-129°C). \(^{24}\) \(^1\)H-NMR (400 MHz, CDCl\(_3\), 25°C, TMS) \(\delta\): 7.20 (d, 2H, \(^3\)J\(_{H-H}\) = 5.0 Hz, H\(_3\)), 7.08 (s, 2H, H\(_6\)) 7.06 (d, 2H, \(^3\)J\(_{H-H}\) = 3.5 Hz, H\(_3\)), 7.02 (dd, 2H, \(^3\)J\(_{H-H}\) = 3.5 and 5.0 Hz, H\(_4\)). \(^{13}\)C\({}^1\)H-NMR (100 MHz, CDCl\(_3\), 25°C, TMS) \(\delta\): 142.4 (C\(_2\)), 127.7 (C\(_4\)), 126.1 (C\(_3\)), 124.3 (C\(_5\)), 121.5 (C\(_6\)). IR (neat) cm\(^{-1}\): 1790 (C=C), 1143, 1282, 1038, 943, 850, 694. **ESI-MS:** (Acetonitrile) m/z 193.0146 ([M+H]\(^+\)) (calc. 193.0146).

3,6-di(2-pyridyl)-4,5-di(2-thienyl)-1,4-dihydropyridazine (64)

In a sealed pressure tube 1,2-di(2-thienyl)ethene (63) (0.10 g, 0.52 mmol) and 3,6-di(2-pyridyl)-1,2,4,5,-tetrazine (62) (0.135 g, 0.57 mmol) were dissolved in toluene (30 mL) and stirred at 180°C for 24 hours. The solution was cooled to room temperature and solvent removed. The residue was purified by column chromatography using ethyl acetate as the eluent to the product (R\(_f\) = 0.7) as an orange solid which was recrystallised from methanol. **Yield:** 0.142 g, 0.354 mmol, 68%. **Melting Point:** 212°C. NMR shows two isomers in solution (see discussion in text). \(^1\)H-NMR (600 MHz, CDCl\(_3\), 25°C, TMS) \(\delta\): 9.38 (s, 1H, H\(_{16}\)), 8.68 (d, 1H, \(^3\)J\(_{H-H}\) = 4.4 Hz, H\(_{22}\)), 8.65 (d, 0.7H, \(^3\)J\(_{H-H}\) = 4.4 Hz, H\(_1\)), 8.60 (d, 0.3H, \(^3\)J\(_{H-H}\) = 4.4 Hz, H\(_{11}\)), 8.17 (d, 0.7H, \(^3\)J\(_{H-H}\) = 8.0 Hz, H\(_2\)), 8.08 (d, 0.3H, \(^3\)J\(_{H-H}\) = 8.0 Hz, H\(_3\)), 7.77 (dt, 0.3H, \(^3\)J\(_{H-H}\) = 1.4 and 8.0 Hz, H\(_3\')), 7.68 (dt, 0.7H, \(^3\)J\(_{H-H}\) = 1.4 and 8.0 Hz, H\(_2\')), 7.54 (m, 2H, H\(_{19}\) and H\(_{20}\)), 7.36 (m, 0.3H, H\(_4\)), 7.24 (m, 1H, H\(_{21}\)), 7.21 (m, 0.7H, H\(_4\)), 7.14 (m, 2H, H\(_{11}\) and H\(_{16}\)), 7.13 (d, 1H, \(^3\)J\(_{H-H}\) = 3.7 Hz, H\(_9\)), 6.99 (d, 1H, \(^3\)J\(_{H-H}\) = 3.7 Hz, H\(_{14}\)), 6.93 (dd, 1H, \(^3\)J\(_{H-H}\) = 3.7 and 5.1 Hz, H\(_{10}\)), 6.91 (dd, 1H, \(^3\)J\(_{H-H}\) = 3.7 and 5.1 Hz, H\(_{15}\)), 6.05 (s, 1H, H\(_3\)). \(^{13}\)C-NMR (100 MHz, CDCl\(_3\), 25°C, TMS) \(\delta\): 153.8 (C\(_6\)), 151.4 (C\(_{18}\)), 149.0 (C\(_{20}\)), 148.3 (C\(_1\)), 148.2 (C\(_1\)'), 147.4 (C\(_5\)'), 146.5 (C\(_5\)), 145.2 (C\(_8\)), 141.5 (C\(_{13}\)), 140.1 (C\(_{17}\)), 136.6 (C\(_3\)'), 135.9 (2*C, C\(_3\) and C\(_{12/13}\)), 127.2 (C\(_9\)), 126.8 (C\(_{10}\)), 124.3 (C\(_3\)), 121.5 (C\(_6\)), 114.3, 1282, 1038, 943, 850, 694. **ESI-MS:** (Acetonitrile) m/z 193.0146 ([M+H]\(^+\)) (calc. 193.0146).
126.6 (C₇), 125.6 (C₁₂₁₃), 125.1 (C₁₁), 124.8 (C₆), 124.7 (C₄'), 124.2 (C₁₁), 123.3 (C₁₄), 122.7 (C₄), 121.1 (2*C, C₂ and C₂'), 101.0 (C₁₂₁₃), 37.5 (C₇). IR (neat) cm⁻¹: 3350 (N-H), 3102, 1564 (C=N), 1468, 1286, 1262, 1151, 1038, 993, 826, 788, 704, 622. ESI-MS: (Methanol) m/z 401.0914 ([M+H]+) (calc. 401.0895).

