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Towards An Organic Ferromagnet

A thesis presented by John N. Devine to the
University of St. Andrews in application for
the degree of Doctor of Philosophy

July 1999



Declarations

I, John Neil Devine, hereby certify that this thesis has been composed by myself, that it is a record of my own work and that it has not been accepted in partial or complete fulfilment of any other degrees or professional qualification.

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Date 10.12.99

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Acknowledgements

Having entered the chemical industry within the past six months, I have grown accustomed to the phrase " Yes, but does it add value?". This question, and the financial aspects of industry never fail to remind me of how much I enjoyed the chemistry carried out in St. Andrews and I would like to express my sincere thanks to everyone who made this possible.

Special thanks must go to Professor John Walton for his patience, guidance and motivation throughout this project and for basically making me a better chemist. I will always appreciate Prof. Waltons supervision technique, and feel I have benefited greatly from it. I would also like to thank Dr Joe Crayston for his helpful advice, discussions and insight into the electrochemical and physical aspects of this project and also for his optimistic enthusiasm.

I would like to acknowledge the Defence Research Agency for financial support and also thank my industrial supervisors Dr. Marcia Hohn and Dr. Eamon Colclough for fruitful discussions.

Whilst working in Lab 410 I have had the privilege of working with a number of good friends and colleagues. I would especially like to thank Paul Baguley (gluefoot), Mo Afzal (what about that peak there Mo?) and Ahmed Iraqi (What I would do) for two very enjoyable years and latterly Andrew McCarroll and Leon Jackson. Thanks must also go to Matt Wheatley for his work on end-capped quaterthiophenes.

I cannot fail to mention the superb friendship of Stephen McMahon (the flasher) and Rick White who made my stay more enjoyable and provided many sources of amusement. I would also like to acknowledge the fellow players, past and present, of the all conquering Chemistry Department Football Team "Steaua Needarest'.

The help and advice offered and received from Prof. Rob Field, Dr Jim Naismith, Dr. Alan Aitken, Jim Bews, Bobby Cathcart, Melanja Smith, Colin Smith, Brian Walker and Sylvia Smith are also greatly appreciated.

I would especially like to thank Elaine Angus for her love support and understanding and for making the effort to be together, despite the travelling and effort required.

Finally, I am indebted to my parents for giving me the opportunities which they never had. The love, support and encouragement I have received from them has been unconditional and words could never fully express my gratitude or how lucky I have been to have them as parents. You are truly amazing.

Abbreviations and Symbols

A	Acceptor
b.p.	Boiling Point
br, s, d, t, q, m	Broad, singlet, doublet, triplet, quartet, multiplet
BuLi	<i>n</i> -Butyl lithium
CV	Cyclic Voltammetry
D	Donor
DDQ	2,3-Dichlorodicyanobenzoquinone
DEI	Desorption electron impact
DMAP	Dimethylaminopyridine
DMF	Dimethylformamide
DME	Dimethoxyethane
ESR	Electron Spin Resonance
Ether	Diethyl ether
FCU	Ferromagnetic Coupling Unit
GCMS	Gas chromatography mass spectroscopy
h, min	Hours, minutes
IR	Infra-red
<i>J</i>	Spin-spin coupling constant in Hz.
M	Mol dm ⁻³
M ⁺	Molecular ion
MO	Molecular Orbital
mmol	Millimoles
m/z	Mass to charge ratio
m.p.	Melting point
MeCN	Acetonitrile
NMR	Nuclear Magnetic Resonance
NBS	N-Bromosuccinimide

Abstract

A brief description of the basic concepts of magnetism are followed by a review of the various models proposed for the development of an organic ferromagnet, with particular emphasis on the topological and polaronic models. This is followed by an outline of our design characteristics and synthetic strategy in producing novel alkylated thienyl phenylene polymers.

A literature and practical investigation into the regioselective methods of coupling 3-alkylthiophenes *via* transition metal catalysed coupling reactions such as Kumada, Suzuki and Stille led to high yields of dialkylbithiophenes from the palladium catalysed coupling of thienyl stannanes **60**, **62**, **70** and **71** with 2-bromo-3-alkylthiophenes **25** and **63**. An efficient separation technique was also developed in order to afford the desired 3,4-dialkylbithiophenes **27** and **67**.

Modified Suzuki coupling conditions were established by modelling the reaction of two equivalents of 3-alkylthiophene with 1,3-phenylene bis(1,3,2-benzodioxaborole) **30**. These conditions were then utilised in the formation of monomers **31**, **77**, **83** and **84** from the Suzuki coupling of two equivalents of **27** or **67** with **30**. Monomers **85** and **99** were synthesised via Suzuki and zinc mediated coupling reactions respectively and served as a comparison of ferromagnetic coupling units and also helped address the issue of π dimerisation.

Polymerisation studies showed that the monomers were polymerised and doped more efficiently using electrochemical, rather than chemical techniques. The resultant doped polymers were characterised by UV-vis spectroscopy, cyclic voltammetry and high frequency low temperature ESR which provided direct evidence for polaronic species and also allowed the number of unpaired electrons per mole of polymer to be calculated. The effect of temperature on the linewidth of the ESR spectra of **P84**, **P85** and **P99**, was also investigated.

Synthetic attempts to produce an end-capped 1,3-phenylene bis(quarterthiophene) **102** are also detailed.

Chapter One

Introduction

An Introduction to Magnetism

Long one of nature's most fascinating phenomena, magnetism was once thought useful to thieves, effective as a love potion and also as a cure for gout or spasms. It was even claimed that a lodestone (Fe_3O_4) pickled in the salt of a sucking fish had the power to attract gold. Today these beliefs have been put aside, but magnetism is no less remarkable for our modern understanding of it.

Since the discovery of the lodestone many different magnetic materials have been developed, almost all based on transition metals such as iron, nickel and cobalt. In contrast, the theory of magnetism has progressed more slowly. The reason why early theoretical models were not valuable must, in some part, be due to the fact that any theory of magnetism must be based on two inherently quantum mechanical concepts: electron spin and the Pauli exclusion principle. As such only the 20th century has produced a competent model for magnetism and that model continues to evolve.

Today the challenge in magnetic materials is directed towards the design and preparation of organic ferromagnets. The purpose of this introduction is to provide a review of the theoretical models that have been proposed in the development of organic ferromagnetic materials and the subsequent experimental and analytical work involved in evaluating these models. It will however be necessary to briefly touch upon the physical properties of magnetism, and on transition metal ferromagnets, in order to provide a greater understanding of the challenge involved in designing organic ferromagnetic materials.

1.0 Basic Facts on Magnetism

The magnetic behaviour of solids is complex and many different types of magnetism can be distinguished: diamagnetism, paramagnetism, antiferromagnetism, ferrimagnetism, ferromagnetism, metamagnetism *etc.* In all cases the ultimate carrier of the magnetic effect is the same, the magnetic moment of the electron. The many different forms of magnetic phenomena arise as a result of the number of ways in which these moments can be coupled together.

In the presence of a magnetic field, magnetic dipoles within a material become partially orientated. The magnetic dipole moment per unit volume is referred to as the magnetisation M . The unit of magnitude of the magnetisation vector M is Am^{-1} . For isotropic substances the magnetic susceptibility χ is defined by $\chi = M/H$ where M and H are the magnitudes of magnetisation and magnetic field vectors respectively.

Diamagnets, Paramagnets and Ferromagnets

These various types of magnetic materials are classified according to their bulk susceptibility. If a substance is diamagnetic, containing only spin paired electrons, the magnetic response opposes the applied field and the magnetic susceptibility is small and negative. In a paramagnetic substance, that is one which contains unpaired electrons, the density of magnetic lines of force within the sample are intensified, therefore χ is small, positive, independent of the magnetic field intensity and decreases with increasing temperature. In a ferromagnetic substance, where all the spins are parallel to one another, χ is positive, large, dependent on the magnetic field, temperature and history of the sample.

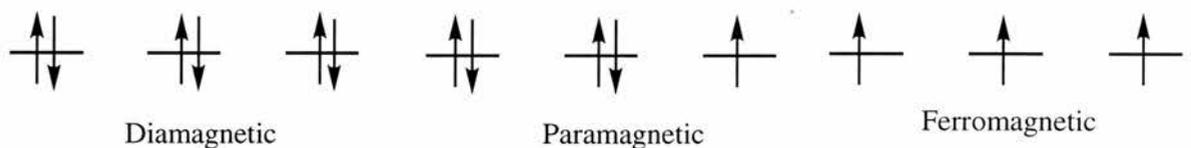


Figure 1. Schematic representation of spin coupling in a diamagnet, paramagnet and ferromagnet.

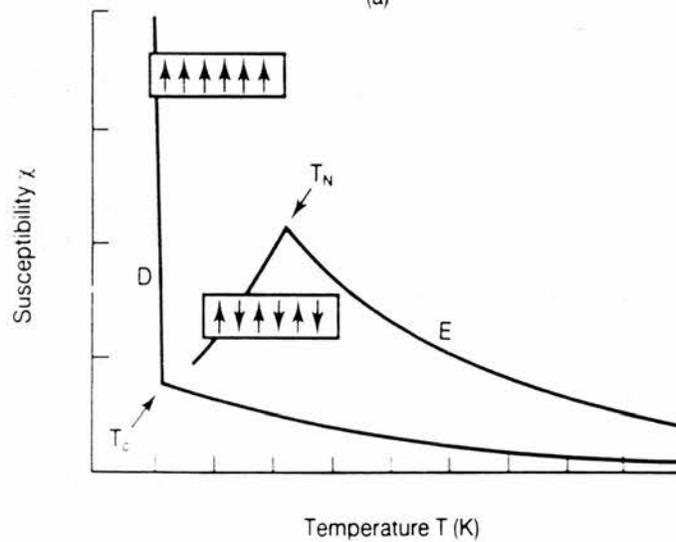
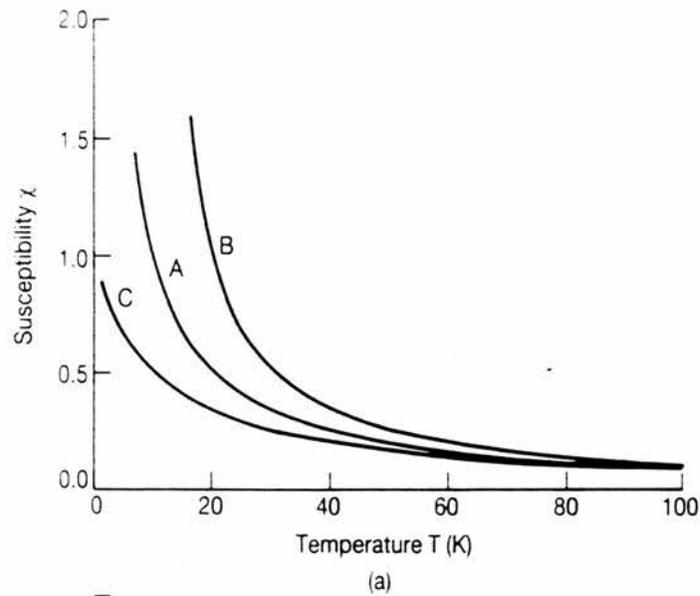


Figure 2 (a) Graphical representation of the Curie law(1.1) and the Curie Weiss law (1.2). Curve A = Curie law, curve B = Curie-Weiss law with $\theta= +10$, curve C = Curie-Weiss law with $\theta= -10$. **(b)** Schematic representation of the susceptibilities of an antiferromagnet and a ferromagnetic polycrystalline substance as a function of temperature. Curve D = thermal variation of the susceptibility for a ferromagnet. Curve E = thermal variation of the susceptibility for an antiferromagnet.

Figure 2 (a) shows the temperature dependence for the susceptibility of a paramagnetic material which can follow either the Curie Law (1.1) or the Curie Weiss law (1.2) in which C and θ are constants and T is the absolute temperature.

$$\chi = C/T \quad (1.1)$$

$$\chi = C/(T-\theta) \quad (1.2)$$

For a pure paramagnet (non-interacting spins) θ is zero and the Curie law applies but if local ferromagnetic coupling exists, θ is positive, whereas local antiferromagnetic coupling (anti-parallel spins) gives a negative value for θ . For substances that show bulk ferromagnetism a transition occurs at a temperature known as the Curie temperature, T_c , leading to a phase in which there is long-range parallel ordering of spins. Below this temperature the susceptibility rises to a very high value, **Figure 2b**. Although ferromagnets below the Curie temperature exhibit long-range ordering of spins a sample may still not behave like a magnet since this ordering occurs within domains. The domains themselves are randomly orientated and cancel each other out, however application of a magnetic field will magnetise the sample. When the field is turned off the magnetisation curve shows hysteresis and the sample retains some magnetisation.

Molecular Magnets

By far the most important class of materials are the ferromagnets. This statement can be made unreservedly both from practical and theoretical viewpoints. The applications which these materials find are very diverse. In engineering applications, for example, ferromagnets are used because of their high permeabilities which enable high magnetic inductions to be obtained with only modest magnetic fields, their ability to retain magnetisation and thereby act as a source of field, and of course torque on a magnetic dipole in a field can be used in electric motors. It is perhaps somewhat surprising that the few ferromagnetic elements in the periodic table should be so technologically vital.

Anticipated Properties of Molecular Magnetic Materials¹

- | | |
|---------------------------|---|
| 1 Insulating | 2 Low density |
| 3 Low magnetic anisotropy | 4 Optical changes |
| 5 Low elastic modulus | 6 Tuning of properties <i>via</i> organic chemistry |
| 7 Processability | 8 Low environmental contamination |
| 9 Solubility | 10 Photo magnetic effect |

Many of the properties given above are a direct consequence of the non-metallic nature of the materials. The first obvious application would be the replacement of existing bulk magnets or magnetic recording devices. The saturation magnetisation, M_s , for molecular/organic based magnets are comparable to metallic magnets on a mole basis. However, their inherently large molecular weights and low densities result in smaller saturation magnetisation on either a volume or mass basis. Furthermore, since bulk magnets are sold on an energy product per volume basis, it is clear that high energy products are unlikely to be achieved and thus molecular magnets are unlikely to compare well with existing magnets.

Materials with magnetic moments parallel to the plane of a film or disk form the basis for magnetic tapes and disks. Increased data density requires larger demagnetisation fields and this produces the need for materials with larger coercive fields such as $[\text{Fe}^{\text{III}}(\text{C}_5\text{Me}_5)_2]^+ [\text{TCNE}]^-$ and so molecular based magnets may be useful as magnetic recording media.

Optical disks, which have a high data density, could be an increasingly important data storage system. Such technology relies upon the magneto-optic effect. A rotation of polarised light is required and the effect is greatest when the magnetic moments are perpendicular to the plane of the substrate. Magneto-optic effects have yet to be studied for an organic/molecular magnet, and therefore molecular magnets remain a potential recording media for optical disks.

As a consequence of their insulating nature a variety of optical properties may be expected i.e. photomagnetic switches and also polarised light manipulation in integrated optical devices. Finally, biocompatibility may lead to several potential applications that include magnetic imaging and transducers for medical implants.

Before beginning this review on molecular ferromagnets we should perhaps ask why the need for such materials exists. The significance of the realisation of organic ferromagnetism cannot be over emphasised. From a theoretical point of view, extended ferromagnetic exchange interactions through *s* and *p* orbitals will be novel and may provide valuable insights into the very phenomenon of magnetism. From a practical point of view, the extensive synthetic flexibilities offered by organic systems will enable the fine tuning of solid state magnetic characteristics. The fabrication of electronic devices at a molecular level is an area of intense research activity with tempting possibilities of application in modern computer technology.² Similar development of molecular magnetic systems will be of immense technological value.

1.1 Magnets Based on Transition Metal Complexes

The mechanism of spin-coupling in molecular magnets differs from that in metals like iron. There are two distinct mechanisms: direct exchange and indirect, or superexchange. A relevant example of direct exchange is Hund's rule of maximum multiplicity.³ This 'rule' predicts that atomic carbon will have a triplet ground state. Four of its six electrons are spin paired (in 1*s* and 2*s* orbitals) but the two remaining electrons which occupy degenerate 2*p* orbitals, are predicted to have parallel spins. Hund's rule is also applicable to molecular and intermolecular situations; however, it must be applied with caution. In atomic, molecular or intermolecular situations, the interaction which lies behind the rule is only significant if the half-filled orbitals are orthogonal but represent electron distribution which overlap significantly in space. This 'orthogonal but co-extensive' requirement is always met for co-centred atomic orbitals.

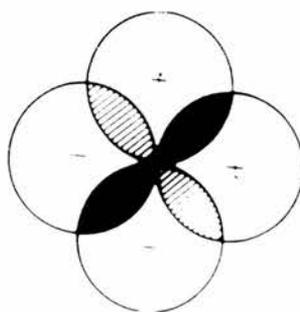
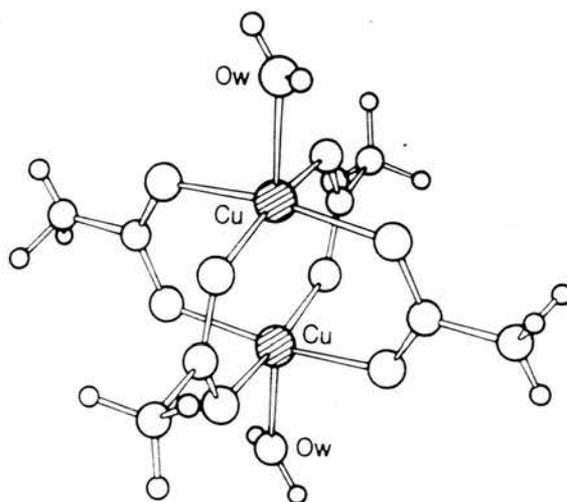


Figure 3, Singly occupied 2*p* orbitals of atomic carbon exhibiting co-extensive, orthogonal orbitals.

This interaction is not always fulfilled between molecular orbitals and so the rule can break down. One of the main themes of research into high spin organic compounds has been the limitation of Hund's rule in situations where direct exchange dominates. However, the study of polynuclear transition metal complexes has shown a very different problem, namely that a strong coupling of spins was observed over distances which were too great to be attributed to direct interactions between half filled metal ion *d*-orbitals. In cases where this exists the interaction is mediated through the ligands and the mechanism of spin-interaction is known as superexchange. An example of this type of interaction can be observed in the copper acetate complex, 1.

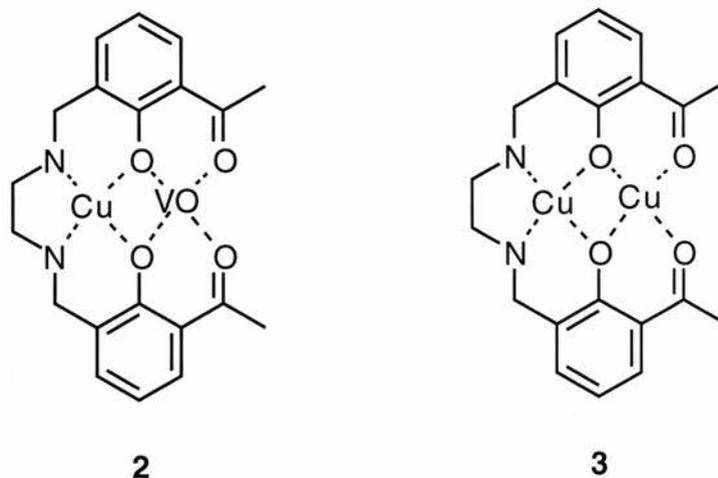


1

The crystal structure of this compound shows that it contains isolated pairs of copper ions which interact strongly through exchange forces, each pair forming a low energy singlet and a high energy triplet state. This interaction does not occur through direct bonding but through the acetate ligands.

These ligand-mediated 'superexchange' interactions have been the subject of a detailed systematic study by Kahn,⁴ who chose to study bimetallic complexes. The sign and strength of interaction varies widely from system to system but, similar to direct exchange, it depends

ultimately on the symmetry of the 'magnetic' orbitals and their overlap density. For example, comparison of the two complexes $\text{CuVO}(\text{fsa})_2\text{en}\cdot\text{CH}_3\text{OH}$ **2** and $\text{CuCu}(\text{fsa})_2\text{en}\cdot\text{CH}_3\text{OH}$ **3**, where $(\text{fsa})_2\text{en}^{4-}$ is the bichelating ligand derived from the Schiff base *N,N*-(2-hydroxy-3-carboxybenzylidene-1,2-diamine).



In each of these compounds the magnetic sites interact ($\text{Cu}(\text{II}), s = 1/2$ and $\text{V}(\text{IV})\text{O}, s = 1/2$) to give rise to a singlet and a triplet ground state. In compound **3** the orbitals have the same symmetry and overlap leading to a singlet ground state ($J = -650 \text{ cm}^{-1}$). In compound **2** however the orbitals are orthogonal and co-extensive. This stabilises the triplet which becomes the ground state ($J = +120 \text{ cm}^{-1}$). Kahn⁵ has developed this strategy in the design of bimetallic chains containing metal ions of differing spins, held together by bridging ligands. This approach produced one of the earliest true molecular magnets namely $\text{MnCu}(\text{pbaOH})(\text{H}_2\text{O})_3$ ($\text{pbaOH} = 2\text{-hydroxy-1,3-propanediylbis(oxamato)}$) [$T_c = 4.6 \text{ K}$]. Its structure consists of alternating bimetallic chains assembled within the crystal lattice in such a way that along the chain axis the shortest interchain separations are $\text{Mn}\cdots\text{Cu}$ instead of $\text{Mn}\cdots\text{Mn}$ and $\text{Cu}\cdots\text{Cu}$, **Figure 4**. This strategy is reminiscent of an idea put forward by McConnell as early as 1963.⁶ The overall ferromagnetic coupling between the ferrimagnetic chains occurs through the interaction between strong positive and weak negative spin densities belonging to the neighbouring chain. The positive and negative spin densities are provided by $S_{\text{Mn}} = 5/2$ and $S_{\text{Cu}} = 1/2$ respectively. The $\text{Mn}(\text{II})\text{-Cu}(\text{II})$ interaction through the oxalato bridge is indeed strongly antiferromagnetic. This interpretation is substantiated by the fact that

$\text{MnCu}(\text{pba})(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}$ does not order ferromagnetically due to the fact that the shortest interchain interactions are now $\text{Mn} \cdots \text{Mn}$ and $\text{Cu} \cdots \text{Cu}$.

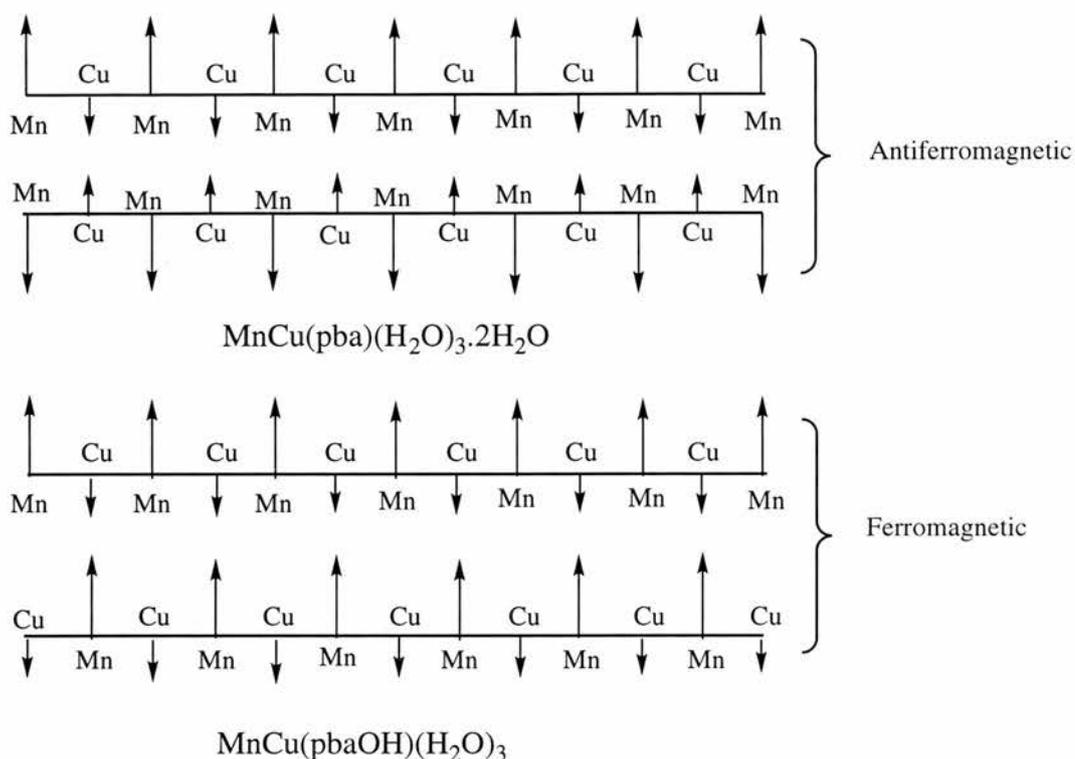


Figure 4

Gatteschi developed this idea by choosing ligands which contain free radicals, namely nitroxides, and investigated the interactions between metal ions and the stable organic radicals.⁷ When the nitroxide binds through its oxygen atom to a paramagnetic metal ion, the spins can orientate themselves anti-parallel to one another or preferentially parallel to one another resulting in ferromagnetic coupling. The sign of the coupling of a nitroxide directly bound to a metal ion is again dependent on orbital overlap considerations as shown in **Figure 5**, where only the top left interaction is orthogonal and co-extensive.