2-(3,6-di(2-pyridyl)-5-(2-thienyl)-2,5-dihydropyridazinyl)-4,7-di(2-pyridyl) thieno[2,3-d]pyridazine (65)

In a sealed pressure tube, 1,2-di(2-thienyl)ethene (63) (0.40 g, 2.08 mmol) and 3,6-di(2-pyridyl)-1,2,4,5,-tetrazine (62) (0.5 g, 2.11 mmol) were dissolved in toluene (30 mL) and stirred at 180°C for 72 hours. The solution was cooled to room temperature and solvent removed. The residue was purified by column chromatography using ethyl acetate as the eluent to the product (R_f = 0.4) a yellow solid which was recrystallised from methanol. **Yield:** 0.28 g, 0.46 mmol, 44%. **Melting Point:** 210-212°C. IR (neat) cm⁻¹: 3351 (N-H), 3057, 1565 (C=N), 1468, 1342, 1261, 1178, 993, 85, 789, 705, 622. ESI-MS: (Chloroform) m/z 607.1495 ([M+H]+) (calc. 607.1487).

Oxidation of di-thienyl pyridazine 64 - Synthesis of 66a-c
Part 7: Experimental.

3,6-di(2-pyridyl)-4,5-di(2-thienyl)-1,4-dihydropyridazine (64) (50 mg, 0.13 mmol) was dissolved in dichloromethane (150 mL) and cooled to 0°C. Nitrous gases (prepared via the addition of 6 M aqueous sodium nitrite (50 mL) to concentrated hydrochloric acid (30 mL)) were passed through the solution for 30 minutes. The solution was quenched with aqueous sodium hydrogen carbonate until no further gas evolved (~60 mL) and the organic layer was extracted with dichloromethane, dried with magnesium sulfate and solvent was evaporated to give a purple solid which was purified by column chromatography using dichloromethane as the eluent (R_f = 0.9). **Yield:** 42 mg, 0.053 mmol, 82%. NMR shows three tautomers in solution (see discussion in text). **^1H-NMR** (600 MHz, CDCl_3, 25°C, TMS) δ: 9.41 (s, 2H, H_15), 8.65 (d, 2H, ^3J_H-H = 4.6 Hz, H_1), 8.54 (d, 2H, ^3J_H-H = 3.7 Hz, H_14), 8.01 (d, 2H, ^3J_H-H = 7.9 Hz, H_{11/12/13}), 7.61 (m, 2H, H_{2/3/4}), 7.56 (d, 2H, ^3J_H-H = 4.5 Hz, H_16), 7.55 (m, 6H, 2 * H_{2/3/4} and H_{11/12/13}), 7.30 (m, 2H, H_{11/12/13}), 6.99 (dd, 2H, ^4J_H-H = 1.1 Hz and ^3J_H-H = 5.3 Hz, H_8), 6.80 (dd, 2H, ^4J_H-H = 0.8 Hz and ^3J_H-H = 3.4 Hz, H_6), 6.67 (d, 2H, ^3J_H-H = 4.5 Hz, H_9), 6.00 (s, 2H, H_5).

5,5’-dimethyl-2,2’-bisthiophene (68)\(^{25}\)

[Diagram of 5,5’-dimethyl-2,2’-bisthiophene (68)]

2,2’-bisthiophene (4.0 g, 24.05 mmol) was dissolved in tetrahydrofuran (40 mL) and cooled to -40°C. To this green solution 2.5 M n-butyl lithium (21.2 mL, 53.0 mmol) was added dropwise and the solution was stirred for 45 min at -40°C. To this methyl iodide (4.9 mL, 78.3 mmol) was added dropwise over 20 min and the solution warmed to room temperature. The brown solution was extracted with diethyl ether and solvent was removed. This was purified by column chromatography using hexane as the eluent to give the product (R_f = 0.8) as a white solid. **Yield:** 1.87 g, 9.6 mmol, 40%. **Decomposition Temperature:** 146°C. **^1H-NMR** (400 MHz, CDCl_3, 25°C, TMS) δ: 6.92 (d, 2H, ^3J_H-H = 3.5 Hz, H_3), 6.68 (qd, 2H, ^4J_H-H = 1.0 Hz and ^3J_H-H = 3.5 Hz, H_4), 2.51 (d, 6H, ^4J_H-H = 1.0 Hz, H_6). **^13C[^1H]-NMR** (100 MHz, CDCl_3, 25°C, TMS) δ: 138.0 (C_5),
135.1 (C\textsubscript{2}), 125.3 (C\textsubscript{4}), 122.4 (C\textsubscript{3}), 14.9 (C\textsubscript{1}). **IR (neat)** cm\(^{-1}\): 3066, 1475, 1434, 1089, 1025, 741, 691.

**3,3’-dibromo-5,5’-dimethyl-2,2’-bisthiophene (69)**\(^{26}\)

![](image)

5,5’-dimethyl-2,2’-bisthiophene (68) (1.0 g, 5.15 mmol) was dissolved in dimethylformamide (20 mL). To this n-bromosuccinimide (1.83 g, 10.3 mmol) in dimethylformamide (15 mL) was added and the solution was stirred for 16 hours. The mixture was poured into water (80 mL) and extracted with diethyl ether (3 x 40 mL). The solution was then washed with brine (60 mL) dried over magnesium sulfate and solvent was removed to give a yellow oil. Addition of methanol (3 mL) gave the product as a yellow solid after 24 hours. **Yield:** 0.95 g, 2.7 mmol, 52%. **Melting Point:** 54°C. **\(^{1}\text{H}-\text{NMR}\):** (400 MHz, CDCl\textsubscript{3}, 25°C, TMS) \(\delta\): 6.77 (q, 2H, \(\textbf{4}^J_{\text{H-H}} = 1.0\) Hz, H\textsubscript{4}), 2.51 (d, 6H, \(\textbf{4}^J_{\text{H-H}} = 1.0\) Hz, H\textsubscript{6}). **\(^{13}\text{C}\{^{1}\text{H}\}-\text{NMR}\):** (100 MHz, CDCl\textsubscript{3}, 25°C, TMS) \(\delta\): 141.7 (C\textsubscript{5}), 128.7 (C\textsubscript{4}), 126.7 (C\textsubscript{2}), 111.3 (C\textsubscript{3}), 15.6 (C\textsubscript{6}). **IR (neat)** cm\(^{-1}\): 2916, 1520, 1426, 1307, 1170, 968, 871, 689, 786. **EI-MS:** (Acetonitrile) m/z 350.8516 ([M+H]\(^+\)) (calc. 350.8512).