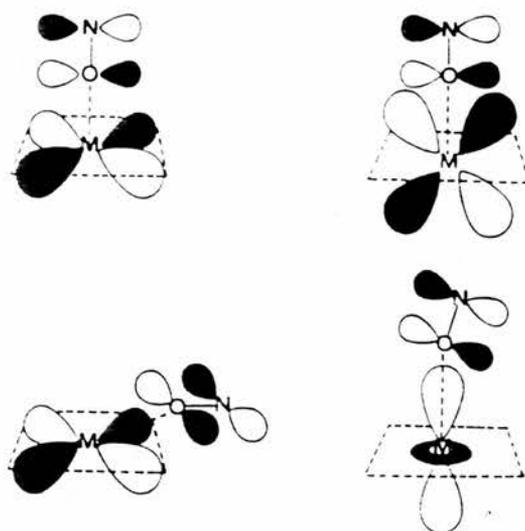
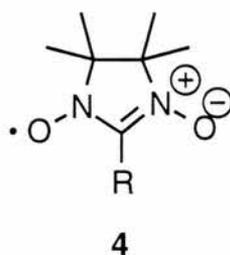


Figure 5

Simple nitroxides can interact with only one metal ion at a time and therefore cannot readily form extended magnetic structures. Gatteschi synthesised a series of compounds using the bridging bidentate nitronyl nitroxide ligands i.e. 2-alkyl-4,4',5,5'-tetramethylimidazoline-1-oxyl-3-oxide, [NIT(R)], **4**.⁸



If the two oxygens present in the NO groups bind to two different metal ions a polymeric structure can be formed, with effective pathways to transmit the magnetic interactions between the metal ions, leading to polymeric chains in which there are alternating spins on the metal and on the ligand. Gatteschi discovered that above 20K the manganese centres complexed to hexafluoroacetylacetonate (hfac) ligands where R = *i*-Pr, Et or *n*-Pr behave as typical ferromagnetic chains, but at low temperatures [$T_c = 7.6, 8.1, 8.6$ K for R = *i*-Pr, Et, *n*-Pr] a

three dimensional ferromagnetic ordering occurs and the magnetic moment rapidly increases. The ferromagnetic phase transition observed has been attributed to dipolar interactions between chains. A lower transition temperature was observed for the analogous Ni complexes and this can be explained by the smaller spin of nickel which makes the dipolar interaction less effective. The interaction between metal ions and radicals is very strong within the chains but unfortunately the chains are very well shielded from one another. Since ferro- or ferri-magnetic order can be achieved only in three dimensions, because one dimensional materials can order only at 0K, the critical temperatures can only be increased if the interactions between the chains are enhanced. In order to do this Gatteschi chose to either introduce additional donor atoms on the NIT(R) radicals in order to increase the number of metal ions to which an individual radical can be bridged or by using co-ligands other than hfac, which favour the formation of adducts between the metal ions and the weak radical ligands but very efficiently shield the chains from one another. The most encouraging results were in the case of $\text{Mn}[(\text{pfbz})_2]_2\text{NIT}(\text{R})$, pfbz = pentafluorobenzoate, and R = Me or Et, which orders magnetically at temperatures as high as 20K. The nature of the phase transition is not clear, however, there is evidence that they behave as weak ferromagnets.⁷

1.2 Models for Organic Molecular Magnets

This section will review the key models proposed for the development of an organic ferromagnet and the experimental work involved in evaluating these models.

Negative Spin Density Product Model

The earliest proposal for achieving ferromagnetic interactions between organic free radicals was put forward by McConnell in 1963⁹. McConnell stated that 'radicals with large positive and negative atomic π -spin densities which pancake such that atoms with positive spin density are exchange coupled to atoms with negative spin density should result in a ferromagnetic exchange interaction'. McConnell's model therefore relies upon the construction of a crystal

lattice of radicals in such a way that atoms with opposite spin densities are aligned side by side for each pair of radicals, **Figure 6**.

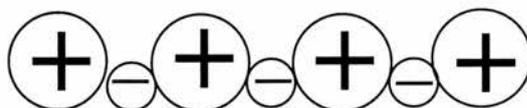


figure 6, Schematic representation of the ideal alignment of spin densities in the McConnell model.

The overall exchange interaction between two aromatic radicals A and B with spins S_A and S_B can be approximated by the Hamiltonian.

$$\langle H \rangle = -JS_A S_B = \sum J_{ij}^{A^B} * S_i^A S_j^B$$

Where S_i^A and S_j^B are the π electron spins on atoms i and j of molecules A and B respectively. McConnell's argument is based on the fact that the exchange interaction between atoms is ferromagnetic if J_{ij}^{AB} and the product $S_i^A S_j^B$ have the same sign. Since the largest exchange interactions J_{ij}^{AB} are usually negative, the product $S_i^A S_j^B$ should be negative by design if the interaction is to be ferromagnetic. This is possible if some atoms on A and B have negative spin densities and the orientations of A and B are such that spin densities of opposite signs couple most efficiently. Thus the trick is to exploit an inherently antiferromagnetic coupling to produce ferromagnetism.

The mechanism described above relates to pairwise ferromagnetic exchange, not bulk ferromagnetism which requires ferromagnetic exchange in three dimensions. To achieve ferromagnetic exchange, routes to spin pairing must be avoided. This requires the use of stable free radicals such as tetracyanoethylene [TCNE] $^{\bullet-}$ or tetracyano-*p*-quinodimethane [TCNQ] $^{\bullet-}$ radical anions which do not easily dimerise and contain atoms with unequal positive and negative spin densities such that it is conceivable that they might form a structure that complies with McConnell's requirement.¹⁰ However, of the numerous structures reported, the overlap required to satisfy the McConnell model has never been achieved. Even stable radicals undergo dimerisation to form diamagnetic species.¹¹ A number of competing reactions such as

carbon-carbon bond formation between $C(CN)_2$ moieties on adjacent TCNQ molecules have also been reported.¹² Cleverly designed stable radicals with the proper solid state packing were synthesised by Izuoka *et al.* in order to test McConnell's model, **Figure 7**.¹³

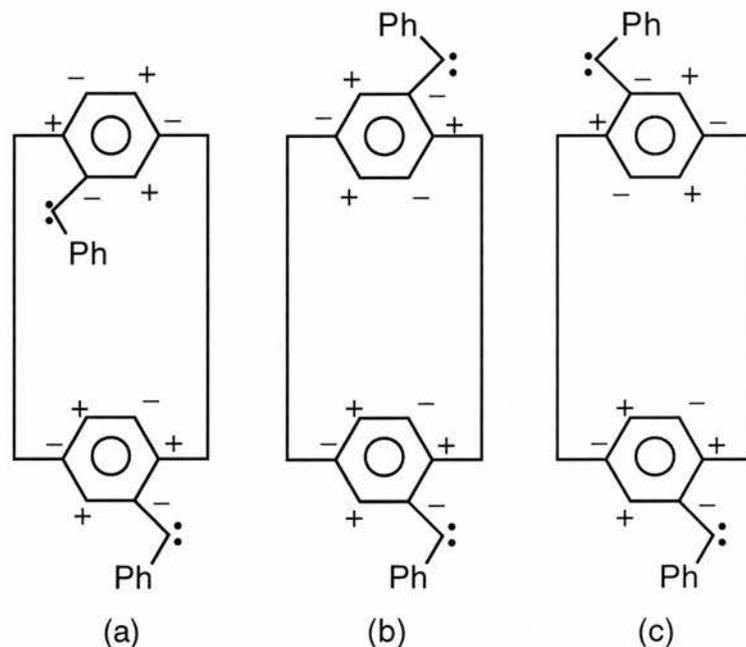


Figure 7, Showing (a) the *pseudo-ortho*, (b) *pseudo-meta* and (c) *pseudo-para* bis(phenylmethylene)[2,2-*para*-cyclophanes].

Among the three isomers of bis(phenylmethylene)[2,2-*para*-cyclophanes] only the *pseudo-ortho* and *pseudo-para* isomers satisfy McConnell's condition in that the sign of the spin density product at each interacting site is negative, leading to ferromagnetic coupling of the two triplet carbenes and a quintet ground state as observed by ESR. The overlapping mode in the *pseudo-meta* isomer leads to antiferromagnetic coupling and hence a singlet ground state. This provided the first experimental demonstration that the spin distribution of the π electrons in the layered benzenoid can determine the ferro- or antiferromagnet interaction between carbene units.

Charge Transfer Complexes

In 1967, at a Robert Welch Foundation Conference, Mulliken delivered a lecture on charge transfer complexes.¹⁴ In normal ion radical charge-transfer solids, intermolecular spin pairing (antiferromagnetism) is a result of the mixing of a ground state and a singlet back charge-transfer state of a charge transfer pair, **Figure 8**.

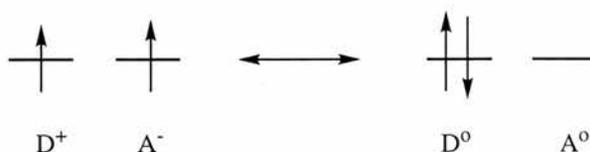


Figure 8

Following Mulliken's lecture McConnell proposed a detailed model utilising specific charge transfer complexes to produce molecular ferromagnets.¹⁵ McConnell claimed that if an ionic charge transfer pair (D^+A^-) could be built that had a back charge-transfer excitation to a neutral triplet state rather than a singlet state then the D^+A^- pair could also be a triplet due to mixing of the charge transfer state with the ground state, **Figure 9**.

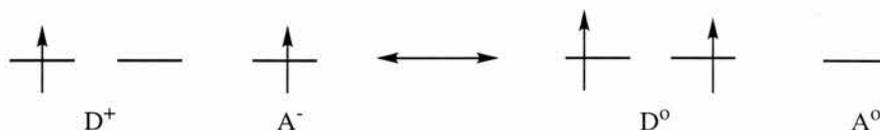


Figure 9

If this mixing of a high spin arrangement is present between adjacent donors and acceptors in a multi-dimensional array within a solid, then macroscopic parallel alignment and thus ferromagnetic behaviour of solids should be possible. Although Mulliken's lecture and McConnell's theories were published they were not widely available and as a result remained largely unknown until the work of Miller and Epstein¹⁶ and also Breslow¹⁷ and co-workers.

The essence of McConnell's model is that if an excited state, E_s , with $m_s = 1$ arising from either a $m_s = 1$ donor D , or a $m_s = 1$ acceptor A , but not both, formed by either virtual retro charge-transfer ($D^0 + A^0 \leftarrow D^{\bullet+} + A^{\bullet-}$ or virtual forward ($D^{2+} + A^{2-} \leftarrow D^{\bullet+} + A^{\bullet-}$) charge transfer, admixes with the ground state, GS, then ferromagnetic coupling will be stabilised. The model relies on four basic criteria being fulfilled.

- (i) Formation of a complex of the type $A^{\bullet-}, D^{\bullet+}$ where $A^{\bullet-}$ is the radical anion of the acceptor and $D^{\bullet+}$ the radical cation of the donor.
- (ii) Crystallisation as mixed $(A^{\bullet-}, D^{\bullet+})_n$ not discrete $(A^{\bullet-})_n$ and $(D^{\bullet+})_n$ stacks.
- (iii) Significant admixture of the excited state A^{2-}, D^{2+} .
- (iv) Either A^{2-} or D^{2+} to be a ground state triplet species.

By using Hund's rule as applied to molecules and biradicals¹⁸ the lowest energy excited state that can virtually admix with the ground state can be identified enabling the prediction of the magnetic coupling.¹⁹ McConnell's model is best illustrated by considering a doubly degenerate partially occupied molecular orbital (POMO) containing three electrons i.e. d^3 which acts as the radical cation donor and a radical anion acceptor, $A^{\bullet-}$, with a non degenerate s POMO containing one electron. For this $D^{\bullet+}/A^{\bullet-}$ pair in the absence of spin interactions two ground states (ferromagnetic and anti-ferromagnetic) are possible, **Figure 10**. They exist at equal energy and lead to simple paramagnetic behaviour.

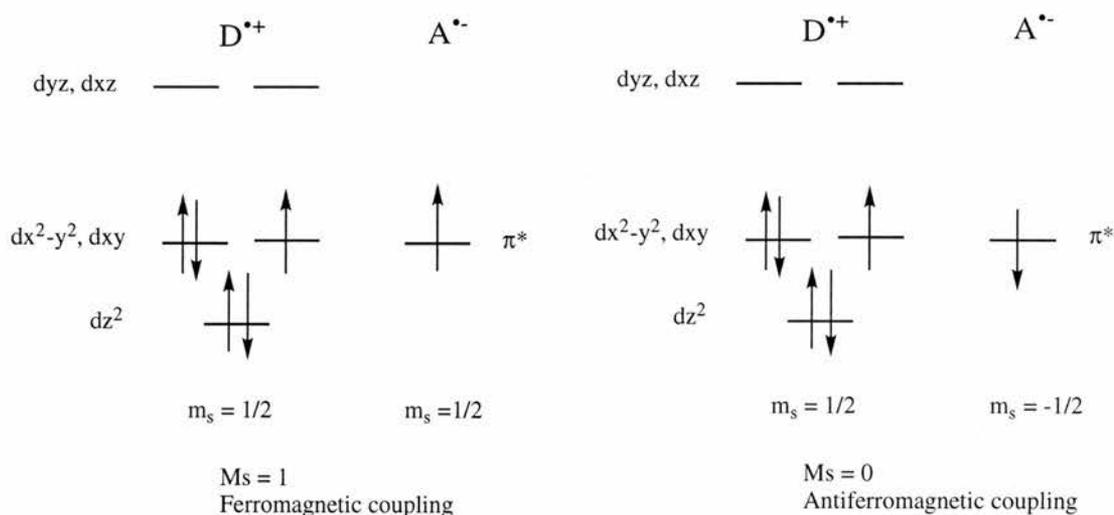


Figure 10

Spin interactions between the ions can lead to lowering of the ferromagnetic ground state, GsFC or antiferromagnetic ground state, GsAF. The ground state lowered is the one with the greatest probability of admixing with the lowest energy virtual charge transfer excited state. Magnetic coupling can therefore be predicted for a specific direction of charge transfer. For example if retro charge transfer occurs ($A^{\bullet-} \rightarrow D^{\bullet+}$), $D^{\bullet+}$ can only accept a $m_s = -1/2$ electron and GsAF has a $m_s = -1/2$ electron whereas GsFC does not, hence the admixture of the EsAF $A \rightarrow D$ will lower the GsAF leading to antiferromagnetic coupling, **Figure 11**.

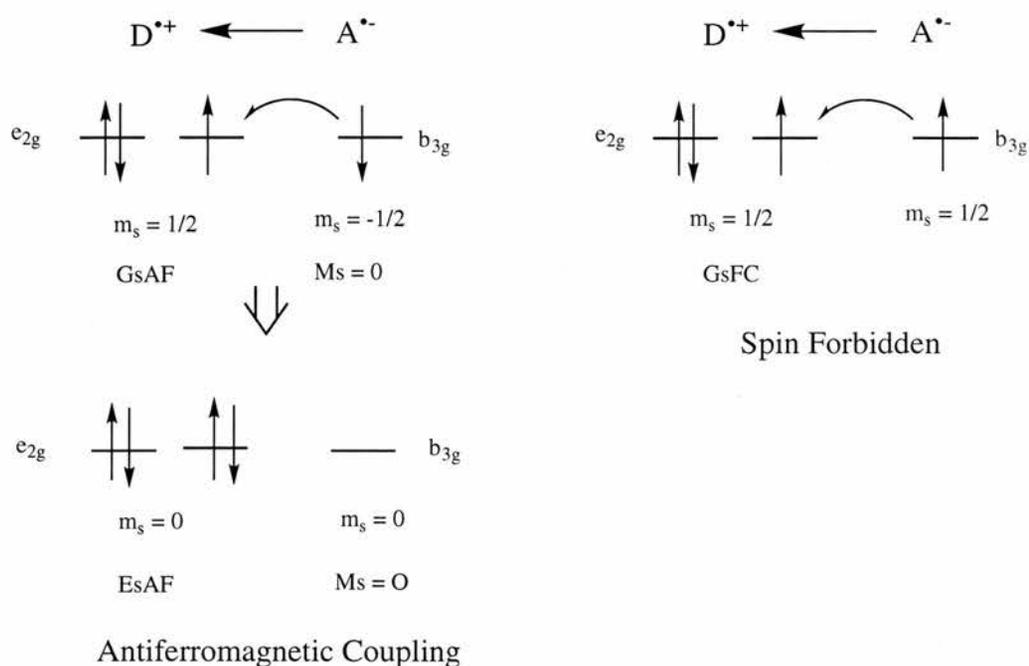


Figure 11

For virtual forward charge transfer, excited states $EsFC^{D \rightarrow A}$, $EsAF^{D \rightarrow A}$, and $EsAC^{D \rightarrow A}$ are possible, **Figure 12**. From Hund's rule the most easily lost $D^{\bullet+}$ electron has $m_s = -1/2$ and can only be transferred to the ferromagnetically coupled $A^{\bullet-}$, **Figure 12 (a)**. Transfer of a $m_s = 1/2$ electron to an antiferromagnetically coupled $A^{\bullet-}$ requires admixture of higher excited states, **Figure 12 (b) and (c)**. Thus forward charge transfer to the ferromagnetically coupled ground state may lead to ferromagnetic behaviour.

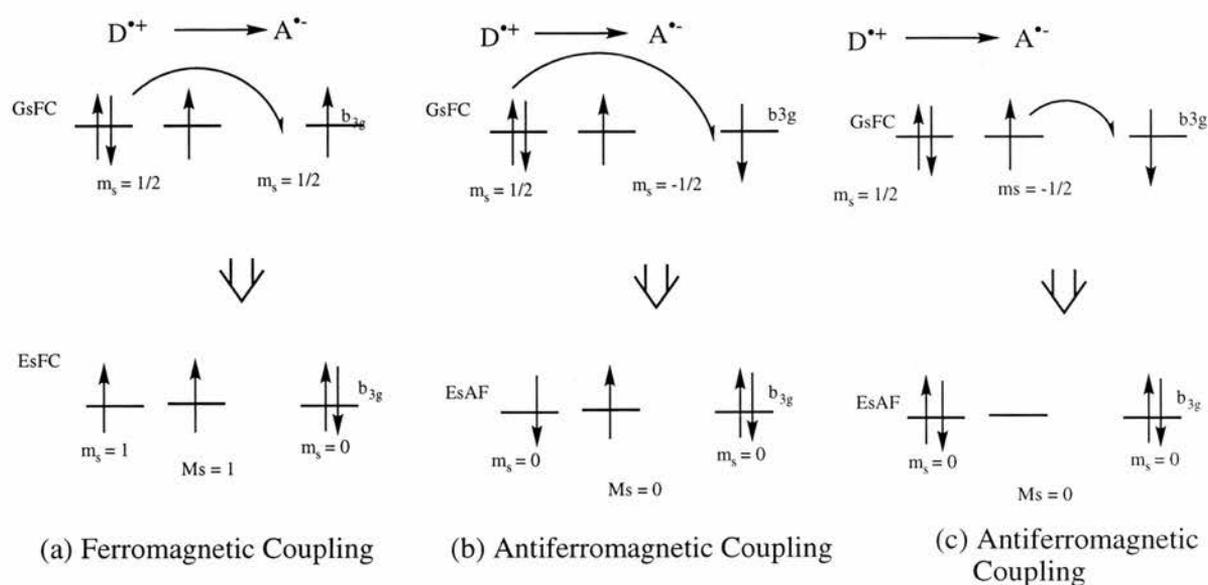
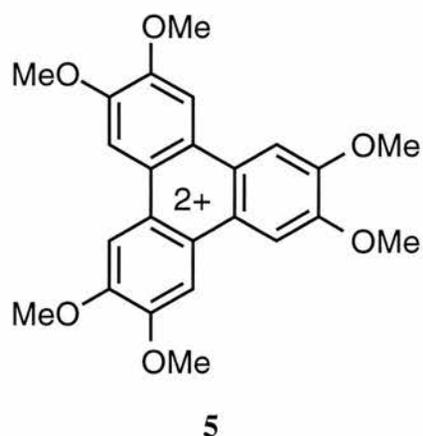


Figure 12

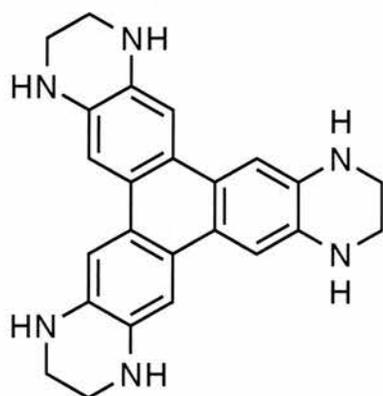
The seminal example of this was observed in $[\text{Fe}^{\text{III}}(\text{C}_5\text{Me}_5)_2]^{\bullet+}[\text{TCNE}]^{\bullet-}$ in which bulk ferromagnetic behaviour was observed ($T_c = 4.8\text{K}$).²⁰ According to the McConnell mechanism the driving force behind its ferromagnetism is the triplet ground state character of $[\text{Fe}^{\text{III}}(\text{C}_5\text{Me}_5)_2]^{2+}$. This leads to ferromagnetic coupling between $[\text{Fe}^{\text{III}}(\text{C}_5\text{Me}_5)_2]^{\bullet+}$ and $[\text{TCNE}]^{\bullet-}$ both within the stack and between out of registry adjacent stacks giving the full three dimensional coupling of spins required for bulk ferromagnetism. Although the application of the McConnell mechanism to these systems has been challenged,²¹ it provides a simple rationalisation, if the direction of charge transfer is known, to the nature of magnetic coupling.

Since McConnell's initial model there have been many modifications in an attempt to enhance the ease with which molecules could be synthesised to prove or disprove the model. Breslow suggested an improvement to the McConnell model in 1982.¹⁶ This model stemmed from Breslow's earlier work on cyclic conjugated systems with $4n \pi$ electrons which led him to propose that $4n \pi$ electron cyclic conjugated systems could have the potential to behave as ground state triplets providing these systems have C_3 or greater symmetry. The symmetry of such molecules leads to degeneracy in some molecules, while the presence of $4n \pi$ electrons leads to half occupancy of a degenerate orbital pair and consequent spin unpairing and single occupancy of each orbital. However, there is no guarantee that a symmetrical $4n \pi$ molecule will have a triplet ground state and therefore Curie Law studies must be performed to ensure

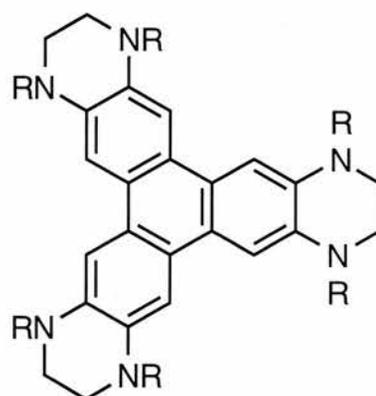
the ground state is not a singlet. Species such as $C_5H_5^+$ and $C_5Cl_5^+$ were known to have triplet ground states, however these molecules are chemically unstable. Breslow then synthesised triphenylene derivatives following a report by Parker in which it was claimed hexamethoxytriphenylene (HMT) dication **5** was a ground state triplet.²²



The (HMT) dication has no real chemical stability and to form the dication requires high positive potentials, limiting the search for suitable anion acceptors. Breslow modified this molecule producing various hexaaminotriphenylene derivatives, **6** and **7**, which have greater stability and form the relevant dication at much lower potentials i.e. ($HET \rightarrow HET^{2+} 0.271 V$) compared to ($HMT \rightarrow HMT^{2+} 0.85 V$), $HET = 2,3,6,7,10,11$ -tris(N,N' -diethylenediamino)triphenylene.

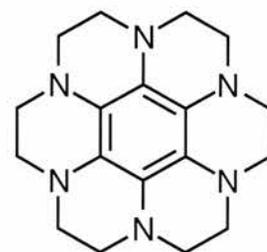


6



HET

7



HOC

8

Breslow claimed these molecules were ground state triplets and these dications were subsequently used in tests of Breslow's own model. When these dications have triplet spin multiplicity a forward charge transfer from D^+A^- to $D^{2+}A^{2-}$ is required, **Figure 13**.

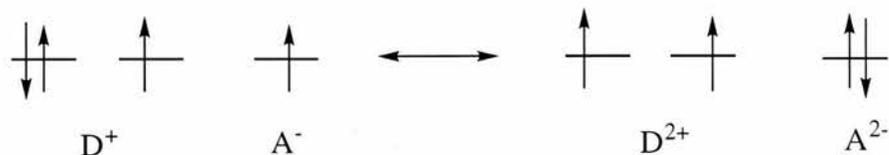
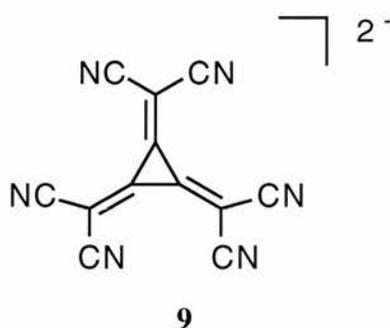


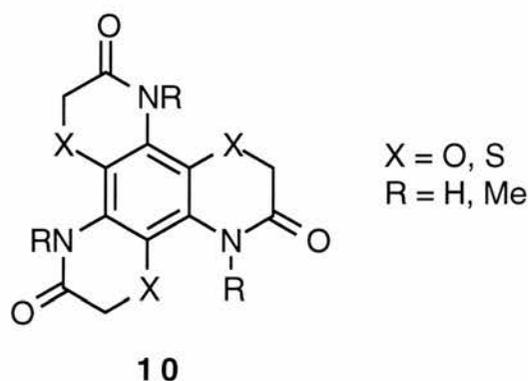
Figure 13

This leads to greater charge on the molecules than McConnell's original proposal and favours the alternating donor-acceptor stacking required for donor-acceptor mixing. The interactions of donor and acceptor in the solid must favour substantial forward transfer and disfavour back charge transfer such that the neutral singlet charge transfer configuration is high in energy. For forward charge transfer to occur the donor and acceptor must be of similar potentials. It is also crucial that the donor has a stable triplet as one of its redox forms. The preference is for as large a triplet-singlet energy gap as possible in order to stabilise the spin parallel arrangement. Most challenging is maintaining the threefold symmetry of the donor which effectively provides the degeneracy. To examine this model Breslow used the hexacyano compound **9** as an acceptor.

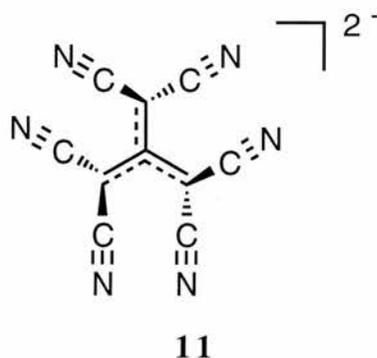


This required alteration of the donor, $R = Et$ being replaced by the more electron withdrawing $R = CHF_2CH_2$ in order to match the donor/acceptor potentials, thus providing the correct amount of charge transfer in the solid. Despite satisfying the conditions of the model, namely

alternating donor-acceptor stacking, partial second charge transfer and a triplet donor cation, the material was found to exhibit antiferromagnetic coupling. This may be a result of the instability of the triplet ground state of the donor, a loss of degeneracy resulting from a loss of symmetry of the donor in the complex (i.e. Jahn Teller distortion) favouring the singlet ground state or the intermolecular interactions may not be general or multidimensional enough. Breslow²³ turned his attention to hexaazaoctadecahydrocoronene, **8** (HOC), which has a larger gap between singlet and triplet energy states and also HET variants such as **10** since sulphur atoms on the edge of electrically conducting organic stacks can facilitate sideways interactions between the stacks. However the non-planarity of these systems made them much more difficult to oxidise.