**5,5’-dimethyl-2,2’-bithiophene-3,3’-dicarbaldehyde (70)**

![](image)

3,3’-dibromo-5,5’-dimethyl-2,2’-bisthiophene (69) (1.0 g, 2.84 mmol) was dissolved in tetrahydrofuran (40 mL) and cooled to -78°C. To this 2.5 M n-butyllithium (2.27 mL, 5.68 mmol) was added and the solution stirred for 2 hours. Dimethylformamide (3 mL) in tetrahydrofuran (10 mL) was then added dropwise and the solution warmed to room
temperature over 16 hours. 10% aqueous hydrochloric acid (20 mL) was added and the solution extracted with dichloromethane to give a yellow solution. This was purified by column chromatography using dichloromethane as the eluent to give the product (R_f = 0.6) as a yellow solid. **Yield:** 350 mg, 1.38 mmol, 49%. **1H-NMR** (400 MHz, CDCl₃, 25°C, TMS) δ: 9.87 (s, 2H, H₇), 7.29 (s, 2H, H₄), 2.55 (s, 6H, H₆). **13C{¹H}-NMR** (100 MHz, CDCl₃, 25°C, TMS) δ: 184.0 (C₇), 142.5 (C₃), 140.0 (C₂), 139.5 (C₅), 124.3 (C₄), 14.8 (C₆). **IR (neat)** cm⁻¹: 3316, 2815, 2727, 1664 (C=O), 1541, 1448, 1357, 1198, 1123, 966, 834, 771, 718. **ESI-MS:** (Chloroform) m/z 273.0027 ([M+Na]⁺) (calc. 273.0020).

(67)²⁷

![Structure 67](image)

5,5′-dimethyl-2,2′-bithiophene-3,3′-dicarbaldehyde (70) (100 mg, 0.399 mmol) and 3-ethyl-5-(2-hydroxyethyl)-4-methylthiazolium bromide (19.6 mg, 0.078 mmol) were dissolved in tert-butanol (20 mL). To this 1,8-Diazabicyclo[5.4.0]undec-7-ene (17.9 mL, 0.12 mmol) was added and the solution stirred for 24 hours at 60°C. The reaction was quenched with 10% hydrochloric acid (60 mL) and allowed to oxidise in air for 2 hours. The solution was then extracted with dichloromethane dried over magnesium sulfate and solvent was removed to give a purple solid. This was purified by column chromatography using dichloromethane as the eluent to give the product (R_f = 0.4) as a purple solid. **Yield:** 9 mg, 0.036 mmol, 9%. **1H-NMR** (400 MHz, CDCl₃, 25°C, TMS) δ: 7.11 (q, 2H, ¹J_H-H = 1.2 Hz, H₄), 2.48 (d, 6H, ¹J_H-H = 1.0 Hz, H₆). **13C{¹H}-NMR** (100 MHz, CDCl₃, 25°C, TMS) δ: 174.5 (C₇), 142.8 (C₂), 140.5 (C₃), 134.8 (C₅), 125.2 (C₄), 15.3 (C₆).
7.7 References

Annex
Table 1 - Crystal data and X-ray experimental details for compounds 3, 6, 16, 17 and 18.