The dication of HOC was prepared and its role in charge transfer complexes investigated by Miller²⁴ and co workers who found that crystalline salts of $[\text{HOC}]^{2+}$ with $(\text{C}[\text{C}(\text{CN})_2]_3)^{2-}$, **11** and $(\text{C}_3[\text{C}(\text{CN})_2]_3)^{2-}$ were in fact ground state singlets and that $[\text{HOC}]^{+\bullet}[\text{TCNE}]^{\bullet-}$ showed strong antiferromagnetic interactions.



Another modification of McConnell's model was proposed by Torrance²⁵ who suggested that a stack of highly symmetric radicals could have spins in degenerate orbitals which should have a triplet excited state as a consequence of the radical cation/anion of the molecule which has the appropriate filling, **Figure 14**.

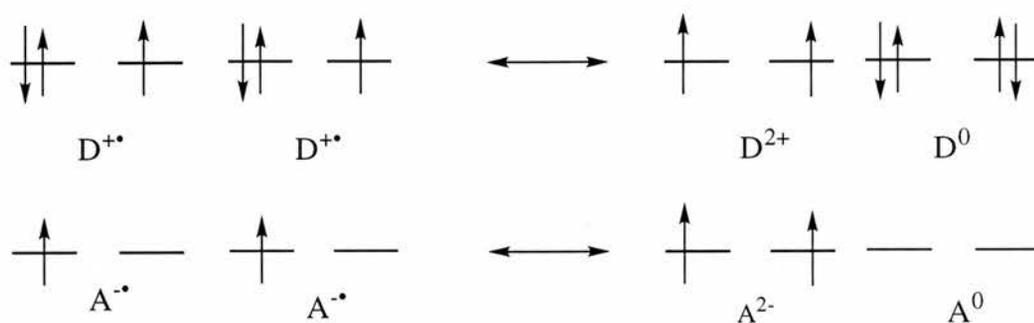
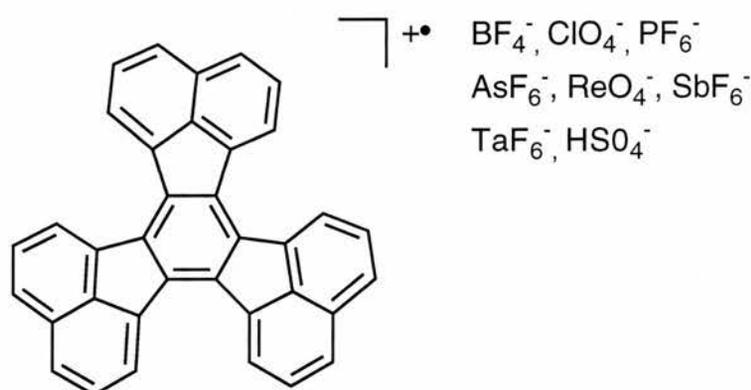


Figure 14



12

Torrance made stable radical cation salts of decacyclene, **12**, with the anions shown. These salts have the stoichiometry (decacyclene)₃X₂ where X is the anion. Magnetic susceptibility measurements revealed that these materials were not ferromagnetic. This may be due to unknown complications in the structure of the complex, distortions of the structure which destroy the symmetry, the width of the band formed by orbital overlap being too large compared to Hund's rule, intraatomic exchange, or there may be complicating effects such as spin orbit interactions. Breslow's compounds were ideal candidates for Torrance's model but were found to be anti-ferromagnetic.

Torrance also suggested linking together symmetric molecules in a way which maintained symmetry, **Figure 15**, which could then be oxidised to produce spins.²⁶

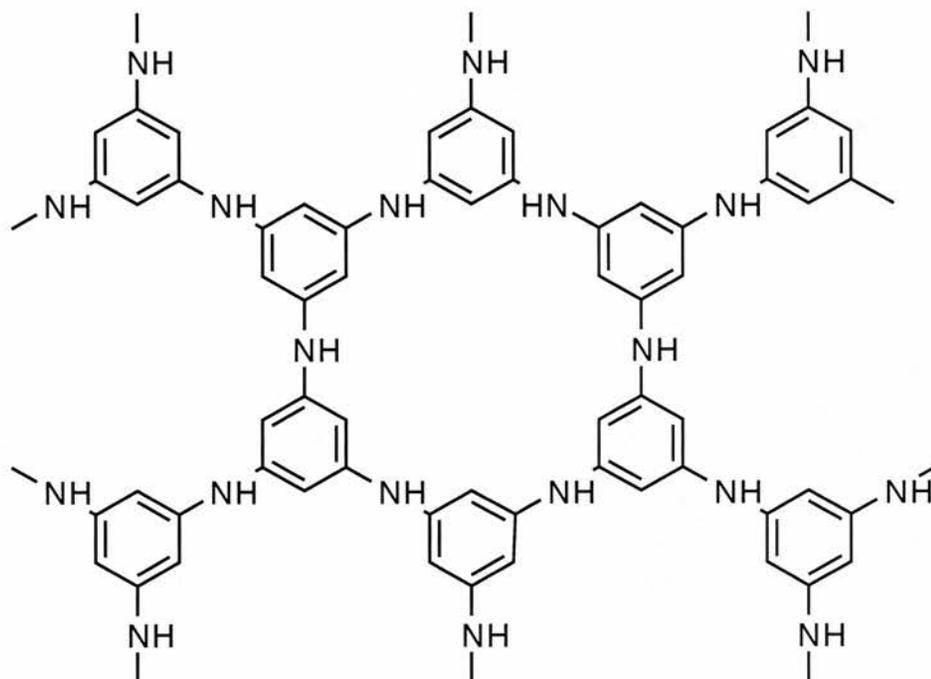


Figure 15

Torrance claims that such a molecule may have been produced in the reaction of triaminobenzene with iodine which yielded a black insoluble polymer which on rare occasions showed the presence of small amounts of ferromagnetic material however these results proved irreproducible.

Soos and co-workers attempted to extend the superexchange mechanism established in inorganic solids to organic stacked complexes.²⁷ In a mixed $R^{\bullet}SR^{\bullet}S$ stack, an excited triplet state may be obtained if the spacer molecule S has degenerate orbitals into which the radical R^{\bullet} spins are transferred during virtual excitation, **Figure 16**. This requires the orbital degeneracy of S to be maintained in the solid complex and this is only possible if the orientation of R^{\bullet} is such that the perturbations on the degenerate MO's of S are equal. A spacer with degenerate HOMO or LUMO should allow ferromagnetic coupling *via* charge transfer

when radicals are orthogonal to each other. Soos used ion radicals based on strong organic donors such as N,N,N',N'-tetramethyl-*p*-phenylene diamine (TMPD) **13** and strong organic acceptors such as tetracyanoquinodimethane (TCNQ) **14**.

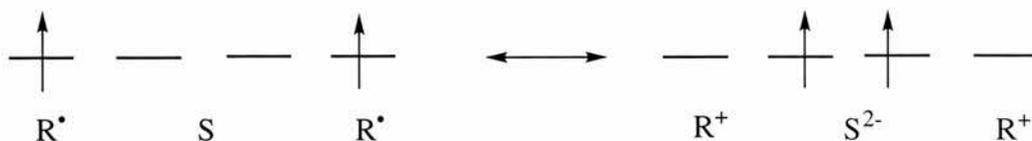
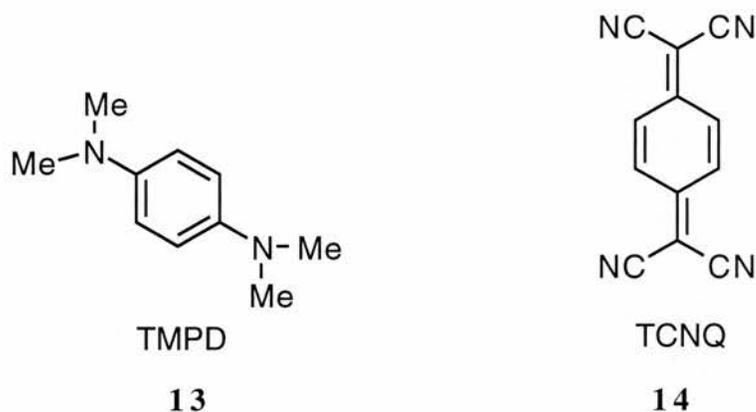
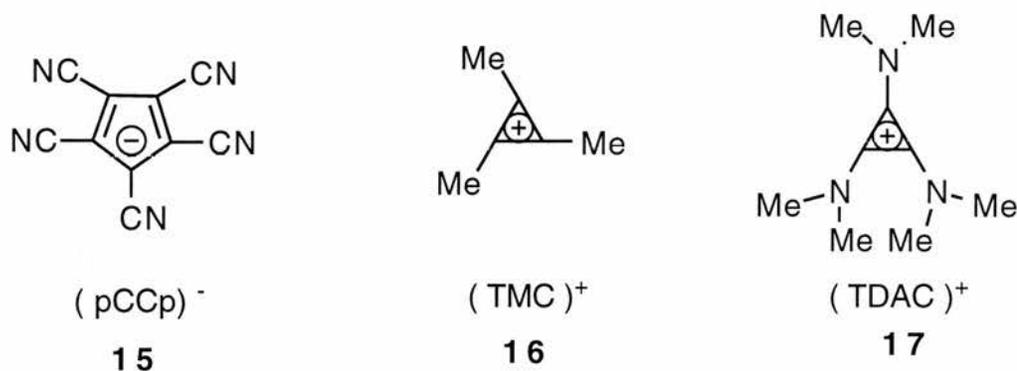


Figure 16

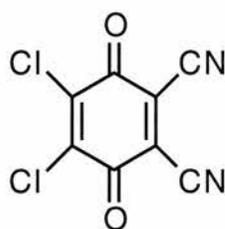


Appropriate spacers for the ion radicals are closed shell anions X^- like pentacyanocyclopentadienide (pCCp) **15** which has a degenerate HOMO or cations X^+ such as trimethylcyclopropenium (TMC) **16** or tris(dimethylamino)cyclopropenium (TDAC) **17** which have degenerate LUMO's.



The coulombic interactions present should promote mixed stacking $D^+X^-D^+X^-$ or $A^-X^+A^-X^+$. The preparation of a TMPD:pCCp complex in which the dihedral angle was 41° rather than the

required 90° resulted in weakly antiferromagnetic interactions.²⁸ Other complexes produced by Soos include a 1:1 TDAC:DDQ (2,3-dichlorodicyanobenzoquinone) complex **18**. This however was found to have a dimerised stacking pattern of $X^+A^-A^-X^+$ by X-ray crystallography ruling out the possibility of superexchange.¹⁹ It was proposed that this was due to the strong tendency of DDQ^- ions to dimerise due to strong dipolar attraction and the exchange interactions of DDQ^- ions. However, replacing DDQ by TCNQ, which does not have a permanent dipole, failed to improve matters.²⁹



DDQ

18

Wudl and co-workers proposed another variation of McConnell's model based on a ferromagnetic organic metal.³⁰ Following work to design molecules which would be stable, neutral diradicals, with the intent of generating neutral organic metals, Wudl suggested that the neutral donor could be a triplet and the acceptor could be the radical ion derived from the donor, **Figure 17**. This would allow the generation of homomolecular stacks which could give rise to ferromagnetic organic molecules.

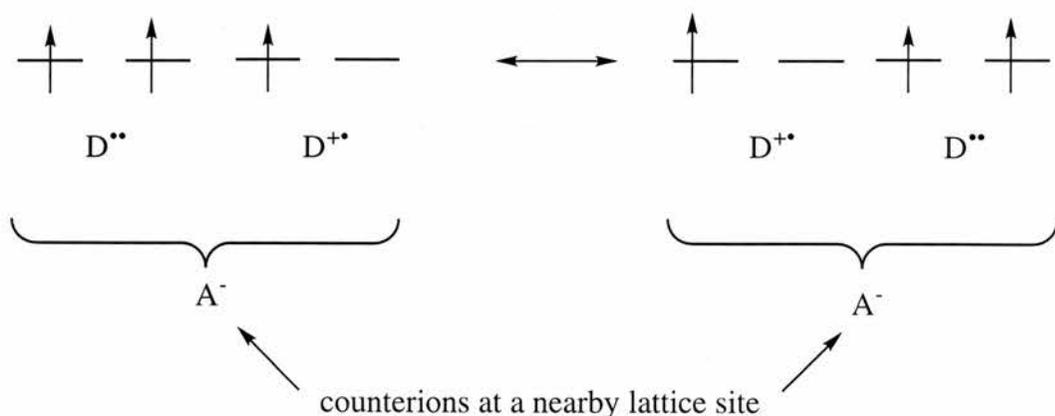
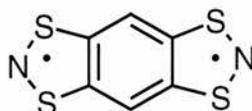


Figure 17

This differed from McConnell's model in that the stoichiometry is D_2A and species either side of the double arrow are identical satisfying the spin conservation rules. Wudl therefore required stable donor radicals which have a triplet ground state and do not dimerise or polymerise. Cross-linking had never been observed in compounds containing a $[-S-N-S]^{\bullet}$ group, prompting a study of benzobisdithiazole **19**.



19

The biradical **19** was found to exist as an oligomer in solution and in the solid state by ESR spectroscopy which also showed that if monomeric forms of **19** existed they would adopt a singlet rather than triplet ground state.

In 1991 it was discovered that buckminsterfullerene exhibited superconductivity upon doping with alkali metals.³¹ Structural studies had shown that interstitial holes in the fullerene's face centred cubic structure could accommodate metal ions³² and cyclic voltammetry had shown that C_{60} and C_{70} could easily be reduced.³³ Theoretical calculations had also determined that the LUMO and HOMO were triply and five fold degenerate respectively.³⁰ It was proposed that such a large number of degenerate levels could lead to unusual electronic and magnetic properties. Wudl utilised the strong acceptor properties in C_{60} to form a 1:1 charge transfer complex with TDAE, **Figure 18**.³⁴

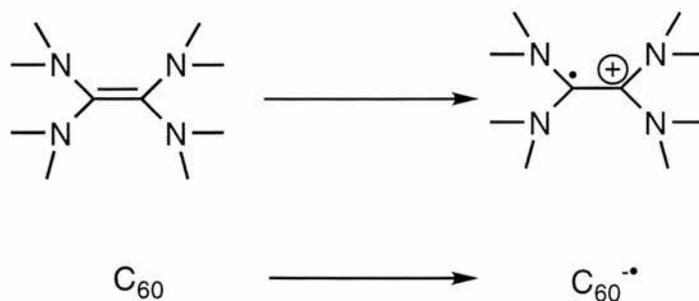
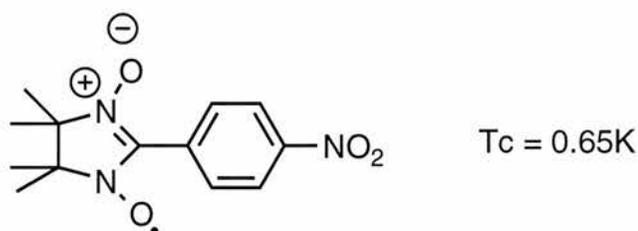


Figure 18

Magnetic susceptibility measurements showed that this complex underwent a transition to a state in which the spins ordered ferromagnetically. These measurements also indicated that at 16K the material showed magnetisation without remanance. This lack of retention of magnetism outside an applied field was thought to indicate a transition to a soft itinerant ferromagnet.

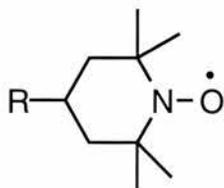
Organomagnetic Materials Based on Nitroxide Radicals

The discovery of *p*-nitrophenyl nitronyl nitroxide, **20**, the first ever organic bulk ferromagnet by Kinoshita and co-worker came in 1991.³⁵



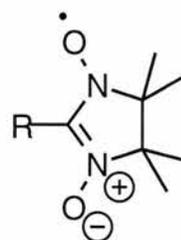
20

Today there are over twenty organic ferromagnets many based on nitroxide containing materials. Nitroxide radicals are fairly stable and can be further stabilised by conjugation with π electrons of aromatic systems or by substitution with bulky substituents. Radicals such as TEMPO **21** and nitronyl nitroxide **22** have been central to the development of organomagnetic materials.



TEMPO

21

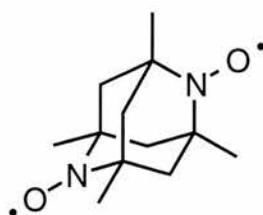


Nitronyl nitroxide

22

The unpaired electrons of nitroxides in singly occupied molecular orbitals (SOMO) are localised mainly on the N-O moiety, delocalised between nitrogen and oxygen and in nitronyl nitroxides, between both NO groups. The general strategy in designing nitroxide containing magnetic materials is to prepare molecules with large intramolecular spin polarisation, minimise the intermolecular overlap integrals between the SOMO's of the unpaired electrons of a radical and the vacant or doubly occupied molecular orbitals of neighbouring molecules.

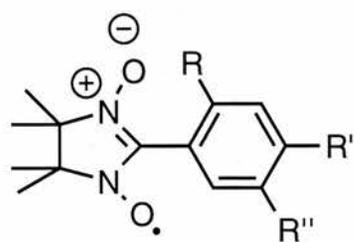
In 1993 Rassat and co-workers suggested that 1,3,5,7-tetramethyl-2,6-diazadamantane-N, N'-dioxyl, **23**, in addition to exhibiting intramolecular ferromagnetic interactions, should also take part in intermolecular ferromagnetic interactions due to the three dimensional network of NO chains.³⁶



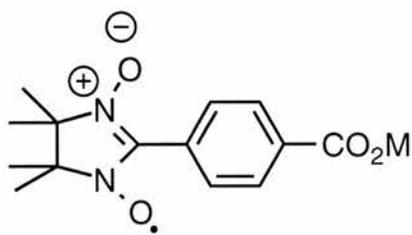
$$T_c = 1.48\text{K}$$

23

Further work followed in an attempt to either arrange the spin sources through hydrogen bonding effects in compounds such as **24**³⁷ or through control of the coulombic interactions.³⁸ Inoue and Iwamura, in compounds **24** and **25**, tried to control the molecular and spin arrangements in these molecules by the interactions with ferromagnetic interactions shown in some of them (**25a** and **25c**).³⁹

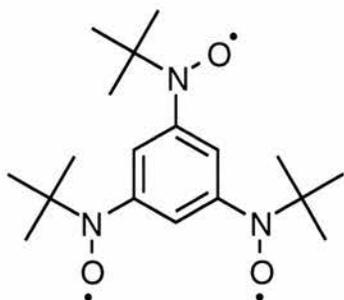


24 R, R'' = OH, R' = H
T_c = 0.5K

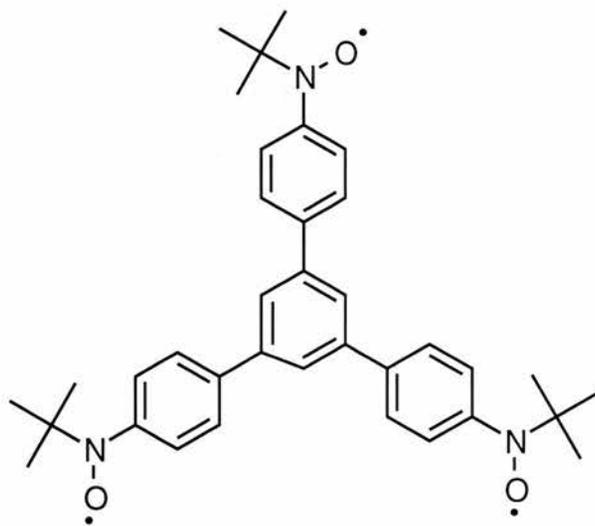


25 a. M = Li
b. M = Na
c. M = K

Multi-spin systems bearing nitroxide radicals have received attention in the design of molecular magnets. Iwamura and co-workers produced the triradicals **26** and **27**.



26



27

They found that compound **27** had a stronger intermolecular spin interaction than **26** and has a quartet ground state.⁴⁰ Despite many other attempts to produce radical crystals with a high T_c value, Rassat's radical which has a T_c = 1.48K remains the highest obtained.

1.3 Charge Transfer Complexes Containing Nitroxide Radicals

Recent attempts to produce charge transfer complexes employing acceptors with donors carrying nitroxide radicals have focused on tetrathiafulvalene (TTF) or aromatic alkyl amine

donors carrying nitroxide radicals, coupled with DDQ or TCNQF₄ acceptors. These have mainly proved unsuccessful in producing ferromagnetic charge transfer salts. Sugimoto *et. al.* succeeded in developing a ferromagnetic charge transfer salt based on pyridinium substituted imadizolin-1-oxyl with TCNQF₄ or hexacyanobutadiene acceptors, **Figure 19**.⁴¹

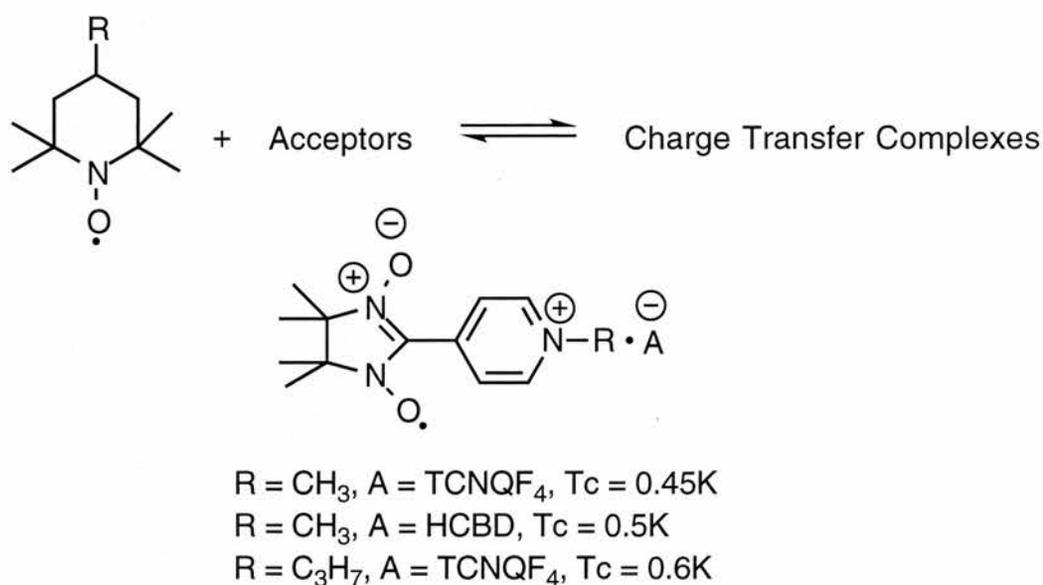
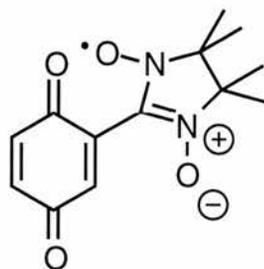


Figure 19

Limited success has also been achieved using acceptor molecules, most commonly benzoquinone derivatives, to carry stable nitroxide radicals. Sugawara and co-workers observed ferromagnetic interactions in a radical anion salt carrying nitronyl nitroxide **28**, in the absence of a donor, i.e. the nitroxide radical itself acts as a donor.⁴²



28

Nakatsui and Awzai investigated⁴³ alkylamino-TEMPO derivatives **29a-d** by the reductive amination of 4-oxo-tempo with alkyl amines using sodium cyanoborohydride, **Figure 20**.⁴⁴

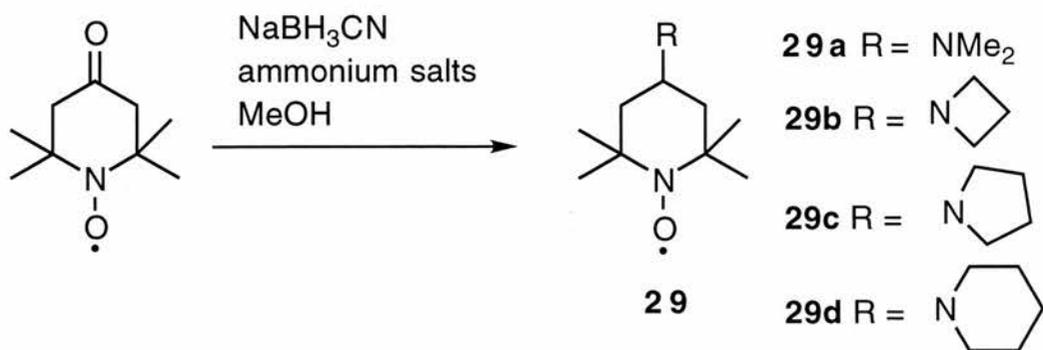


Figure 20

Compound **29d** exhibited ferromagnetic interactions with a Weiss constant of 0.5K.

1.4 Topological Model

The topological model can be simply explained by considering the trimethylenemethane biradical first reported by Dowd⁴⁵ as a ground state triplet. This can be thought of as two methyl radicals connected 1,1 to ethylene. Alternatively two methyl radicals can be connected 1,2 to ethylene (butadiene) which is a ground state singlet. i.e. connectivity (topology) determines the nature of spin-coupling. This also applies to benzene moieties where *m*-benzoquinodimethane has a triplet ground state and acts as a strong ferromagnetic coupling unit whereas its *ortho*- and *para*-isomers are ground state singlets and act as antiferromagnetic coupling units, **Figure 21**.