<table>
<thead>
<tr>
<th>Compound</th>
<th>3</th>
<th>6</th>
<th>16</th>
<th>17</th>
<th>18</th>
</tr>
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<tbody>
<tr>
<td>Empirical formula</td>
<td>C₂₂H₁₆FeS</td>
<td>C₂₂H₁₆FeS</td>
<td>C₁₈H₁₂S₃</td>
<td>C₁₈H₁₂S₃</td>
<td>C₁₀H₆S₂</td>
</tr>
<tr>
<td>Formula weight</td>
<td>368.26</td>
<td>368.26</td>
<td>324.46</td>
<td>324.46</td>
<td>190.27</td>
</tr>
<tr>
<td>Temperature (K)</td>
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<td>293(2)</td>
<td>296(2)</td>
<td>293(2)</td>
<td>298(2)</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>P₂₁/c</td>
<td>P₂₁/c</td>
<td>P₂₁/c</td>
<td>P₂₁/c</td>
<td>Pbcn</td>
</tr>
<tr>
<td>b (Å)</td>
<td>10.137(5)</td>
<td>10.066(2)</td>
<td>9.814(2)</td>
<td>9.5408(19)</td>
<td>9.5408(19)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>8.208(4)</td>
<td>8.0643(16)</td>
<td>20.233(4)</td>
<td>33.268(7)</td>
<td>7.578(4)</td>
</tr>
<tr>
<td>α (°)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
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<tr>
<td>β (°)</td>
<td>92.198(11)</td>
<td>92.27(3)</td>
<td>100.91(3)</td>
<td>97.90(3)</td>
<td>90</td>
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<tr>
<td>γ (°)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Volume(Å³)</td>
<td>1777.0(13)</td>
<td>1696.9(6)</td>
<td>1517.8(5)</td>
<td>3135.1(11)</td>
<td>875.7(9)</td>
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<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated) (Mg/m³)</td>
<td>1.376</td>
<td>1.441</td>
<td>1.420</td>
<td>1.375</td>
<td>1.443</td>
</tr>
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<td>Absorption coefficient (mm⁻¹)</td>
<td>0.965</td>
<td>1.010</td>
<td>0.477</td>
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<td>0.540</td>
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<tr>
<td>F(000)</td>
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<td>760</td>
<td>672</td>
<td>1344</td>
<td>392</td>
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<td>Crystal size (mm)</td>
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<td>0.5 x 0.4 x 0.15</td>
<td>0.36 x 0.18 x 0.14</td>
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<td>Theta range for data collection (°)</td>
<td>2.77 to 24.00</td>
<td>2.25 to 24.99</td>
<td>3.04 to 25.00</td>
<td>2.47 to 25.07</td>
<td>2.68 to 24.97</td>
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<td>Reflections collected</td>
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<td>9600</td>
<td>8435</td>
<td>17869</td>
<td>4351</td>
</tr>
<tr>
<td>Independent reflections [R(int)]</td>
<td>2782 [0.2504]</td>
<td>2965 [0.0277]</td>
<td>2641 [0.0209]</td>
<td>5535 [0.0583]</td>
<td>767 [0.0393]</td>
</tr>
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<td>Data / restraints / parameters</td>
<td>2782 / 104 / 254</td>
<td>2965 / 0 / 218</td>
<td>2641 / 0 / 194</td>
<td>5535 / 0 / 385</td>
<td>767 / 10 / 80</td>
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<tr>
<td>Goodness-of-fit on F²</td>
<td>0.980</td>
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<td>1.182</td>
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<td>1.118</td>
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<td>R₁ [I&gt;2sigma(I)]</td>
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<td>0.0342</td>
<td>0.0505</td>
<td>0.1005</td>
<td>0.0436</td>
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<td>wR₂ (all data)</td>
<td>0.2701</td>
<td>0.0987</td>
<td>0.1483</td>
<td>0.1948</td>
<td>0.0984</td>
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**Table 2** – Crystal data and X-ray experimental details for compounds 19, 22, 27, 32 and 34.