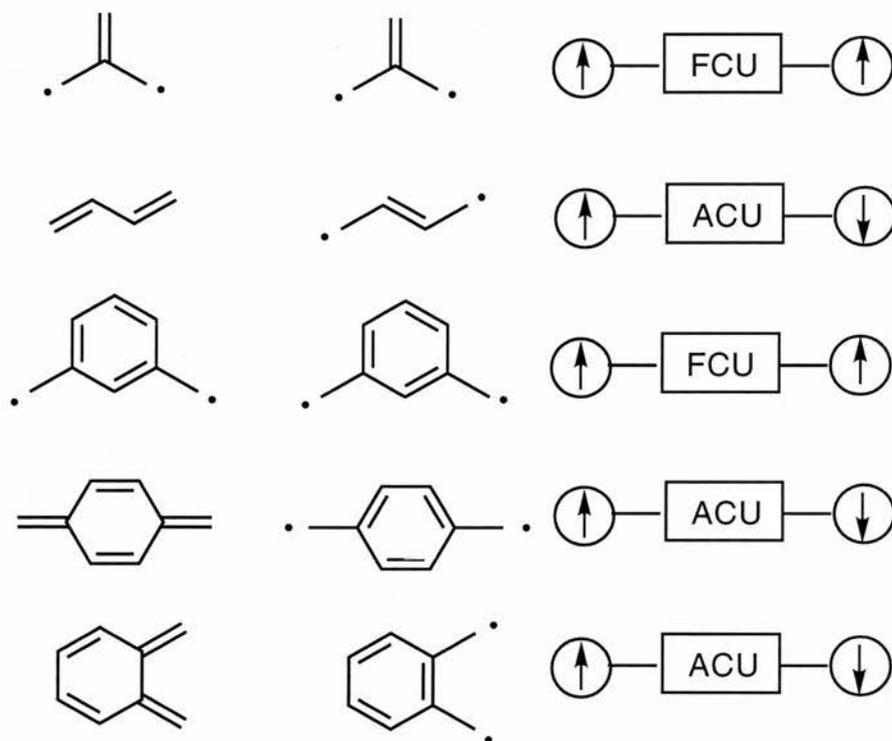
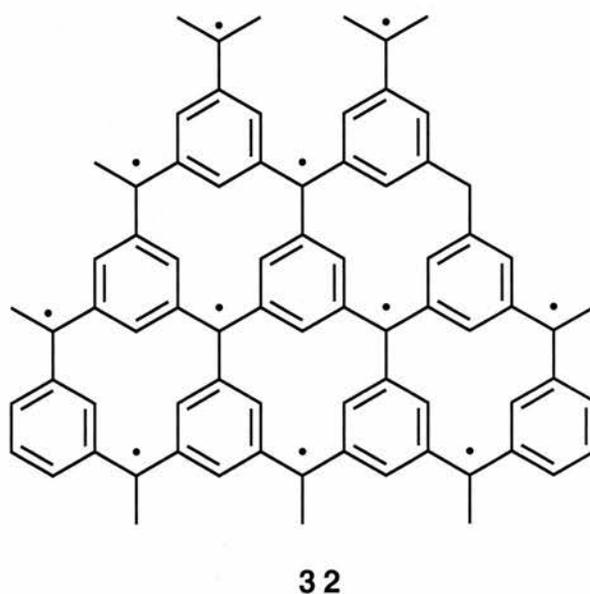
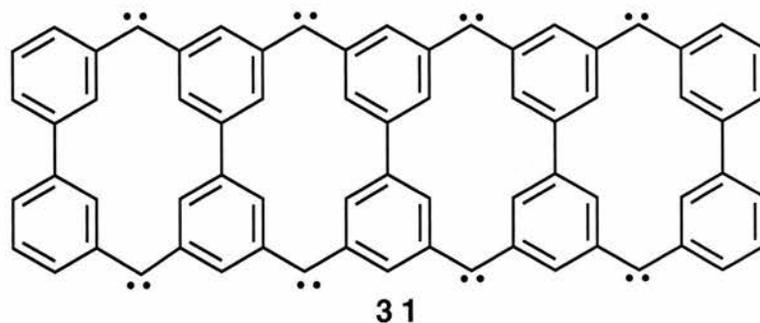
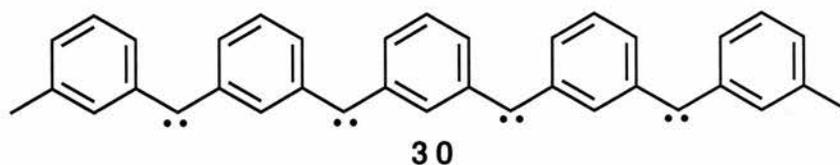


Figure 21

The topological model originated in 1968 with the consideration of the electronic structure of hydrocarbons **30**, **31** and **32**.⁴⁶



These compounds are known as alternant hydrocarbons. A conjugate system is called alternant if its' atoms can be subdivided into two groups denoted by A and A* such that each A* atom is surrounded only by A atoms and *vice versa*. In the case of polycarbenes **30** and **31** it is assumed that one of the atomic orbitals of the divalent carbon participates in conjugation with the ring π electrons while the other remains as a σ type orbital. If the assumption is made that these molecules are co-planar then according to Hückel MO theory or Pariser-Parr-Pople's (PPP) Hamiltonian, these *meta*-substituted alternant hydrocarbons have non-bonding π -molecular orbitals (NBMO's).⁴⁷ The number of π -NBMO's is equal to the number of carbons with unpaired electrons. The energies of the π -NBMO's and the σ type NBMO's are

not equal but are probably close in energy. Therefore the orbitals of these hydrocarbons will be as shown in **Figure 22**.

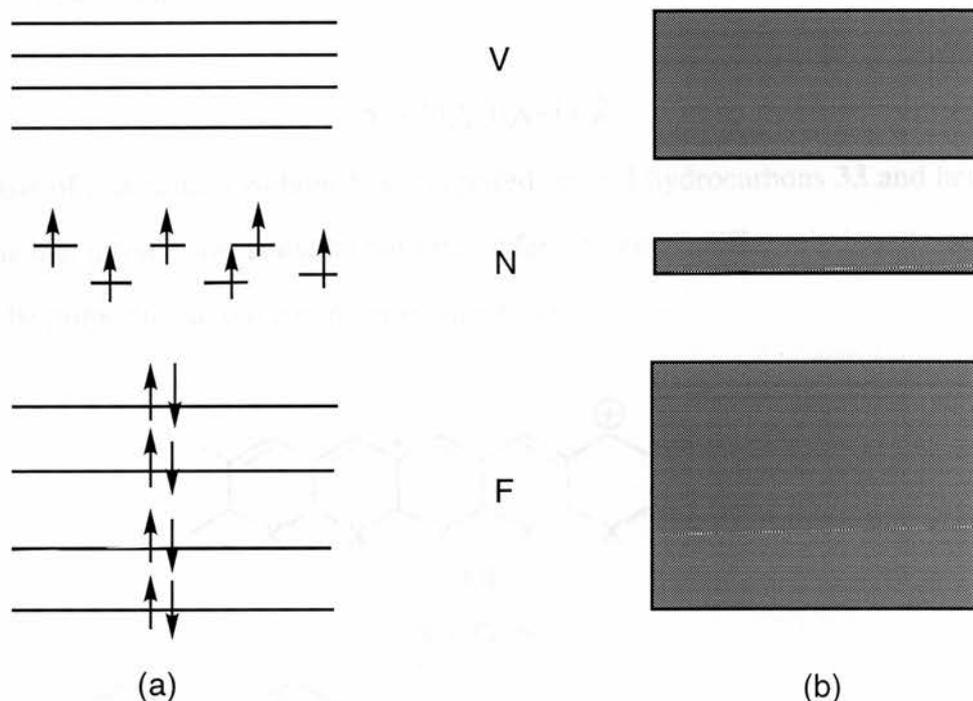


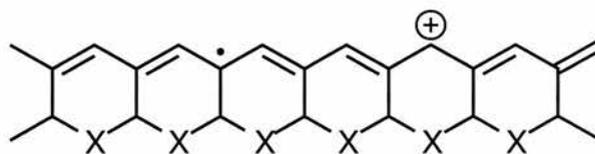
Figure 22

where F indicates the π -MO's doubly occupied by electrons and V indicates the vacant π -MO's in the ground electronic state and N indicates both the π -NBMO's and the σ type n-orbitals. If the orbital energy difference between the non-bonding electrons is sufficiently small then according to Hund's rule³ electrons entering these orbitals will do so singly and with parallel spins as shown in **Figure 22 (a)**. The spin pairing therefore depends on the exchange integral between the π -NBMO's and the σ type n-orbitals and the energy difference between these orbitals. Mataga proposed that when molecules become very large the orbital energies will become almost continuous as indicated in **Figure 22 (b)**, however because of its non-bonding nature the N band will remain sufficiently narrow to support degeneracy and the parallel alignment of spins. Alternatively the band gaps between F, N, and V may become comparable to kT , supporting ferromagnetism only at cryogenic temperatures.

Ovchinnikov proposed an even simpler model to predict ferromagnetic coupling in planar alternant hydrocarbons.⁴⁸ Based on the theorem of Lieb⁴⁹, Ovchinnikov showed that if the number of starred (A^*) and unstarred atoms (A) are not equal, the ground state spin, S , is non zero and is equal to half the difference in their numbers.

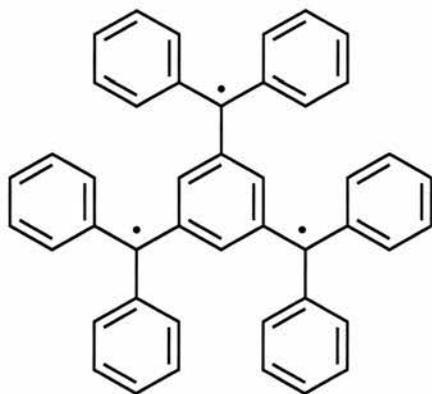
$$S = |n_A - n_{A^*}| / 2$$

On the basis of this result Ovchinnikov suggested several hydrocarbons **33** and heterocycles **34**, **35** which at infinite size could be considered ferromagnetic. The spin in polymers such as **34** would be proportional to the number of chain links.

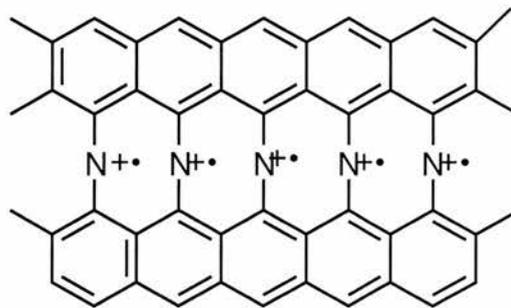


34

$X = O, S$

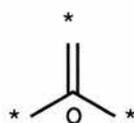


33



35

Klein⁵⁰ *et. al.* supported the possibility of obtaining high spin hydrocarbons on the basis of valence bond models in addition to calculations using classical structures, MO theory, cluster expansions and PPP Hamiltonians. Tyutyulkov and co-workers generalised the observation of Ovchinnikov to include non-alternant, non-kekule systems including those containing heteroatoms. The simplest test for the odd alternant hydrocarbon model is again the trimethylenemethane radical **36** which was confirmed as a ground state triplet.¹²



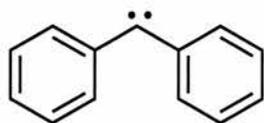
36

$$S = (N^* - N^0) / 2 \Rightarrow (3 - 1) / 2 = 1, \text{ ground state triplet}$$

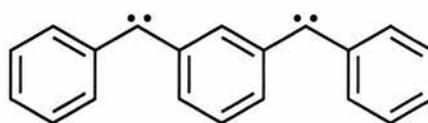
Iwamura and Murata studied systems containing two phenyl nitrene units connected through acetylenic and diacetylenic bridges. It was observed that two triplet nitrenes at *meta*, *para'* and *meta*, *meta'* positions showed ferro and antiferromagnetic interactions respectively.⁵¹ This validated the theory of Ovchinnikov⁴ and Klein⁶ and agrees with a simple rule proposed by Radhakrishnan⁵² which can be applied to a biradical and states that if the number of atoms between radical sites is odd then ferromagnetic coupling occurs and if the number of atoms between sites is even, antiferromagnetic coupling occurs. This provides a simple rule for the design of potential ferromagnetic coupling units.

Early experimental work had already proved that oligomeric derivatives of the model compounds proposed by Mataga such as diphenylmethylene⁵³ **37** and *m*-phenylene-bis-phenylmethylene⁵⁴ **38** have triplet and quintet ground states respectively.

Investigations of phenylene carbenes were initiated by Itoh and co-workers⁵⁵ who studied *m*-phenylene-bis-phenylmethylene **38**, formed by the photolysis of 1,3-bis-(α -diazobenzyl)-benzene and observed a quintet by ESR spectroscopy at 77K.

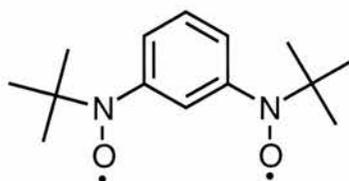


37



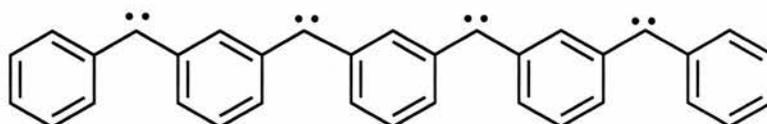
38

Carbenes of this nature are extremely unstable prompting the need for stable radical species. Calder *et. al.*⁵⁶ utilised the stability of nitroxide radicals and linked these through a 1,3-substituted benzene ring to yield biradical **39**.

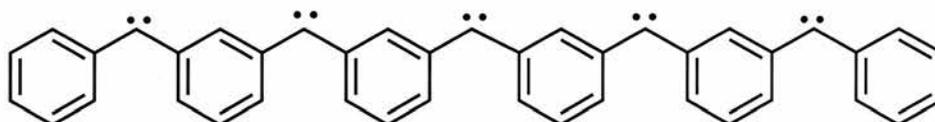


39

Magnetic studies later showed this compound to be a ground state triplet.⁵⁷ This compound however is not fully persistent and isomerises to the aminoquinone imine-N-oxide. Iwamura continued to study polycarbene compounds and in 1985 reported the nonet spin multiplicity of the ground state of tetracarbene **40**.⁵⁸

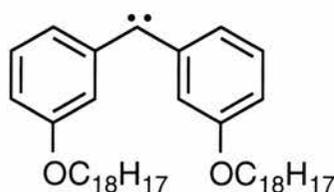


40



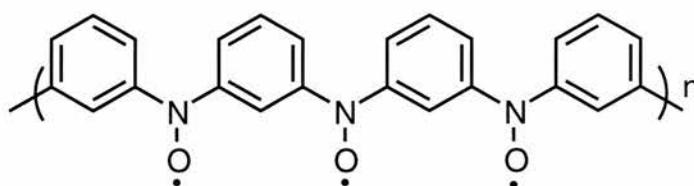
41

It was found that **40** displayed paramagnetic susceptibility with varying temperatures and this was attributed to intermolecular antiferromagnetic interactions. This compound is termed a superparamagnet since the electrons within the molecule are aligned in parallel but the molecules behave independently of one another similar to a paramagnet. Iwamura claimed that partial intermolecular ferromagnetic interactions were observed in **42** by utilising the dispersion forces of alkyl chains which insulate the magnetic interactions between layers.⁵⁹

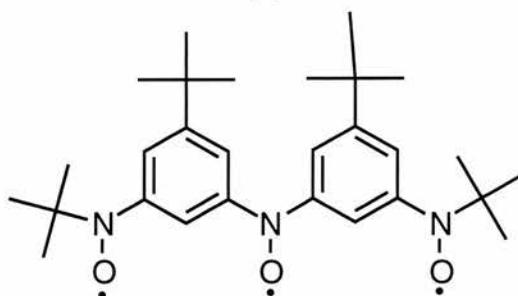


42

Theoretical work on Mataga's model continued using more accurate modelling packages which confirmed the expected ferromagnetic ground state in phenylene carbene polymers.⁶⁰ The synthesis of a $S = 5$ carbene, **41**, was achieved by Iwamura.⁶¹ This compound exhibited the expected undecet by ESR spectroscopy. However, in practical terms the usefulness of these compounds is restricted by their instability. Research therefore diverted to more stable diaryl nitroxide polymers such as **43**.



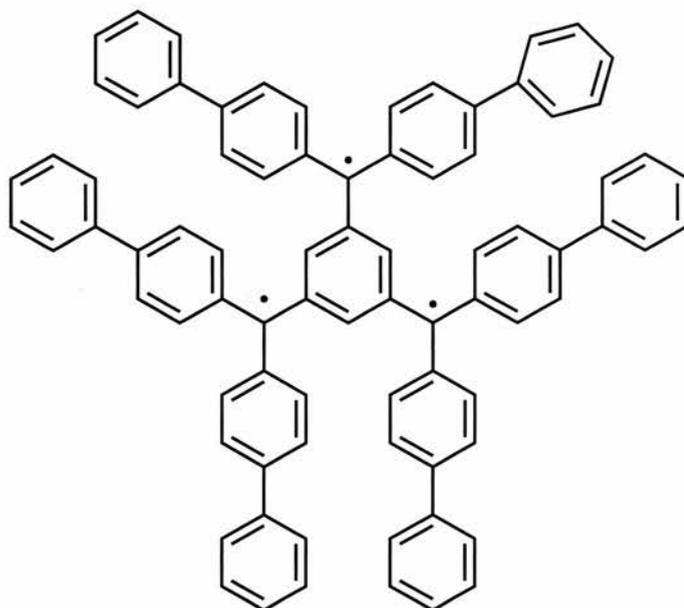
43



44

Compound **44** was synthesised and found to be stable at ambient temperature for several weeks. Measurements of magnetic susceptibility against temperature confirmed a quartet ground state indicating that the intramolecular exchange coupling was strongly ferromagnetic and that perturbation by heteroatoms does not affect the topological model.⁶² Evidence of a band of degenerate NBMO's between bonding and anti-bonding MO's in polyphenylene nitroxides was provided by Tyutyulkov who also showed that these polymers suffer from a smaller degree of spin polarisation in the π -network compared to the analogous carbenes.⁶³ Smaller exchange interactions may indicate that high spin polynitroxides do not exist at ambient temperatures.

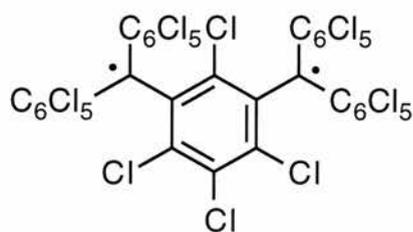
Mataga also proposed that the triphenylmethyl radicals could exhibit ferromagnetic coupling. Compound **45** was found to have a quartet ground state but was prone to rapid dimerisation.⁶⁴



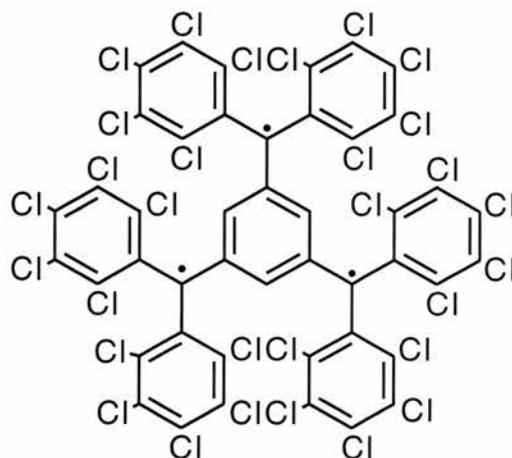
45

Since this observation a series of similar high spin hydrocarbons have been detected such as 1,3,5-tris(phenylmethylene), $S = 3$,⁶⁵ biphenyl-3,3'-bis(phenylmethylene), $S = 0, 1, 2$,⁶⁶ 1,3,5-benzenetrityl[bis(biphenyl-4-yl)methyl], $S = 3/2$ ⁶⁷ and 3,3'-diphenylmethylene-bis(phenylmethylene), $S = 3$.⁶⁸

In an attempt to improve the stability of these compounds. Palacio and co-workers produced a stable biradical, **46**, which had a triplet ground state and had a large separation between the triplet and singlet ground states.⁶⁹ The stability is a result of the restricted rotation of the aryl groups, and also the steric shielding provided by the Cl atoms.

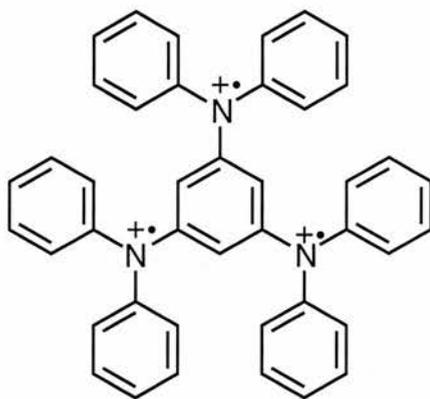


46



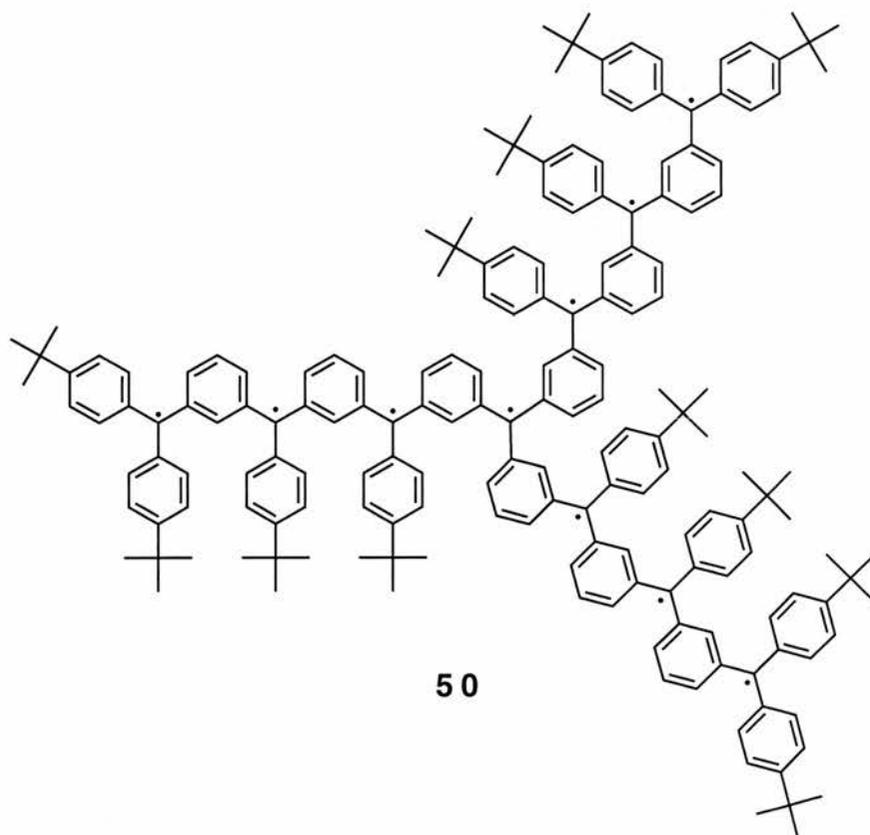
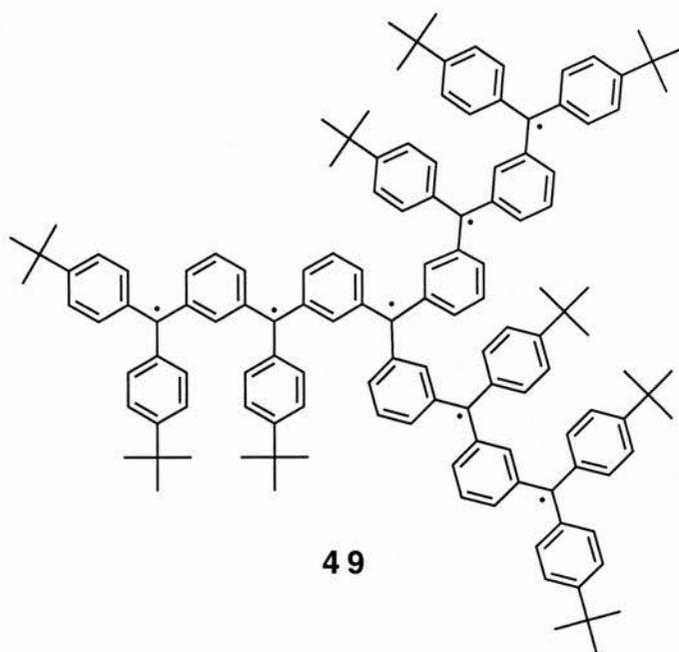
47

Extension to the triradical **47** produced a compound with a quartet ground state which is stable at 250°C in air.⁷⁰ The intramolecular exchange interactions are ferromagnetic and perturbation by electronegative heteroatoms, lack of planarity, and changes in symmetry have little effect on the coupling and therefore it would seem that the topological model can be applied to highly distorted systems. Further evidence of this was provided by Tanaka *et. al.* who observed a quartet ground state in the trication of 1,3,5-tris(diphenylamino)benzene (TDAB), **48**.⁷¹

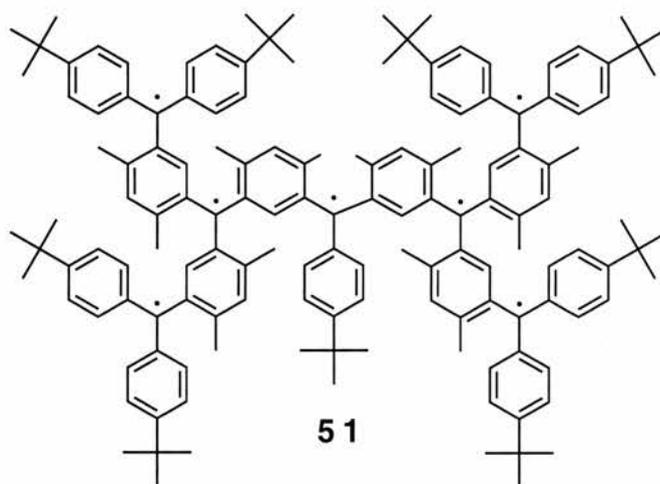


48

The group of Rajca has made significant progress in the design and synthesis of potential organic ferromagnets based on systems which are homologous to *m*-benzoquinodimethane.⁷² Rajca designed and synthesised heptaradical **49** and decaradical **50** based on a 'star branched' topology. These polyradicals showed high spin ground states with strong ferromagnetic coupling ($S = 7/2$ and $S = 5$). Magnetisation data suggests that the intermolecular interactions are ferromagnetic.⁷³



Rajca also designed dendritic polyradicals such as heptaradical **51** in addition to a pentadecaradical and a 31 radical dendrimer.⁷⁴



The average spins for these polyradicals were $S = 3, 7/2, 5/2$ respectively. This is due to the failure to generate spins, hereby known as spin defects. Spin coupling in multi-site radicals such as these is extremely sensitive to these defects due to the interruption of spin coupling paths. It is difficult to overcome this problem unless improved methods of radical generation are developed. The site of the defect is also important, with defects at the inner sites being particularly detrimental. An inner site defect divides the polyradical into uncoupled parts (**Figure 23**) with lower spin, whereas defects at the peripheral sites are relatively innocuous (**Figure 24**), where the circles represent spin sites and the lines are spin coupling paths.