<table>
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<th>Compound</th>
<th>19</th>
<th>22</th>
<th>27</th>
<th>32</th>
<th>34</th>
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<tbody>
<tr>
<td>Empirical formula</td>
<td>C₁₀H₆S₂</td>
<td>C₁₃H₂₀S₂</td>
<td>C₅₅H₉₀C₁₂S₂</td>
<td>C₁₂H₁₀S₂</td>
<td>C₃₈H₆₀S₂</td>
</tr>
<tr>
<td>Formula weight</td>
<td>189.99</td>
<td>546.71</td>
<td>856.05</td>
<td>218.32</td>
<td>797.16</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>153(2)</td>
<td>150(2)</td>
<td>153(2)</td>
<td>150(2)</td>
<td>293(2)</td>
</tr>
<tr>
<td>Crystal system</td>
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<td>Orthorhombic</td>
<td>Triclinic</td>
<td>Orthorhombic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
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<td>Pna₂₁</td>
<td>P-1</td>
<td>Pbca</td>
<td>Cc</td>
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<td>Unit cell dimensions: a (Å)</td>
<td>10.649(2)</td>
<td>10.7129(8)</td>
<td>9.880(2)</td>
<td>12.090(2)</td>
<td>16.666(3)</td>
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<td>b (Å)</td>
<td>11.071(2)</td>
<td>21.7875(16)</td>
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<td>10.884(2)</td>
<td>28.888(6)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>7.6274(15)</td>
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<td>16.781(3)</td>
<td>11.062(2)</td>
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<td>90</td>
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<td>γ (°)</td>
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<td>Volume(Å³)</td>
<td>899.3(3)</td>
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<td>2384.3(8)</td>
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<td>5001.6(17)</td>
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<td>4</td>
<td>2</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated) (Mg/m³)</td>
<td>1.405</td>
<td>1.241</td>
<td>1.192</td>
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<td>1.059</td>
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<tr>
<td>Absorption coefficient (mm⁻¹)</td>
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<td>0.207</td>
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<td>392</td>
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<td>912</td>
<td>912</td>
<td>1712</td>
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<tr>
<td>Crystal size (mm)</td>
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</tr>
<tr>
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<td>1.67 to 25.00</td>
<td>2.80 to 25.00</td>
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<td>4223</td>
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<tr>
<td>Independent reflections [R(int)]</td>
<td>796 [0.0289]</td>
<td>4581 [0.0537]</td>
<td>8384 [0.0264]</td>
<td>1943 [0.0705]</td>
<td>8772 [0.0788]</td>
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<td>Data / restraints / parameters</td>
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<td>4581 / 202 / 398</td>
<td>8384 / 55 / 607</td>
<td>1943 / 0 / 127</td>
<td>8772 / 152 / 523</td>
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<tr>
<td>Goodness-of-fit on F²</td>
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<td>1.016</td>
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<td>wR₂ (all data)</td>
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<td>0.2245</td>
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<td>0.1303</td>
<td>0.1573</td>
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Table 3 – Crystal data and X-ray experimental details for compounds 37, 63, 64 and 65.

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<th>63</th>
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<th>65</th>
</tr>
</thead>
<tbody>
<tr>
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<td>C_{22}H_{22}O_{3}S</td>
<td>C_{10}H_{10}S_{2}</td>
<td>C_{22}H_{16}N_{4}S_{2}</td>
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<td>Triclinic</td>
<td>Triclinic</td>
</tr>
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<td>Cc</td>
<td>P2_{1}/c</td>
<td>P-1</td>
<td>P-1</td>
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<td>9.2328(10)</td>
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<tr>
<td>c (Å)</td>
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<td>10.410(3)</td>
<td>12.9913(13)</td>
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<td>α (°)</td>
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<td>90</td>
<td>106.948(2)</td>
<td>74.680(3)</td>
</tr>
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<td>β (°)</td>
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<td>92.410(7)</td>
<td>95.459(2)</td>
<td>85.560(3)</td>
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<td>γ (°)</td>
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<td>90</td>
<td>94.177(2)</td>
<td>74.900(3)</td>
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<tr>
<td>Volume (Å³)</td>
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<td>465.1(2)</td>
<td>981.49(18)</td>
<td>1397.0(4)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Density (calculated) (Mg/m³)</td>
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<td>Absorption coefficient (mm⁻¹)</td>
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<td>0.509</td>
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<td>F(000)</td>
<td>840</td>
<td>200</td>
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<td>628</td>
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<td>Crystal size (mm)</td>
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<td>0.23 x 0.17 x 0.10</td>
</tr>
<tr>
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<td>1.99 to 25.66</td>
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<td>1197</td>
<td>10356</td>
<td>15624</td>
</tr>
<tr>
<td>Independent reflections [R(int)]</td>
<td>3711 [0.0255]</td>
<td>746 [0.0203]</td>
<td>3449 [0.0230]</td>
<td>5272 [0.0383]</td>
</tr>
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<td>746 / 0 / 55</td>
<td>3449 / 0 / 258</td>
<td>5272 / 0 / 442</td>
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<td>Goodness-of-fit on F²</td>
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<td>1.081</td>
<td>1.075</td>
<td>1.067</td>
</tr>
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<td>R₁ [I&gt;2σ(I)]</td>
<td>0.0438</td>
<td>0.0731</td>
<td>0.0526</td>
<td>0.0494</td>
</tr>
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<td>wR₂ (all data)</td>
<td>0.1184</td>
<td>0.2384</td>
<td>0.1619</td>
<td>0.1261</td>
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