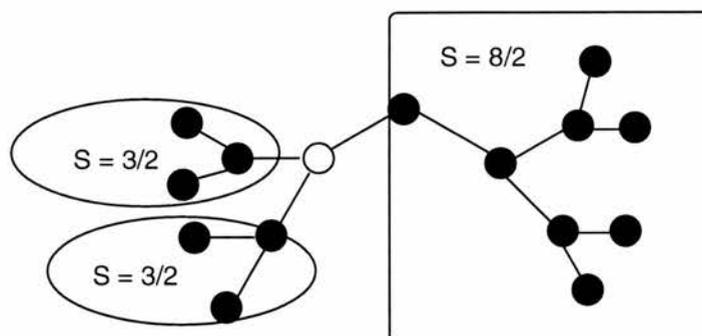


Figure 23

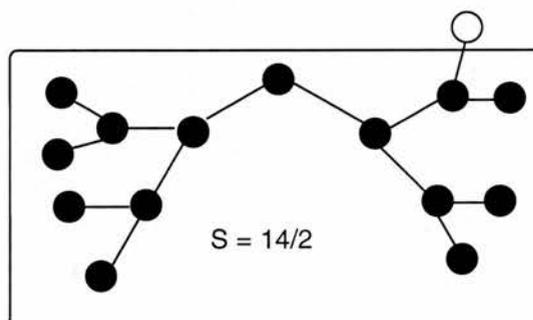
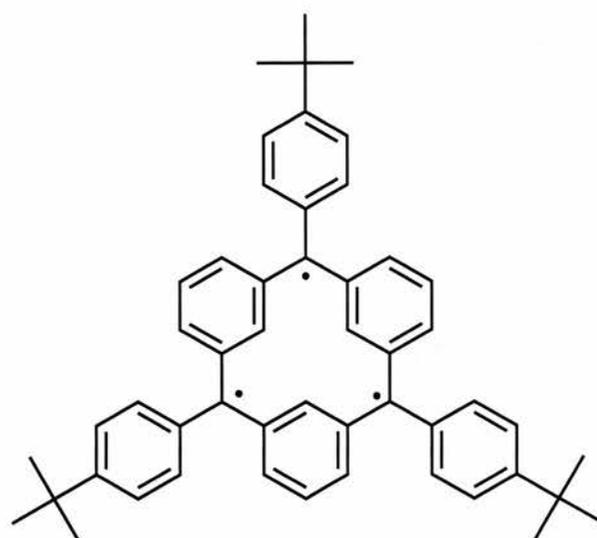
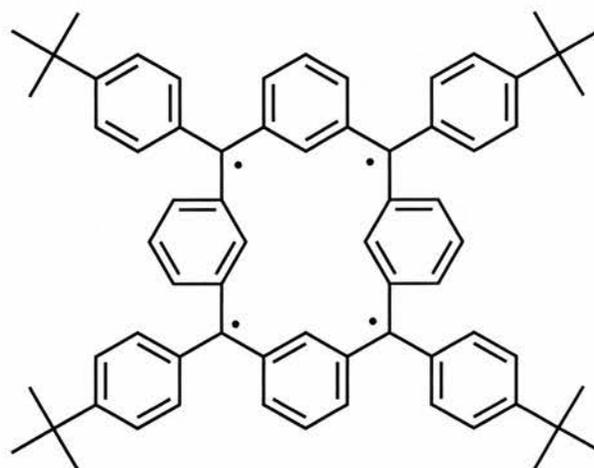


Figure 24

Rajca attempted to overcome the problem of defects by using molecules with multiple coupling paths such as macrocyclic calixarenes which are oblivious to one spin defect.⁷⁵ Triradical calix[3]arene **52** and tetraradical calix[4]arene **53** were synthesised and although **52** was found to dimerise readily, suggesting a lack of steric shielding of the radicals, the steric shielding in the calix[4]arene was sufficient to stabilise tetraradical **53**. The out of plane twisting is moderate enough to preserve ferromagnetic coupling and therefore these macrocycles may be viable building blocks for defect resilient high spin polyradicals.



52



53

However, highly annelated polymacrocyclic systems are difficult to synthesise, though oligomeric fragments which have two strands, **Figure 25**, are accessible by convergent synthetic routes and maintain π conjugation and ferromagnetic coupling in the presence of defects.⁷⁶

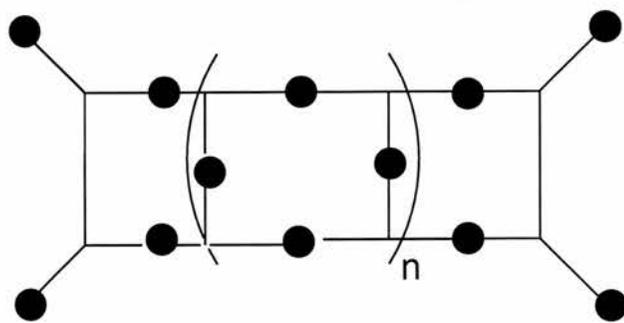
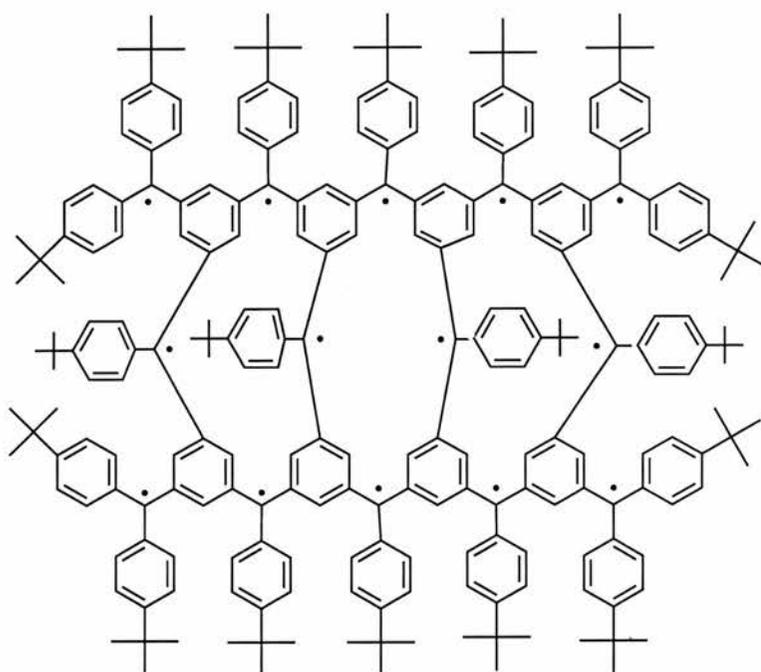


Figure 25



54

Characterisation of **54** by SQUID magnetometry in THF- d_8 /2-MeTHF indicated $S = 6.2$ which is below the theoretical value of 7 expected for strong ferromagnetic coupling of 14 unpaired electrons. Quenching studies showed that approximately 1 deuterium from the solvent was incorporated in **54**, accounting in part for $S < 7$. A study of the temperature dependence of magnetisation indicated that ferromagnetic coupling between spins was not very strong. This was due to an out of plane distortion of the π system. Rajca concluded that the development of 2-D and 3-D ferromagnets would require careful design to accommodate π conjugation, a connectivity compatible with ferromagnetic coupling, steric hindrance to stabilise radicals and yet remain synthetically feasible.

An alternative to the m-phenylene unit was proposed by Rajca, who postulated that sterically unencumbered 3,4'-biphenyl units, **Figure 26**, may possess suitable strengths of spin coupling and also stabilise radicals.⁷⁷

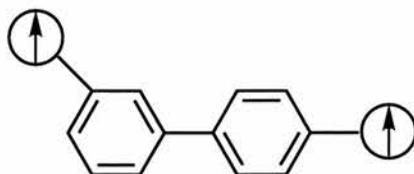
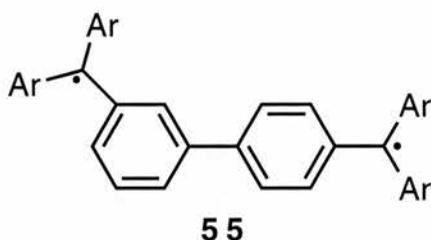
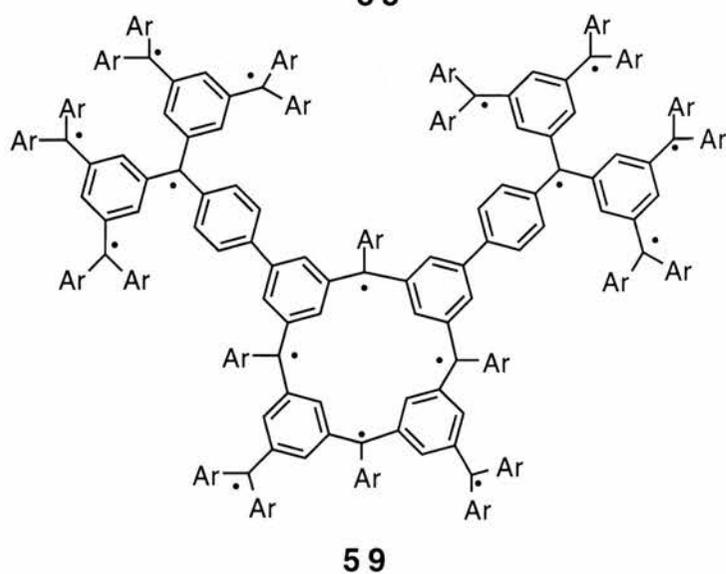
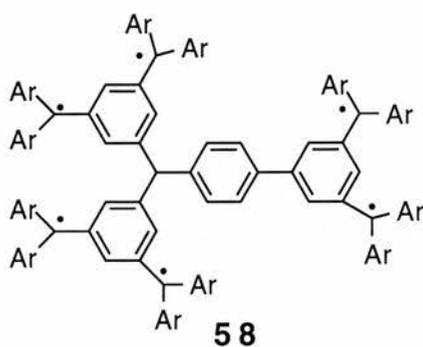
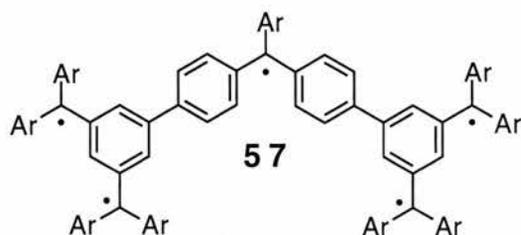
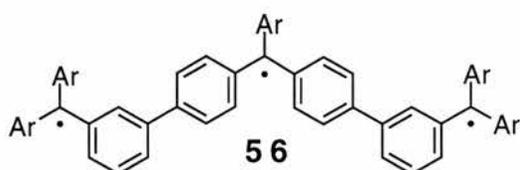


Figure 26



The study of **55**, which is thermally stable and has a triplet ground state suggested 3,4'-biphenyl could be used as a weak ferromagnetic coupling unit. Rajca then postulated that high spin modules should be linked to these weak FCU's to form simple spin clusters, **56-59**. In these spin clusters intramodular ferromagnetic coupling is very strong compared to the weak intermodular coupling through 3,4'-biphenyl units.⁷⁸



Polyradicals **56-58** possess only one site where a single defect may interrupt spin coupling whilst **59** has two such sites. **59** was found to be a $S = 7.2$ hexadecaradical. The estimated yields per site for the generation of unpaired electrons was as high as 98% and the development of spin clusters of this nature led to the synthesis of a polyradical with $S = 10.79$. The four dendritic branches of **60** and the macrocyclic core can be lumped into component spins. The

ferromagnetically coupled pentamer with $S' = 5/2, 5/2, 5/2, 5/2$ and 2 should have a $S=12$ ground state, **Figure 27**.

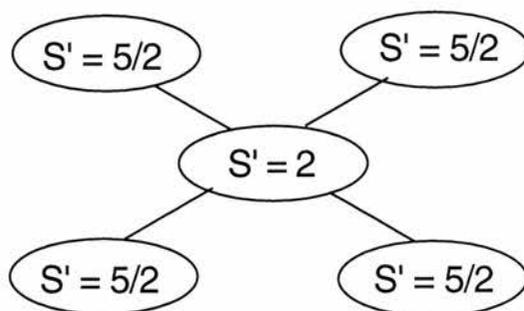
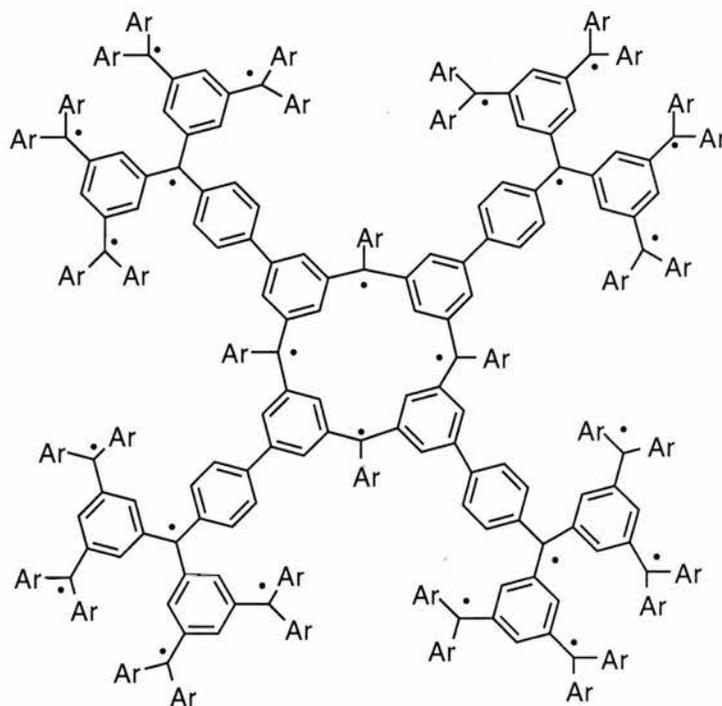


Figure 27



60

A graph of M vs. H/T showed $S \approx 10$ at $5K$. This is the highest spin recorded for an organic ferromagnet and benefits from the fact that only four of the twenty four radical sites are defect sensitive. Rajca is currently working on analogues of **60** in which dendritic branches are replaced by macrocycles.

1.5 Polaronic Model

Fukotome proposed a new class of ferromagnetic conjugated polymers where the spins are generated by doping of conjugated segments. These polymers have an alternating A-B-A-B structure, where A is a block which gives a polaron on doping (spin containing unit, SCU) and B is a block which couples the A block polaron spins in a ferromagnetic fashion (ferromagnetic coupling unit, FCU), **Figure 28**.⁸⁰

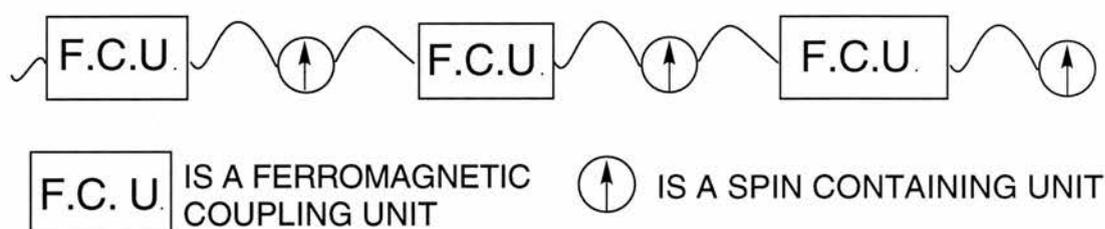


Figure 28

Fukotome suggested the use of oligomeric fragments of conducting conjugated polymers as SCU's such as *trans*-polyacetylene, poly-*p*-phenylene, polypyrrole or polythiophene, which all have an alternative degenerate or nearly degenerate band structure hence a degenerate ground state, **Figure 29**. On doping a conducting polymer with an electron or hole, a polaron, which is an ion radical self trapped in a local lattice distortion, is produced. To obtain ferromagnetic coupling between SCU's the FCU must not have a degenerate or nearly degenerate structure i.e. poly-*m*-phenylene or polyketone type structures, **Figure 30**.

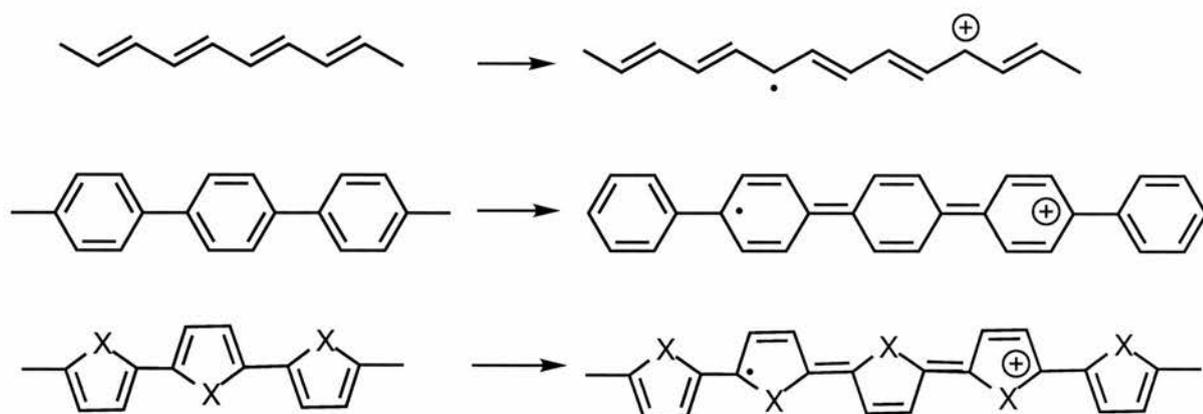


Figure 29

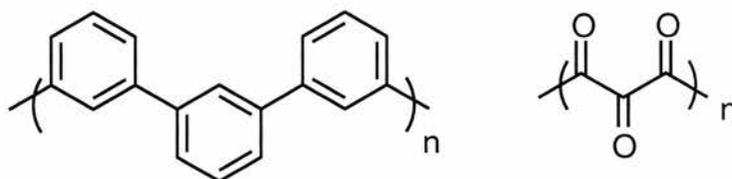
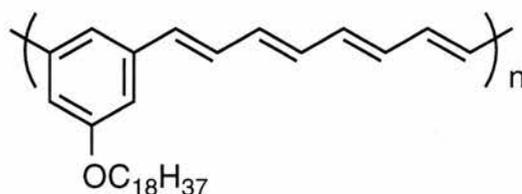


Figure 30

This overcame the problems of instability associated with 'built in' radicals. The polaronic theorem was supported by Tyutyulkov who claimed that the bond structures of these polymers were analogous to that of odd alternant non-classical polymers.⁸¹

The first experimental approach to this model was made by Dougherty and co-workers who employed *m*-phenylene as a ferromagnetic coupling unit and a tetraene as the easily oxidised polaron precursor.⁸² O-alkyl groups were also attached at the 5-position of the phenylene ring to aid solubility. Poly(*m*-phenyleneoctatetraene) PMPOT-18, **61**, was lightly doped with AsF₅ to form polarons which were found to be stable at room temperature. Magnetic studies indicated that $S \geq 2$, suggesting the existence of significant net ferromagnetic couplings in the system. It became clear that the doping was inhomogeneous and that regions of relatively heavier doping allow significant ferromagnetic coupling of the spins, which were found to persist to at least 200K. It could not be confirmed that these results were due to 1-D intramolecular couplings. Some intermolecular antiferromagnetic coupling was also observed at low temperatures.



61

On the basis of molecular orbital calculations and crystal orbital theory, Yamabe considered substituted polyacetylenes as potential 1-D ferromagnets.⁸³ Although the interactions of doped poly(4-oxyphenyl)acetylene were found to be antiferromagnetic, polyacetylene chains with phenoxy radicals as pendants on each alternate site showed possible ferromagnetic couplings. Further theoretical work determined that the interactions of $-C^{\bullet+}H$, $-N^{\bullet+}H$ and $N-O^{\bullet}$ linked

through *m*-phenylene are much stronger than when coupled through a polyacetylene chain and that the interactions would be ferromagnetic. It was also suggested that although bulk ferromagnetism in 1-D systems can only be observed at 0K, there are always weak 3-D interactions such as interchain coupling. Ferro or antiferromagnetic ordering may therefore appear at a finite temperature.⁸⁴

In the majority of polaronic models *m*-phenylene is chosen as the ferromagnetic coupling unit since it is generally considered the best.⁸⁵ Dougherty considered the choice of FCU to be the critical design feature and devised a method of evaluating these units based on a bis(trimethylene)methane containing molecule. These groups provide stable and robust triplets and are coupled to each potential FCU, **Figure 31**. The strength and nature of spin coupling can then be determined by magnetic studies. Further consideration of ferromagnetic coupling units will be presented in chapter 2.

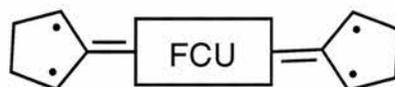
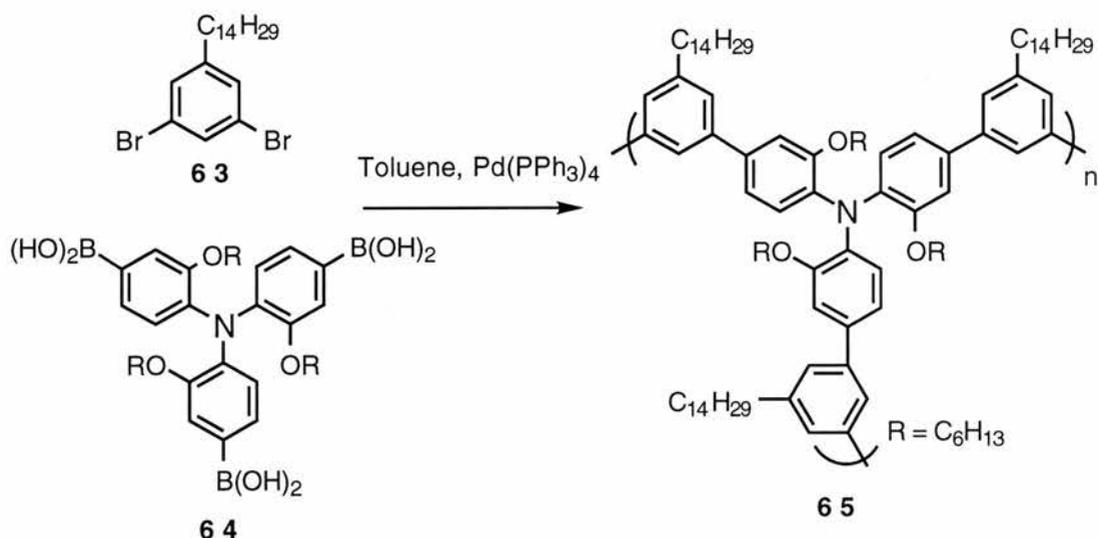
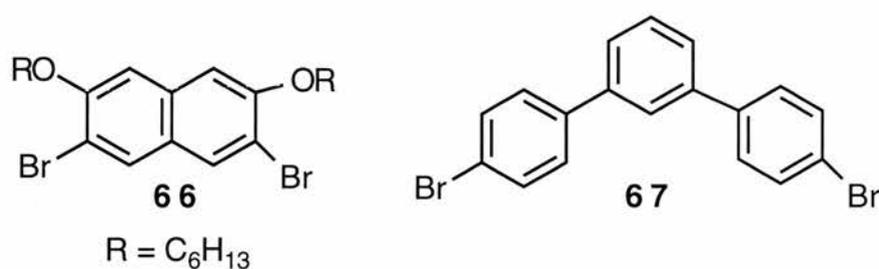


Figure 31

Bushby *et. al.* synthesised a polaronic polymer **65** with $S \approx 5/2$ which featured aryl amines as spin containing units which were linked through *meta*-coupled benzene rings.⁸⁶ Unlike Dougherty's polymer which was one dimensional Bushby's were cross-linked such that each SCU was ferromagnetically coupled to three others in order to counter the effects arising from incomplete doping. The percolation limit, the point at which all spins are aligned, for these systems is estimated to be 70%.⁸⁷ Bushby used spin bearing $N^{\bullet+}$ centres and 1,3,5-trisubstituted benzene rings to extend his structures in more than one dimension. The best results were obtained with the polymer obtained from the Suzuki reaction⁸⁸ between dibromide **63** and the trisboronic acid **64**.

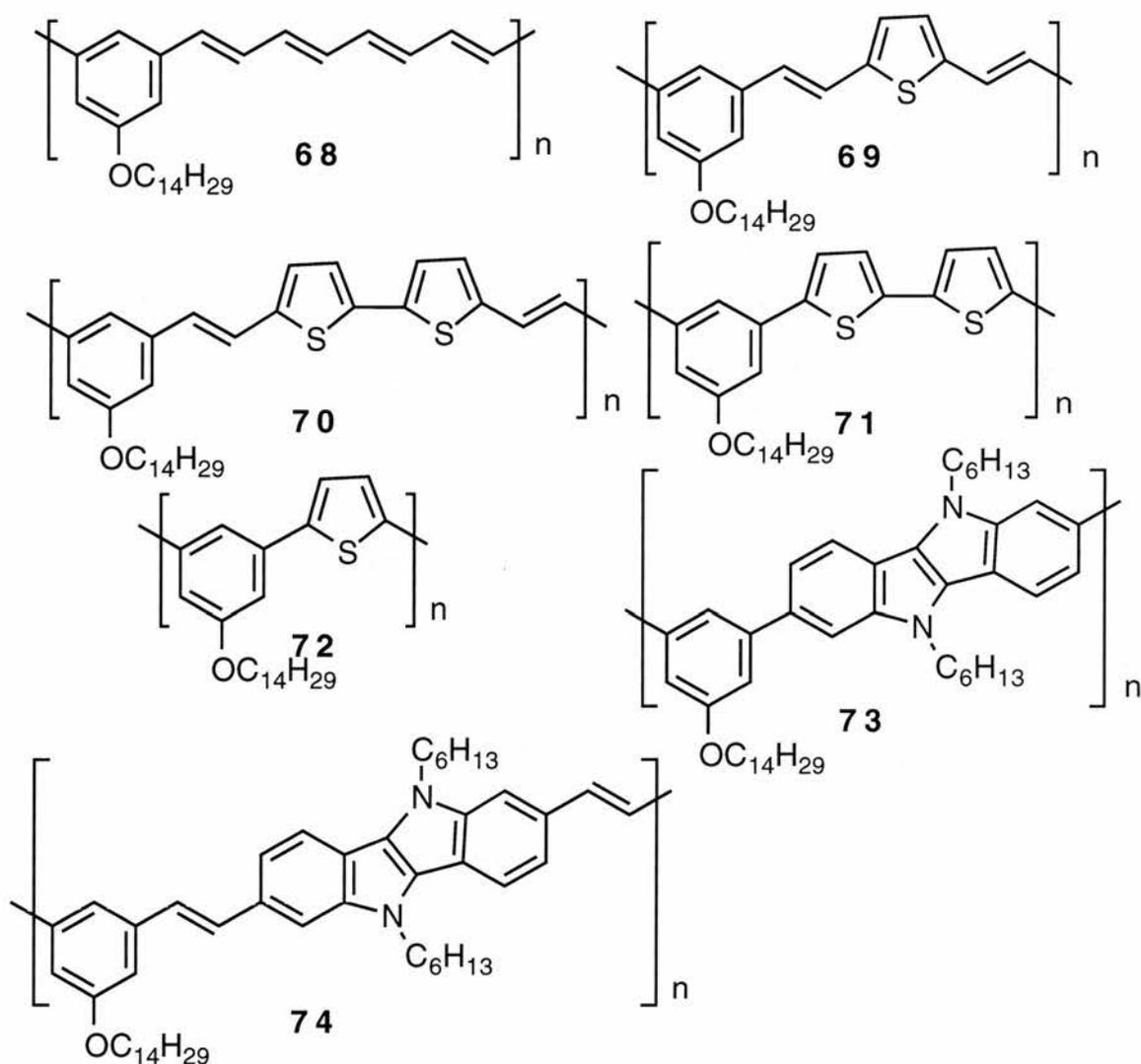


Oxidation of **65** with NO^+BF_4^- resulted in doping levels of approximately 15%, far short of the percolation limit and the 10^3 - 10^4 spins required to sustain a ferromagnetic structure domain. Magnetisation was studied as a function of magnetic field strength, the results obtained suggested that **65** behaved closest to a $S = 5/2$ system. Further studies by Bushby established that a reason for the poor doping levels was due to the difficulty of accommodating large counter ions in a rigid polymer i.e. a steric rather than electrostatic limitation.⁸⁹ In an attempt to rectify this Bushby linked the triarylammonium ions through 2,7-naphthalene **66** and the dibromide **67** rather than 1,3-phenylene.



This 'spacing out' of the monomer units did not lead to higher doping levels with NO^+BF_4^- in dichloromethane. A different doping technique using antimony pentachloride achieved higher doping levels but had a poor reproducibility. It was also found that the thin polymer films required for this method of doping decay rapidly. Polymer **65** could be doped to a level of 40% using SbCl_5 and was found to show $S = 4$ behaviour.

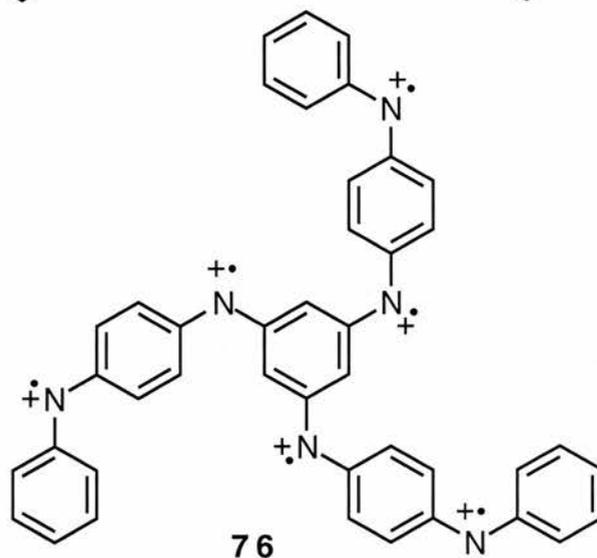
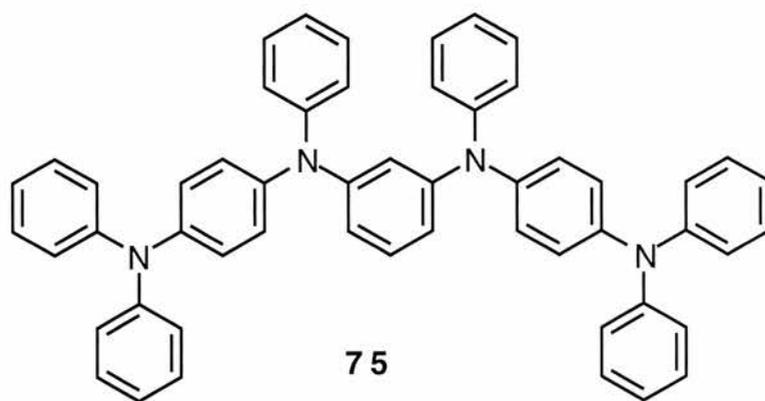
Dougherty continued his work on polaronic ferromagnets proposing a range of potential polaronic magnets, **68-74**, in order to determine which conjugated segments were best suited to producing a large number of spins that interact strongly through the FCU.⁹⁰ Although Dougherty's designs involved 1-D ferromagnets only, the structures shown below were hoped to display short range, high spin ordering.



Polymers **68-74** were produced by Wittig⁹¹ or Suzuki⁸⁸ polymerisation reactions and afforded polymers with an average molecular weight of approximately 10,000 atomic mass units. This was a considerable achievement since insufficient solubility can result in oligomeric chains 'crashing out' of solution. These polymers were doped using iodine or arsenic pentafluoride and subjected to magnetisation studies. The best results were achieved for polymer **73** in

which one third of the monomer units contained a spin. The spins produced were extremely stable with $S > 1/2$ behaviour being observed. However, in general, less than 1 spin per chain was evident in these polymers. The magnetic behaviour is again explained by inhomogeneous doping which occurs due to the creation of a polar environment which favours further doping nearby.

It would appear that a significant problem associated with the polaronic model is achieving the necessary high levels of doping required for ferromagnetic coupling. The use of 'heavy' doping conditions can result in the formation of bipolarons which are spinless dications and thus detrimental to ferromagnetic design. The emeraldine salt of polyaniline cannot accommodate bipolarons due to their instability and these may therefore be used as a basis for designing high spin density polymers. Janssen and co-workers⁹² used this fact in designing N-phenylaniline oligomers comprising alternate *meta* and *para* substituted rings which provide ferromagnetic coupling and radical cation stability respectively.⁹³



Oxidation of **75** with thianthrenium perchlorate afforded the dication radical which was found to have a triplet ground state and showed no decay by ESR spectroscopy after several weeks. A further study involving **76** showed that it also has a high spin ground state and therefore these molecules can be doped to produce stable triplet dication radicals.

A slightly different approach was adopted by Tanaka who constructed co-polymers consisting of π conjugated units as the spin supplier and non π conjugated units containing several sp^3 hybridised atoms as spacers.⁹⁴ The interactions between polaronic units could then be varied by altering the length and atomic species of the spacer unit. The compounds prepared consisted of regularly aligned disilanylene and π conjugated units, the most promising of which appeared to be a quaterthiophene unit, **Figure 32**. Doping polymer **77** was unsuccessful as a result of oligothiophylene units in the chain surrounding the dopant ion

resulting in a partially charged state. The subsequently low spin concentrations prevented the opportunity for polaronic ferromagnetic interactions.

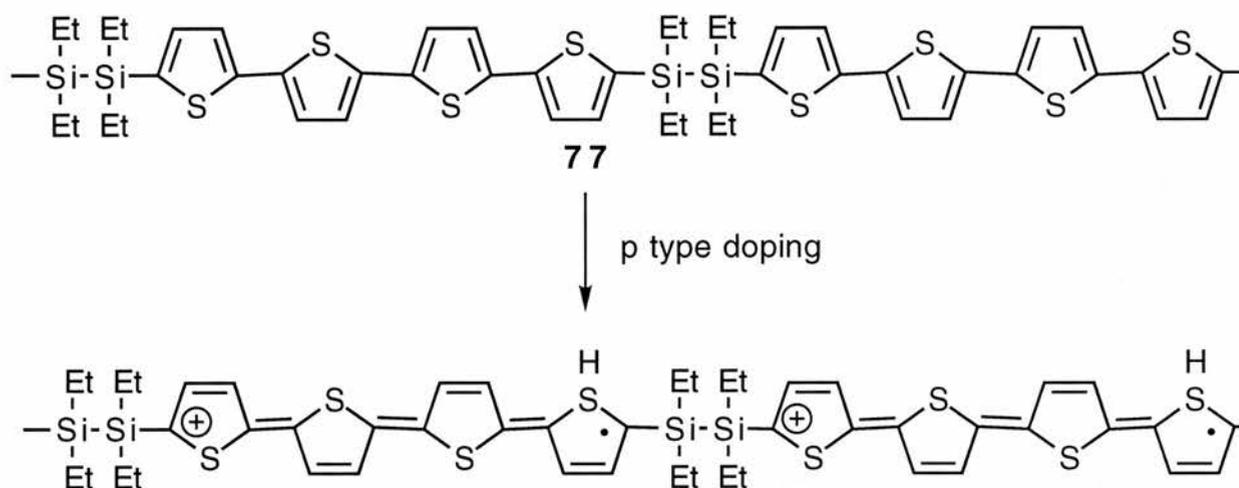
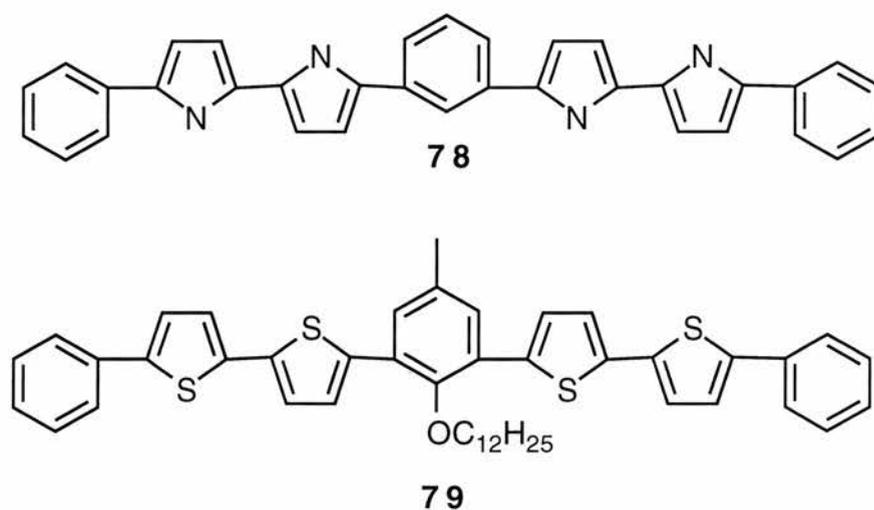


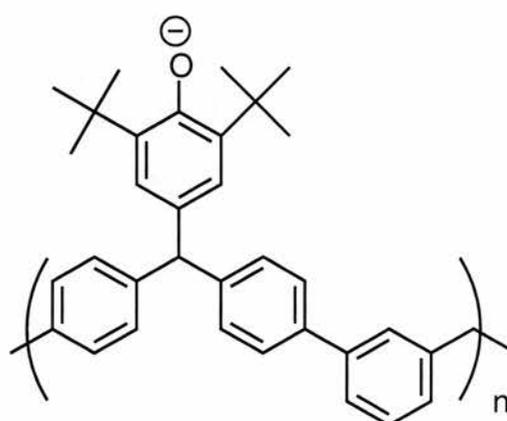
Figure 32

Janssen and co-workers also studied thiophene and pyrrole oligomers such as **78** and **79** which had been protected at the α -position.



From these studies⁹⁵ Janssen claims that cation radicals of oligopyrroles and oligothiophenes can form diamagnetic π dimers in solid state and in solution and that the formation of these diamagnetic π dimers may provide an insight into the low spin concentrations observed in these systems as opposed to inhomogeneous doping. Janssen concludes that it is not possible to obtain high spin molecules based on dopable π conjugated segments containing pyrrole or thiophene.

To date, the most recent improvement of the polaronic model has come from Dougherty who suggests that electrochemically doped poly(*m*-phenylene-fuchsonone) PMPF **80**, is an improvement on other proposed systems in that it provides the first example of electrochemical doping in a polaronic ferromagnet, the first use of a radical anion in a polaronic ferromagnet, the first positive correlation between spin concentration and spin state, the first positive correlation between doping level and spin concentration and the first high spin polaronic system with > 50% spin concentration.⁹⁶



80

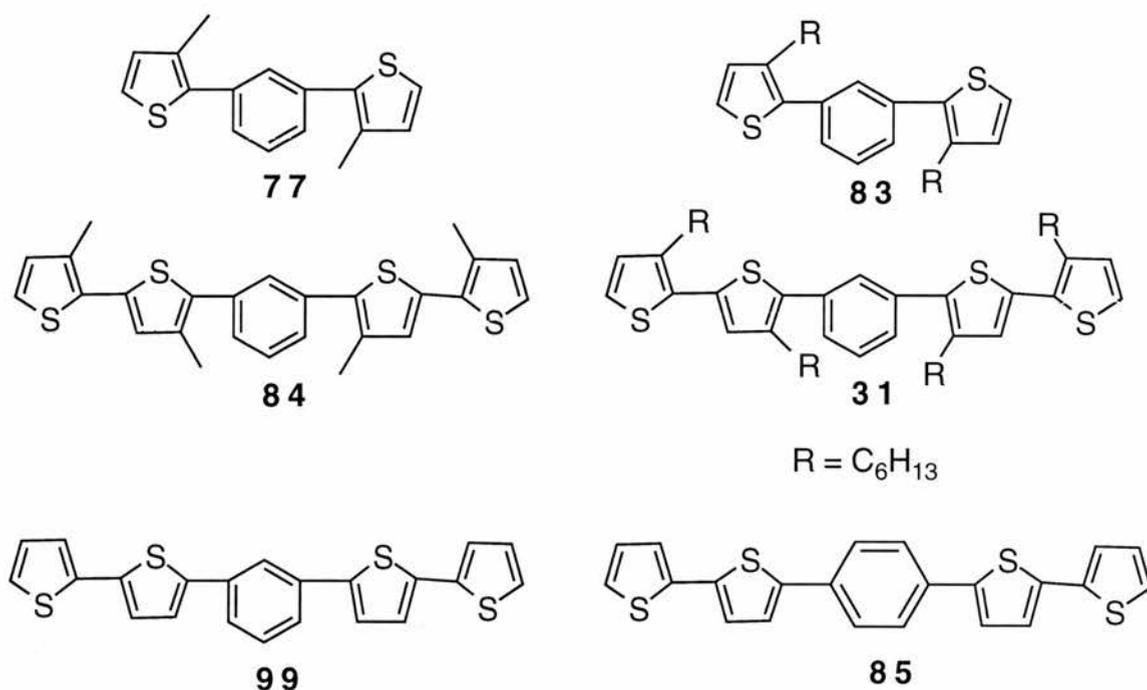
Electrochemical doping of PMPF in THF with *tert*-butylammonium perchlorate as a supporting electrolyte resulted in $S \approx 2$ behaviour at a doping level of 61%. This is a significant result considering each PMPF unit was found to be seven units long at most and therefore the maximum spin expected was $7/2$.

Dougherty has accomplished, thorough homogeneous doping, in producing polymers which are soluble in both doped and undoped states. This is considered an essential for further development in addition to the control of intermolecular antiferromagnetic interactions which would allow the observation of weak intramolecular ferromagnetic interactions.

1.6 Aims and Objectives

Of the earlier strategies for developing organic based magnetic materials, the polaronic ferromagnet remains an appealing target. Early theoretical work by Fukotome suggested that doped conjugated segments, linked by appropriate π topologies, such as *m*-phenylene, could serve as useful spin carriers of novel magnetic materials. It is known from work on organic conducting polymers that doped conjugated organic molecules containing many polarons can be stable at room temperatures. Therefore a polaron would seem a potentially robust spin containing unit. Conducting polymer work also establishes that doping can be a fairly straightforward process by chemical or electrochemical means and is therefore an efficient way to introduce a large number of spins into a system.

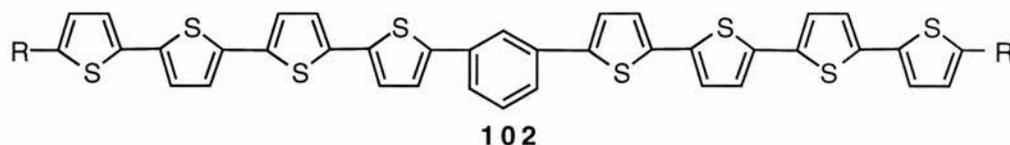
The purpose of my research was to design, synthesise and evaluate potential polaronic ferromagnets, addressing issues such as solubility of polymers, degree of conjugation within the polymer backbone, bipolaron formation, efficiency of doping and methods of polymerisation. This thesis describes the design considerations and synthetic routes towards six different polymers, **P31**, **P77**, **P83**, **P84**, **P85**, **P99**.



Chapter two describes the design features and the various synthetic routes towards monomers **31**, **77**, **83** and **84** using transition metal catalysed carbon-carbon bond forming reactions such as Stille and Suzuki coupling. Chapter 3 details the synthesis of monomers **99** and **85**. **P99** was synthesised in order to provide contrasting information regarding the role of alkyl substituents in aiding solubility, stabilising polarons and preventing π dimerisation, whilst **P85** would allow us to compare a similar polaron unit connected to an anti-ferromagnetic coupling unit.

Chapter 4 describes the physical and electrochemical properties of similar thiophene derivatives and also details the chemical and electrochemical polymerisation of our monomers. The electrochemical characterisation, UV-vis spectroscopy and ESR spectroscopy of **P77-P99** in their doped and undoped states is also discussed, and compared with literature data from related compounds. Unfortunately, due to time considerations, it was not possible to complete a full ESR spectroscopy study of the polymers at a variety of temperatures.

Synthetic routes towards an end-capped 1,3-phenylene-bis-(quaterthiophene) **102** are discussed in Chapter 5. This would have allowed us to investigate the magnetic properties of the di(radical cation) by blocking the sites at which polymerisation occurs.



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Chapter Two

Design and Synthesis of Monomer Units

2.0 Design and Synthesis of Monomer Units

2.1 Design

Of the several strategies for developing organic based magnetic materials we considered the polaronic approach to be the most appealing. Work on conducting polymers has shown that doped, conjugated organic molecules containing many polarons can be stable at room temperature and can be regarded as robust spin containing units (SCU's).¹

The method of spin generation is an important factor. All methods for the generation of unpaired electrons in polyradicals rely on chemical, photochemical or electrochemical reactions that are carried out to generate all unpaired electrons from a suitable precursor. The yields of such reactions are not quantitative and this has a dramatic effect on spin coupling. The best results for spin generation have been achieved by the photolysis of diazo-compounds to afford the corresponding oligocarbenes. However these carbenes are not stable at ambient temperatures. Rajca produced radicals by treating alkyl ethers with a sodium/potassium alloy to create the corresponding anions; further treatment with iodine finally afforded the radicals.² This method generally produces good yields of unpaired electrons, however the failure to generate even a small number of unpaired electrons can significantly affect the spin coupling. In addition this method may not be tolerant of other functionalities present in the precursor molecule.

Again, conducting polymer work has shown that doping conjugated organic segments, to form polaron units, can easily be achieved by chemical or electrochemical methods.¹ Thus the vexing problem of finding efficient ways to introduce spins could be assuaged.

Many approaches to organic magnetic materials produce intractable insoluble materials that are difficult to characterise.³ The polaronic approach can separate polymer synthesis from the

introduction of spins, allowing full characterisation of the polymer, ensuring the desired topology for ferromagnetic coupling has been created, prior to the introduction of spins.

Having decided on polarons as a source of spin, we followed the approach of Dougherty⁴ where the polymer is considered as consisting of two distinct building blocks, a spin containing unit and a ferromagnetic coupling unit, which ensures high spin pairwise interactions between SCU's.

Choosing the Spin Containing Unit

There are many considerations involved in choosing the SCU, however the need for the induced polaron to be as chemically inert as possible must be a primary concern. Stabilising a radical cation suggests increasing delocalisation and so a longer polaron would be advantageous. The introduction of heteroatoms and steric protection are additional strategies for producing stable radical cations.

Another important criterion in selecting potential SCU's is the ease with which the system can be oxidised or reduced. π -Bonded unsaturated polymers which have small ionisation potentials and/or large electron affinities are particularly appealing, since electrons of π character can be relatively easily removed to form a polymeric ion without disruption of the σ bonds which hold the polymer together. As mentioned previously, oxidation or reduction can be achieved electrochemically by subjecting the neutral polymer to the appropriate oxidising or reducing voltage in an electrochemical cell. The charge on the ion is then neutralised by a counter ion from the electrolyte solution. Experimental and theoretical investigations of the evolution of the electronic and transport properties of various conducting polymers have been conducted.⁵ Removing an electron from polythiophene for example, leads to the formation of a polaron whose quinoid like geometry was found to extend over approximately four thiophene rings. Therefore the ideal polaron unit for our system would appear to be a quaterthiophene unit. The removal of a second electron leads to the formation of a bipolaron species, a spinless

dication, which also extends over approximately four thiophene rings, although it has been suggested that such a bipolaron may not be stable due to coulombic interactions present in a dication.⁶ In contrast to conducting polymer work, heavy doping levels are employed to ensure polaron formation. This can lead to bipolaron formation or to degradation of the polymer.

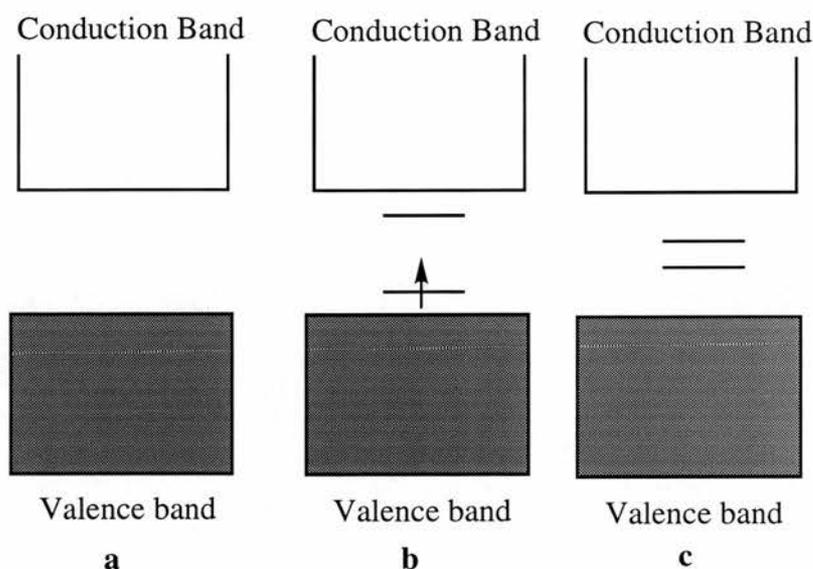


Figure 1

Figure 1 Schematic diagram of band gaps in: **a** neutral polymer, **b** polaron formation and **c** bipolaron formation.

It has been suggested however that if a short enough dopable segment is used, bipolaron formation should be disfavoured due to the coulombic repulsion's inherent in a dication.⁶ Ideally we require a long enough dopable segment to provide stabilisation yet short enough to prevent bipolaron formation. A second factor which favours shorter polaron units is based on a consideration of the effectiveness of the FCU. If *m*-phenylene is the FCU, the simplest high spin system is the biradical *m*-xylene, in which the triplet state is more stable than the singlet by $\approx 10\text{kcal/mol}$. Dougherty and co-workers have shown that the spin coupling strength quantitatively scales with the spin density at the radical centres of the FCU.⁷ If the assumption

is made that spin is roughly delocalised over the length of the polaron then a longer polaron will dilute the spin and diminish the effectiveness of the FCU.

From these considerations we chose quaterthiophene **Figure 2** as the base for our spin containing unit. Stabilisation will be provided by delocalisation and also by the heteroatoms and the unit should be small enough to disfavour bipolaron formation due to electrostatic reasons. A problem associated with quaterthiophene units as SCU's is that long, planar, conjugated π systems are notoriously insoluble and difficult to characterise. A number of potential magnetic organic polymers that are intractable insoluble materials have been produced.³ While these may become technologically important, they are poor vehicles for detailed structural activity studies and thus for developing an understanding of the magnetic properties of films.

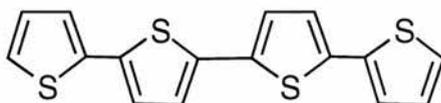


Figure 2

In conducting polymer work, the inclusion of long alkyl chains has improved the solubility characteristics of highly conjugated polymers. These must be carefully incorporated since topological studies of alkylated conducting polymers, and work carried out by Rajca⁸, has shown that the introduction of solubilising groups often causes steric interference which leads to twisting out of conjugation of the polymer backbone. These solubilising groups can be attached to the SCU, FCU or both.

Dougherty attached a hexadecyl chain to the 5-position of a 1,3-phenylene ferromagnetic coupling unit and claimed that it would not interfere with the polymer backbone. We decided to attach the alkyl solubilising groups to the quaterthiophene spin containing unit for a number of reasons.

- i It had been suggested that cations of oligopyrroles and oligothiophenes form diamagnetic π dimers in the solid state and in solution at low temperatures. Recently, Janssen has established that thiophene oligomers linked via 1,3-phenylene form π dimers in solution and concluded that it was not possible to achieve high spin in such systems.⁹ It was also suggested that this dimerisation explained the low spin concentrations observed in similar systems. We postulated that by attaching the solubilising groups to the quaterthiophene unit, steric shielding would prevent π dimerisation from taking place.
- ii The use of solubilising groups at the 5 position of 1,3-phenylene limits the development of the polymer to a 2-D structure. Attaching the solubilising groups to the SCU allows the extension of the structure in 3-D by using 1,3,5-phenylene as the ferromagnetic coupling unit containing unit. This is important since bulk ferromagnetism can only be observed for 2 and 3-dimensional structures.
- iii This approach allows the incorporation of 4, rather than 1 alkyl chain per monomer unit. The alkyl chains can also stabilise the induced polarons but may also hinder the doping process due to steric reasons.

Nature and Position of Solubilising Groups

A clear indication of the relationship between structural homogeneity and improved electrical and optical properties was first observed in Naarman polyacetylene.¹⁰ Given that the degree of π overlap along the chain directly determines the bandwidths, classically prepared polyacetylenes possess larger band gaps than more structurally homogeneous polymers. Similar to classical polyacetylene the standard methods used to make poly(3-alkylthiophenes) generate a large number of defects due to random couplings at the two and five positions of the thiophene ring, **Figure 3**. These structures contain large numbers of thiophene rings that are twisted far out of conjugation due to steric interactions between alkyl chains.

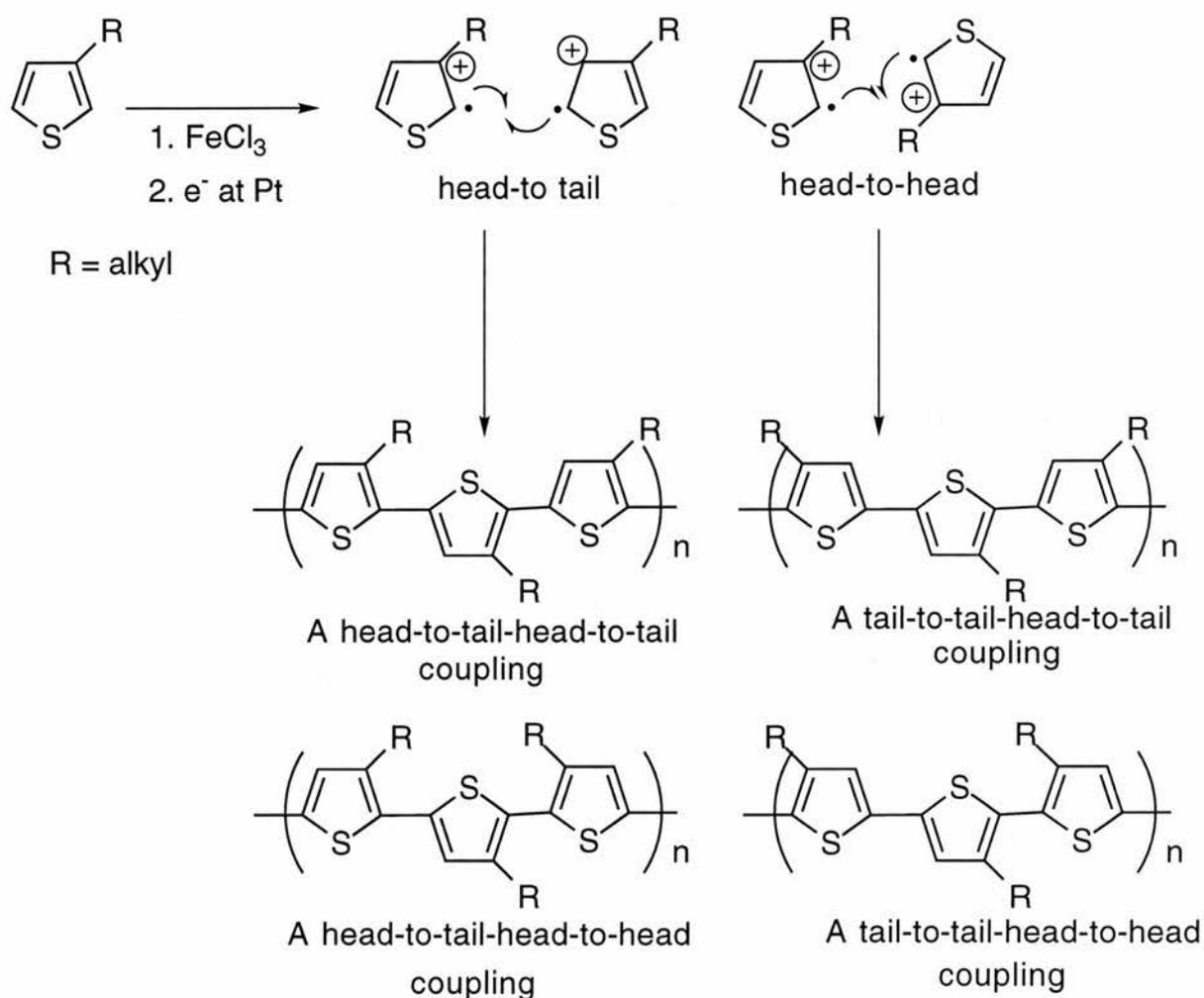
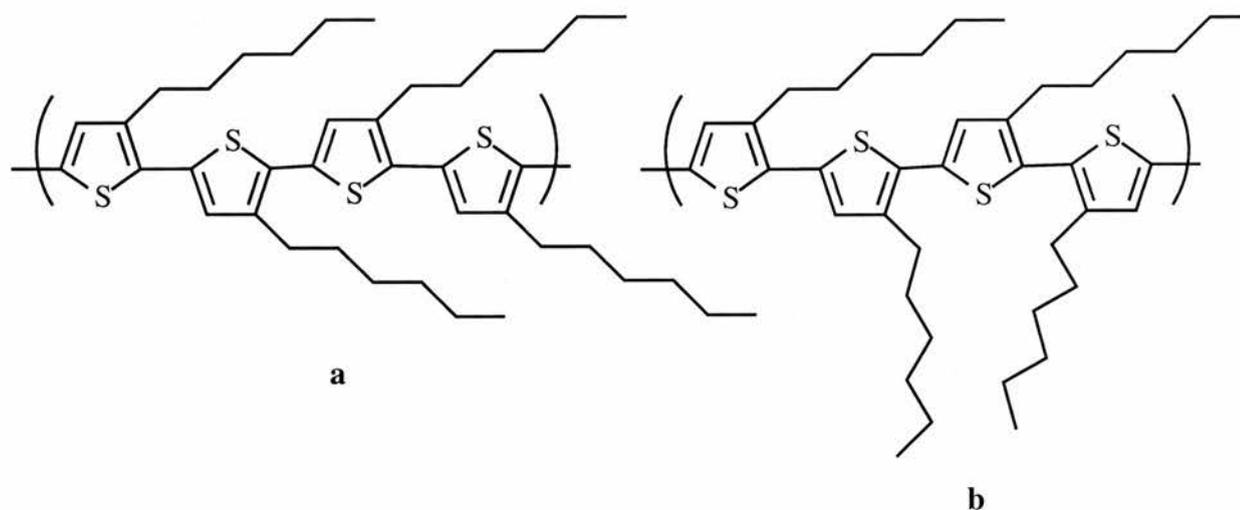


Figure 3

McCullough developed a synthetic route that allows complete regiochemical control to produce structurally homogeneous poly(3-alkylthiophenes).¹¹ Given that the torsion angle between thiophene rings determines the band gaps and the extent of π overlap along the chain. It is absolutely critical to ferromagnetic design to form structurally homogeneous polymers. Examination of model dimers, trimers and tetramers by molecular mechanics and *ab initio* calculations has shown that lowest energy conformational structures, where all rings are coplanar, have the alkyl groups substituted in a head to tail fashion **Figure 4 a**.¹²



Undesirable Coupling:-
 Less conjugation
 Smaller Bandwidths
 Larger bandgaps
 Lower conductivities

Figure 4

We chose the hexyl group as the solubilising group since it should provide solubility yet result in minimal intrachain steric interactions, therefore our spin containing unit was to be a head-to-tail substituted quaterthiophene as shown in **Figure 4 a**.

Design of Ferromagnetic Coupling Unit

Dougherty considered the choice of ferromagnetic coupling units critical to design and began investigating various potential FCU's in the early nineties. Dougherty concluded that magnetism arises when the overlap integral between orbitals is small but the exchange integral remains large. This is possible in fully conjugated, planar π systems with topologies that produce two NBMO's which are degenerate and where the critical issue is the extent to which the NBMO's overlap in space rather than their relative energies.

Dougherty developed a technique to evaluate FCU's which involved linking two robust SCU's through potential coupling units. He used 2-alkylidene-1,3-cyclopentadienyl units which have a large triplet preference, are synthetically accessible and thermally stable. Initial studies focused on the coupling units shown in **Figure 5**.

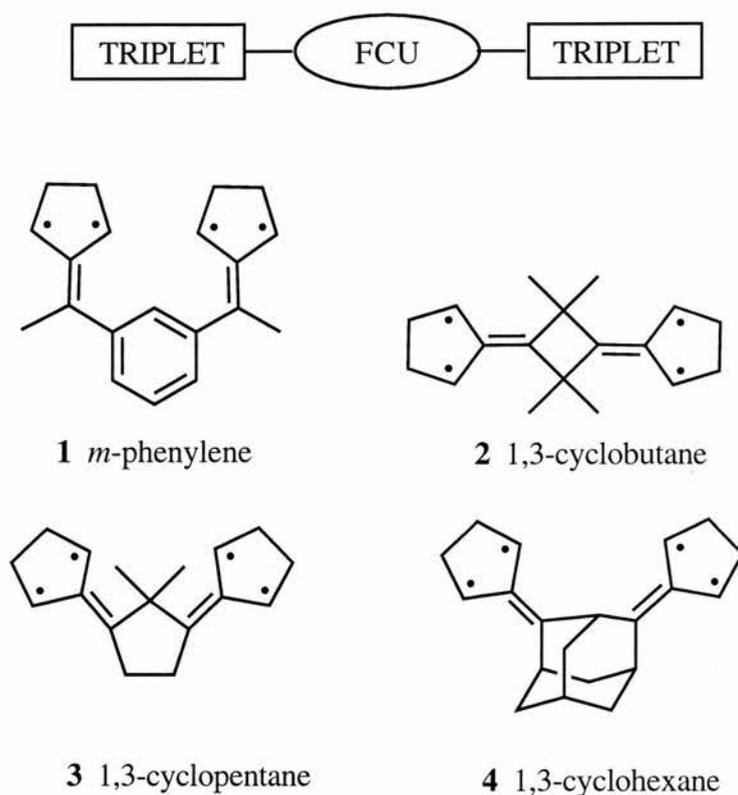
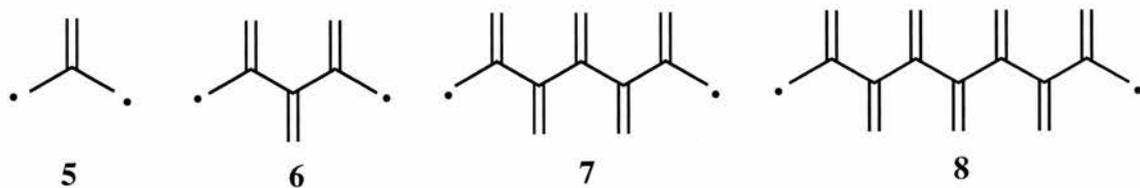
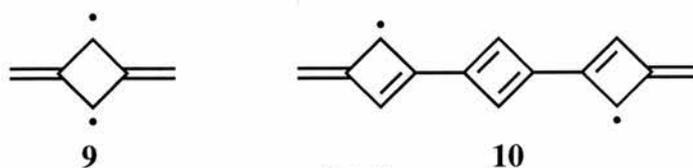


Figure 5

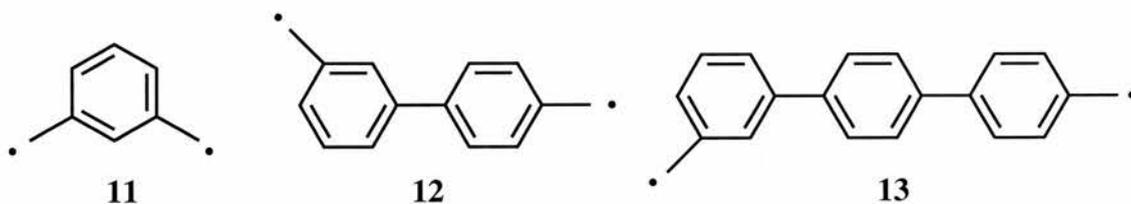
If the groups shown act as ferromagnetic coupling units then a quintet should be observed by low temperature EPR. **1** and **2** were found to be good FCU's whilst **3** acted as a weak FCU, **4** however coupled the spins in an antiferromagnetic fashion. Studies on the strength of spin coupling have been carried out by Li, Ma and Jiang.¹³ Application of the effective valence bond model, proposed by Malrieu and Maynau¹⁴, to biradicals **5-16** allowed the estimation of ΔE_{ST} which relates to chemical reactivity and also reflects the strength of spin coupling between two unpaired sites.



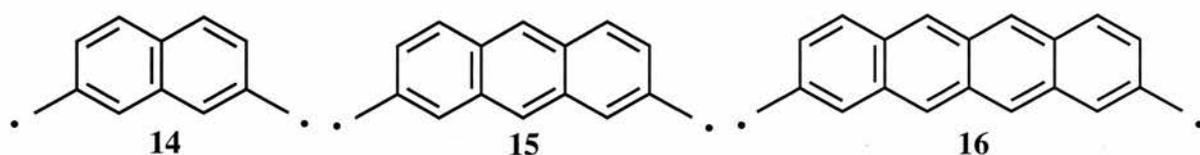
Set A



Set B



Set C



Set D

	ΔE_{ST}			
Set A (5-8)	1.555	0.146	0.029	0.006
Set B (9, 10)	1.492	0.248		
Set C (11-13)	1.146	0.380	0.147	
Set D (14-16)	0.842	0.634	0.487	

Set A decays drastically with increasing topological distance as does Set B. Set C also decreases but in a smoother manner. Interestingly the coupling through three sequential benzene rings is still appreciable. Strong ferromagnetic coupling would appear to emerge in biradicals with a short topological distance between spins and also where numerous spin-coupling paths and large delocalisation effects are present in SCU's. The same group also carried out investigations to determine to what extent the coupling constant in the FCU in

biradicals is maintained in polyradicals and ferromagnetic polymers, using the classical valence bond model based on **a** vinylidene, **b** biphenyl units and **c** *m*-phenylene, **Figure 6**.

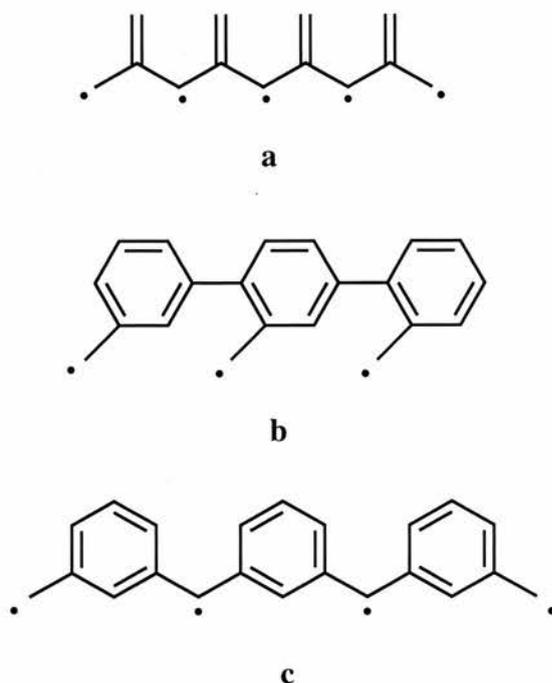


Figure 6

It was found that the coupling constant through vinylidene decreases appreciably from the biradical to the linear triradical. The spin coupling through *m*-phenylene in the biradical is reduced by one third in the linear triradical. The magnitude of coupling through the central *m*-phenylene in a tetradical is lower than the terminal *m*-phenylene and is taken to be a good approximation for a poly(*m*-phenylmethylene) system. The 2,3'- connected biphenyl unit is found to have stronger magnitude of coupling in the linear triradical than in the biradical.

The intramolecular spin-coupling through *m*-phenylene has been extensively studied by a variety of theoretical models and also through experiments designed to characterise the effectiveness of *m*-phenylene as a FCU.¹⁵ By far *m*-phenylene has been proven to be the best FCU for synthesising high spin molecules and truly practical magnetic materials. We therefore chose this as our ferromagnetic coupling unit, which combined with the SCU, describes the target polymer, **Figure 7**.

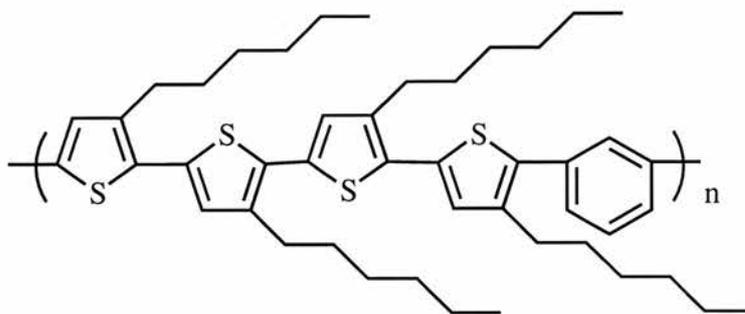
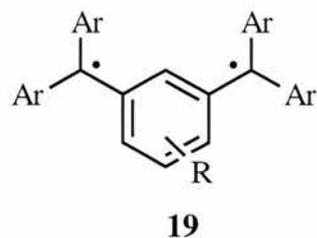
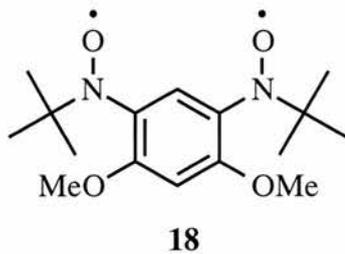
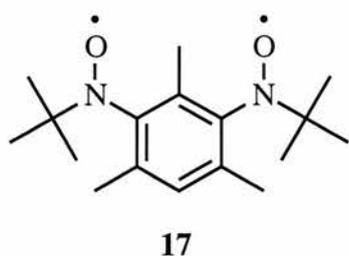


Figure 7

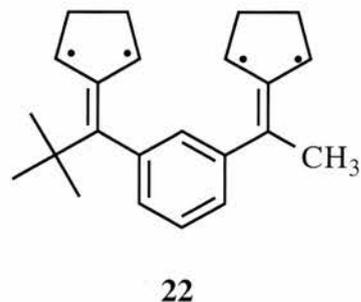
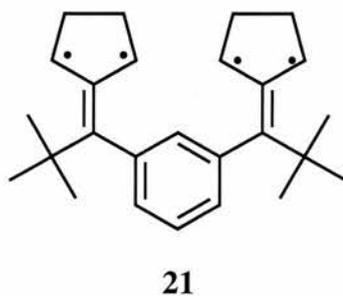
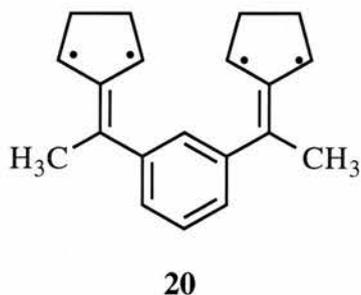
However, in 1995 Iwamura presented an interesting alternative by coupling nitronyl nitroxides through 2,4-substituted thiophene.¹⁶ Iwamura argued that since thiophene rings are more electron rich than benzene, they are better equipped to stabilise radical cations and also that thiophene rings, which are sterically less demanding than benzene, could result in planar polymer backbones. The interactions between the nitronyl nitroxides were found to be ferromagnetic and were larger than those observed through *m*-phenylene, presumably due to an increase in co-planarity hence greater spin polarisation. However, extension to bithienyl units greatly weakened the interactions to the extent that degenerate singlet and triplet states were produced. This was accounted for by the poor delocalisation of the nitroxide's spin into the thiophene ring.

Conformational effects on *m*-phenylene as a FCU

Having decided upon the structure of the target monomers it would be advantageous to be able to estimate the effectiveness of *m*-phenylene in systems where the radical centres may be out of conjugation with the aromatic ring. Several groups have addressed this issue and have found that in highly crowded bisnitroxyls **17**¹⁷ and **18**¹⁸ the two SCU's are twisted completely out of conjugation and the biradicals have singlet ground states. In contrast extremely congested polyaryl derivatives **19** show high spin states despite a large degree of twisting.

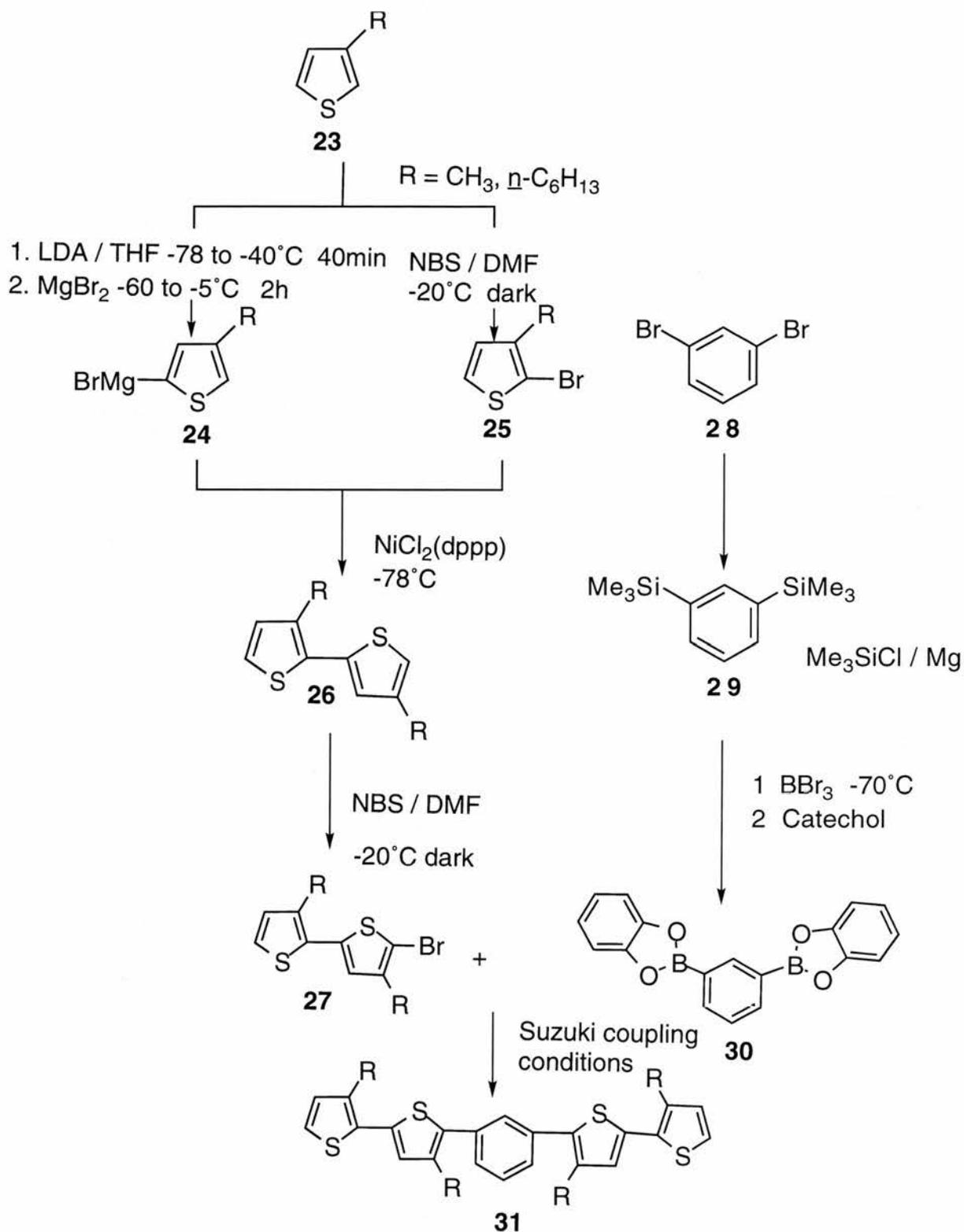


Again using the bistrimethylene methane strategy, Dougherty found that in conditions of modest twisting, **20**, *m*-phenylene remains an effective FCU. Completely twisting both SCU's out of conjugation with *m*-phenylene, **21**, leads to no interactions at all and that having one SCU in plane and one completely out of plane, **22**, still leads to ferromagnetic coupling.¹⁹ It has been proposed that this occurs as a result of a novel mechanism in which antiferromagnetic coupling between a centre of negative spin density and a centre of positive spin density leads to overall ferromagnetic coupling.



2.2 Synthetic Routes Towards a Spin-Containing Unit

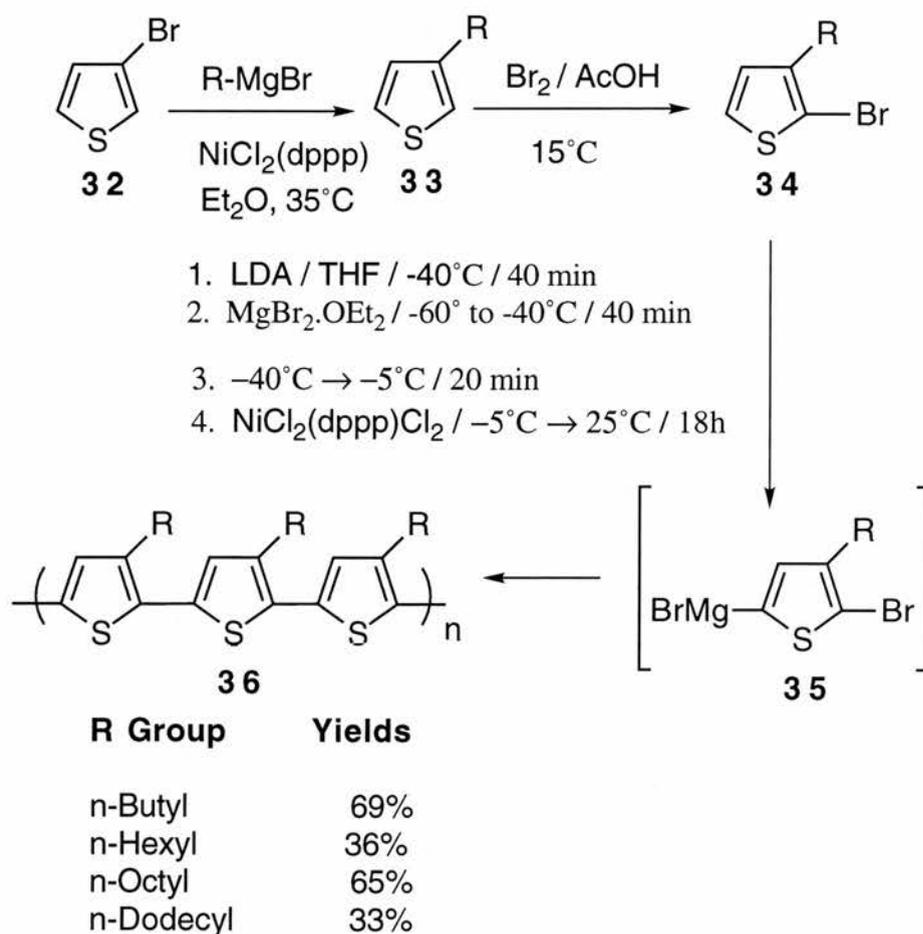
The proposed synthetic strategy towards our desired monomers is shown in **Scheme 1**.



Scheme 1

The key step in the proposed synthesis of monomer **31** was a Suzuki coupling reaction²⁰ involving two equivalents of the regioregular brominated dimer **27** to one equivalent of the bis (boronic ester) **30**. It was thought that the Grignard reaction of 1,3-dibromobenzene **28** with trimethylsilyl chloride followed by reaction of the resulting disilylated product **29** with boron tribromide and subsequent addition of catechol should afford the bis (boronic ester) **30**. It was also envisaged that the head to tail dimer 3,4'-dialkyl-2,2'-bithiophene **26** could be formed exclusively and in good yield by the nickel catalysed coupling of 2-bromo-3-alkylthiophene **25** with 2-bromomagnesio-4-alkylthiophene **24**.

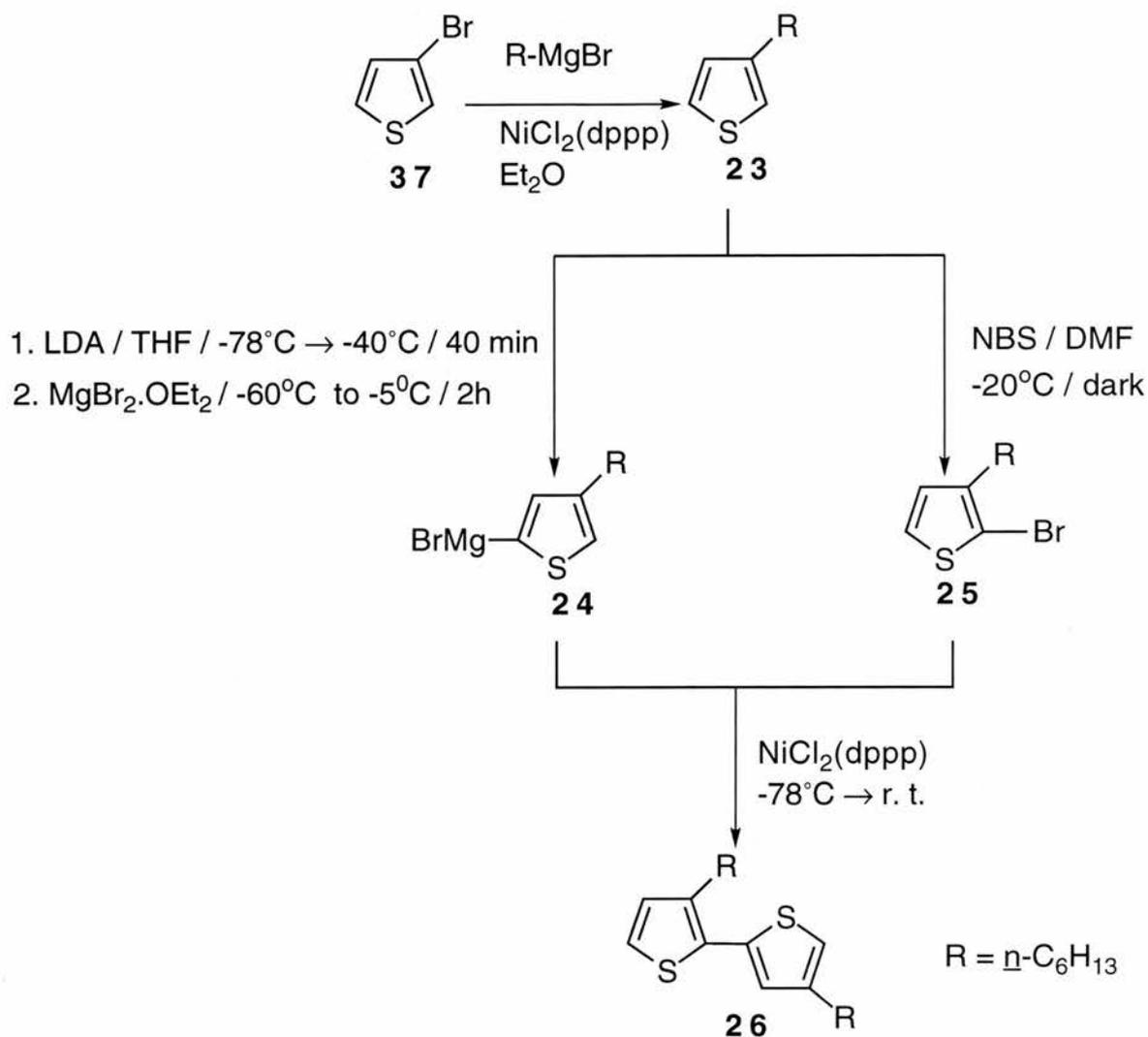
McCullough and co-workers reported the synthesis of structurally homogeneous poly(3-alkylthiophenes) in three steps from bromothiophene, **Scheme 2**.¹⁸



Scheme 2

The polymerisation was performed in a one flask reaction consisting of metallation of 2-bromo-3-alkylthiophene selectively at the 5- position followed by trapping of the 2-bromo-3-alkyl-5-lithiothiophene with magnesium bromide etherate to afford **35**. Subsequent treatment of **35**, in situ with Ni(dppp)Cl₂, led to regiochemically defined head-to-tail coupled poly(3-alkylthiophenes).²¹ One of the key features of this synthesis was the ability to metallate **34** with lithium diisopropylamide in the 5-position, regiospecifically and without scrambling of the organolithium.²² The regiospecific metallation of bromothiophenes and 3-alkylthiophenes occurs at either the 2- or 5-positions on thiophene. Under certain conditions a positional exchange of lithium and halogen can occur, this mechanism is known as 'halogen dance'.²³ Quenching studies by McCullough showed that 2-bromo-3-alkyl-5-lithiothiophenes, generated under the conditions shown in **Scheme 2**, undergo little or no 'scrambling' and are therefore ideal for the desired regiospecific reaction.

We attempted to synthesise 3,4'-dihexyl-2,2'-bithiophene by a modified McCullough reaction, involving the cross-coupling of 2-bromomagnesio-4-hexylthiophene with 2-bromo-3-hexylthiophene in the presence of a nickel chloride diphenylphosphinopropane catalyst, **Scheme 3**.



Scheme 3

A nickel or palladium catalyst is most commonly used for these cross-coupling reactions. In the majority of cross-coupling reactions higher yields are obtained using nickel(II) chloride diphenylphosphinopropane as a catalyst rather than dichloro[1,1-bis(diphenylphosphino)ferrocene] palladium.²⁴

3-Hexylthiophene was prepared by the $\text{NiCl}_2(\text{dppp})$ catalysed reaction of the Grignard of 1-bromohexane with 3-bromothiophene at 0°C , in yields of 50-70%. **23** could be selectively brominated at the 2-position using N-bromosuccinimide (NBS) in dimethylformamide (DMF) at -20°C in the absence of light. This was in contrast to the method of Gronowitz and co-workers who employed $\text{Br}_2/\text{CH}_3\text{COOH}$ as a brominating agent. After brominating with NBS

in DMF, the solvent was removed by distillation producing a dark brown residue. Further distillation resulted in the isolation of a mixture of **23** and **25** in a ratio of 1:4 measured by ¹H NMR spectroscopy. On repeating the bromination reaction, examination of the reaction mixture after the removal of solvent indicated only a small amount of unreacted starting materials present. Therefore it would seem reasonable to assume that the bromination reaction was reversible on heating. Omission of the final distillation step led to yields of 70-80% of 2-bromo-3-hexylthiophene.

The cross-coupling reaction between **24** and **25** was initially carried out using the nickel chloride diphenylphosphinopropane catalyst. Spectroscopy revealed that the reaction mixture contained only 17% of the cross-coupled product. The starting materials were again prepared and the reaction repeated using the palladium catalyst which resulted in the formation of 22% of the cross-coupled product. On both occasions unreacted starting materials represented the remaining material. These poor yields were thought to be a result of the failure to generate sufficient quantities of the components for coupling *in situ*, resulting in only small amounts of 3,4'-dihexyl-2,2'-bithiophene being formed.

A detailed study has been made into the metallation of 3-alkylthiophenes, which reveals that in the reaction of butyl lithium-amine complexes with 3-alkylthiophenes, an increase in steric bulk of the alkyl group directs metallation selectively to the 5-position. For example, in the lithiation of 3-tertbutylthiophene with lithium diisopropylamide, the presence of the 2-lithiated species cannot be detected.²⁵

2-Bromo-3-hexylthiophene was purified by column chromatography to remove trace amounts of unreacted 3-hexylthiophene and having assumed that both components of the coupling reaction should be formed, it was decided to concentrate on the nature and the conditions of the coupling reaction. The cross-coupling reaction takes place at -78°C and is allowed to warm to room temperature overnight. The first variation on these conditions involved increasing the time for metallation and also the temperature at which the cross-coupling reaction was carried

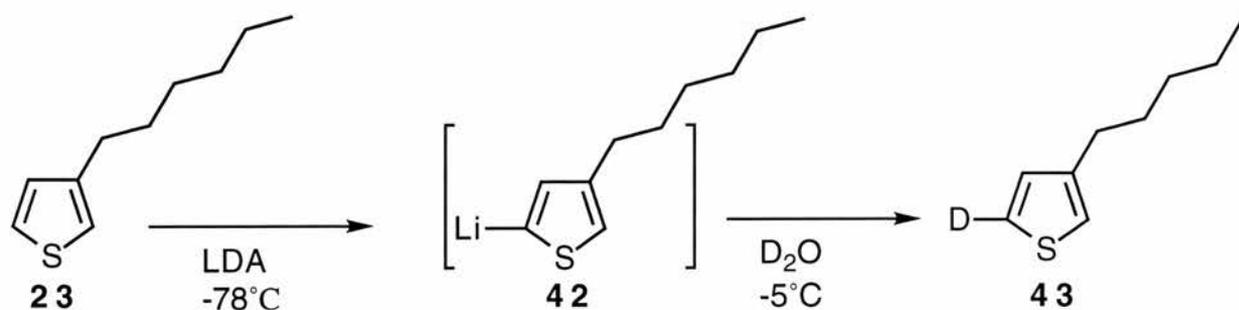
increased from 1 to 2 hours, however no improvement in the yield of cross-coupled product was observed.

The polymerisation of 3-alkylthiophenes using the McCullough method gives a variety of yields of polymer depending on the alkyl substituent. The trend in yields agrees with the assumption that any increase in the steric bulk of the alkyl substituent results in smaller yields of polymer, with the exception of the case in which additional catalyst is added after 12 hours. We decided to alter the alkyl substituent in our coupling reaction and compare the reaction yields. 3-Methylthiophene was brominated using N-bromosuccinimide in chloroform/acetic acid.²⁷ This method was faster and produced 2-bromo-3-methylthiophene in a yield of 85% and also allowed the product to be isolated in high purity without a chromatographic work up. The 2-bromo-3-methylthiophene was then used in a cross-coupling reaction similar to **Scheme 3**.

Spectroscopic analysis revealed that only 10% of the head to tail cross-coupled product 3,4'-dimethyl-2,2'-bithiophene had been produced, suggesting that the reduction of steric bulk had led to no improvement in reaction yield.

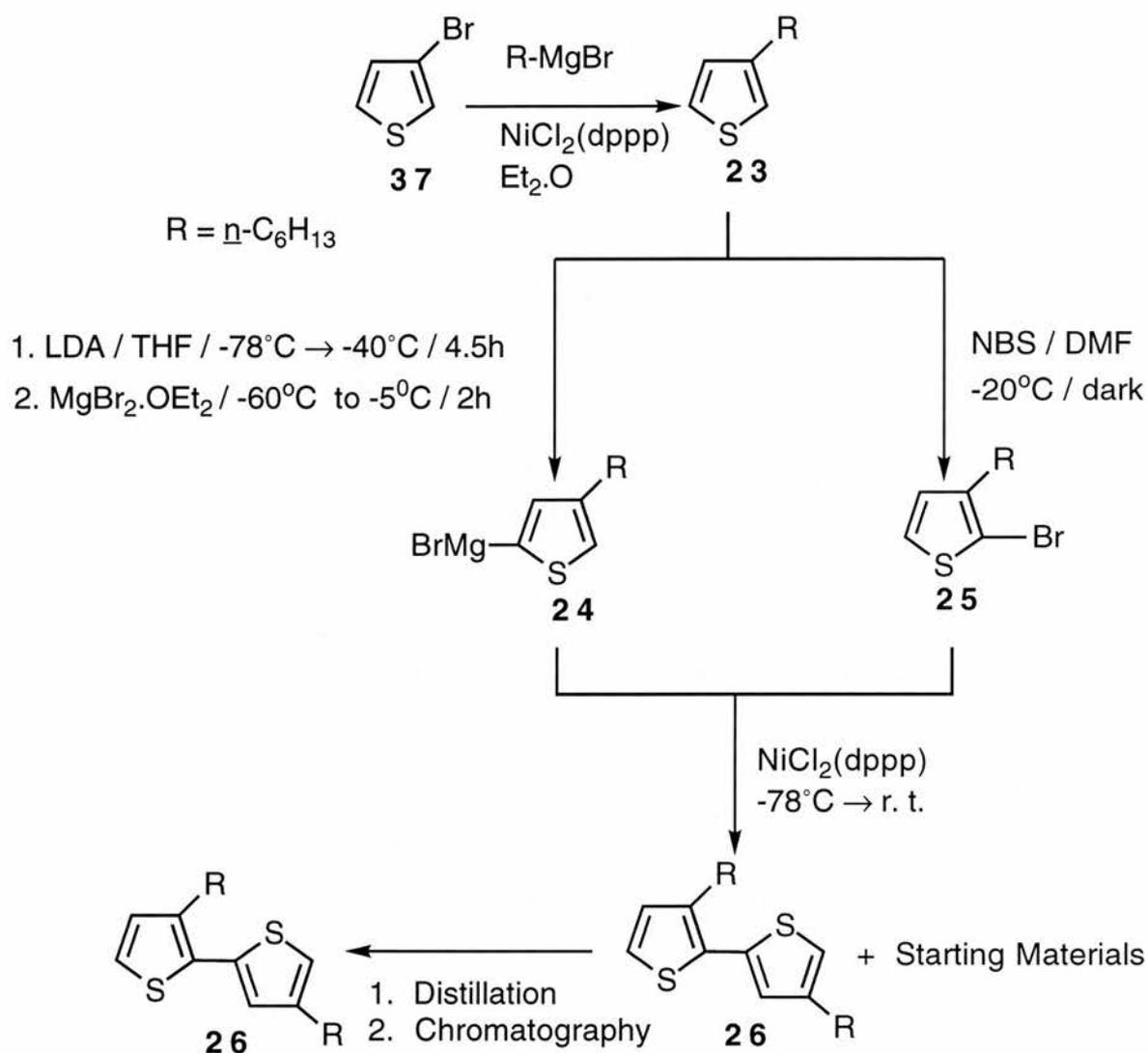
Consultation with Dr. Ronald Elsenbaumer of the University of Texas highlighted the difficulties involved in the cross-coupling reactions of alkylthiophenes. It was suggested that the critical step in these reactions involved the conversion of the lithiated species to the Grignard reagent. The trans-metallation reaction often requires long periods of time for lithiation to occur and may require the use of 4-6 equivalents of magnesium bromide etherate. The original cross-coupling reaction was repeated using 4 equivalents of magnesium bromide etherate and the time for metallation increased to 2 hours. The excess magnesium bromide etherate remained unreacted and was insoluble in the THF solution. Analysis of the reaction product indicated that no coupling had occurred.

Quenching studies with D₂O were carried out to determine if 2-lithio-4-hexylthiophene was formed *in situ*, **Scheme 5**.



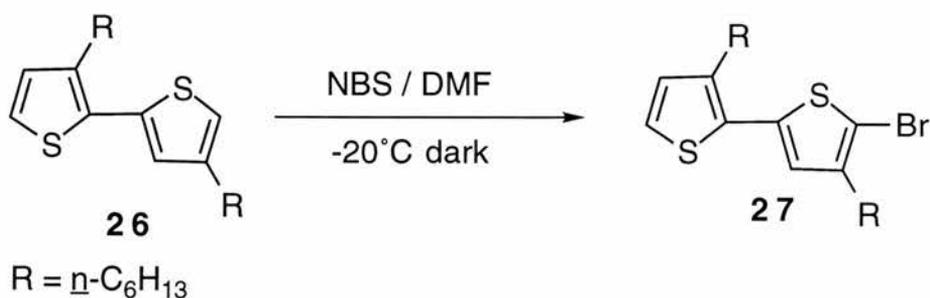
Scheme 5

After quenching 2-lithio-4-hexylthiophene **42** with D₂O the products were analysed by ¹H NMR spectroscopy which indicated that deuterium had completely replaced hydrogen at position -5 and that little or no scrambling of the 2-lithio-4-hexylthiophene had occurred. This was confirmed by 76.8 MHz ²D NMR. As previously mentioned magnesium bromide etherate is insoluble in THF but becomes soluble as it takes part in the trans-metallation reaction. The complete solubility of magnesium bromide etherate, as observed in our reaction, is therefore a good indication that the reaction has occurred. The problematic step would therefore appear to be the actual coupling of **24** with **25** which had been attempted using different catalysts, a range of temperatures and various alkyl side chains, without any increase in the reaction yield. The cross-coupling reaction was repeated and 3,4'-dihexyl-2,2'-bithiophene isolated from the reaction mixture in yields of 15-20%. This was achieved by increasing the time for metallation to 4.5 hours. The crude mixture was then distilled to remove 3-hexylthiophene. The residual oil was then further purified by both dry column flash chromatography and also conventional column chromatography using petroleum ether/ethyl acetate mixture as eluent, to remove 2-bromo-3-hexylthiophene **Scheme 6**.



Scheme 6

The next synthetic step involved the bromination of 3,4'-dihexyl-2,2'-bithiophene using *N*-bromosuccinimide in dimethylformamide at -20°C , in the dark, to afford 5'-bromo-3,4'-dihexyl-2,2'-bithiophene in good yield, **Scheme 7**. This compound was required in order to undergo Suzuki coupling with suitable boronic acids or esters

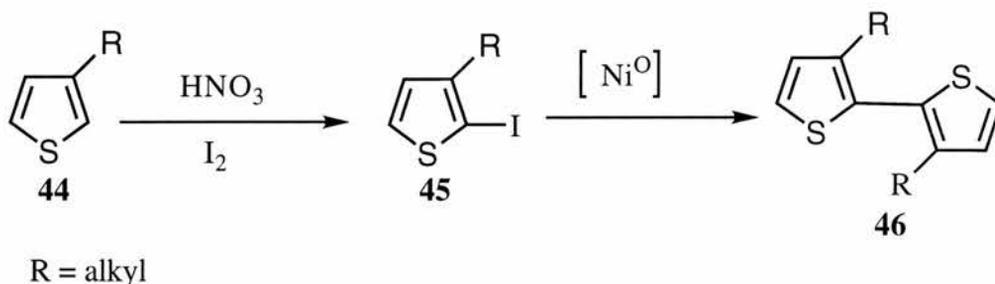


Scheme 7

2.3 Alternative Methods of Regioselective Coupling

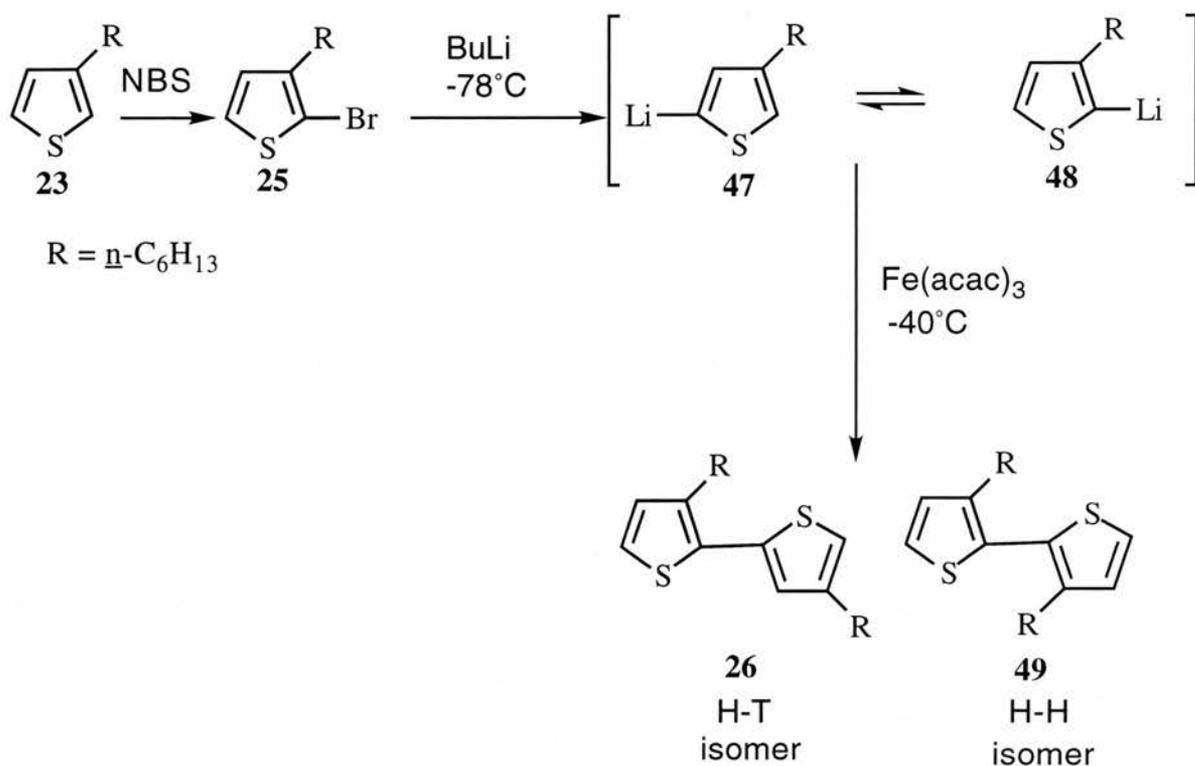
Oxidative Coupling Using Copper(II) and Iron(III) Reagents

It may be convenient to form a differently orientated dimer and there are several ways in which this can be achieved. One method published by Zagorski and Krishe involves lithiation of 3-alkylthiophene followed by an oxidative coupling with CuCl_2 . The lithiation conditions make use of *N,N,N',N'*-tetramethylethylene diamine and butyl lithium solution in dry ether, which is refluxed in the presence of the alkylthiophene for 1 hour. The solution is then cooled to -78°C and 1 equivalent of CuCl_2 added. The reaction yields a 10:1 mixture of 4,4' and 3,3'-dibutyl-2,2'-bithiophene which can be separated by recrystallisation from ether at dry ice temperatures.²⁸ A recent paper by Higuchi and co-workers improved upon the yields of Iyoda *et. al.* whose reaction involved the homo-coupling of 3-alkyl-2-iodothiophenes, **Scheme 8**.²⁹



Scheme 8

The method followed by Higuchi involves the lithiation of 2-bromo-3-hexylthiophene by butyl lithium at -78°C followed by an oxidative homo-coupling in the presence of iron(acetylacetonate) at -78°C .³⁰ 3,3'-Dihexyl-2,2'-bithiophene is formed in yields of 65-75% along with 10-15% of the reduction product, 3-hexylthiophene. An interesting feature of this reaction is observed when there is an increase in both the reaction scale and an elevation of the reaction temperature. If the coupling reaction is carried out at -40°C rather than -78°C a considerable amount of 3,4'-dihexyl-2,2'-bithiophene is obtained in addition to the head to head product, in ratios of between 1:3 and 1:7, **Scheme 9**.



Scheme 9

We therefore carried out the reaction on a large scale (> 20 mmol) and added the oxidant at -40°C rather than the prescribed -78°C in an attempt to increase the ratio of the head-to-tail isomer. The resultant solution was then distilled to remove 3-hexylthiophene and finally purified by column chromatography using silica gel and hexane as eluent. ^1H NMR spectroscopy was used to determine the ratio of head-to-tail and head to head isomers, since the α protons of the alkyl chains of each isomer have different chemical shifts, **Figure 8**.

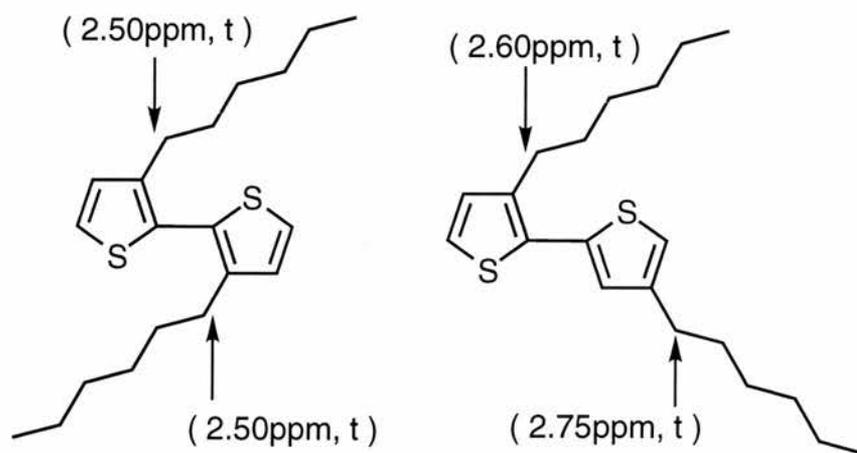
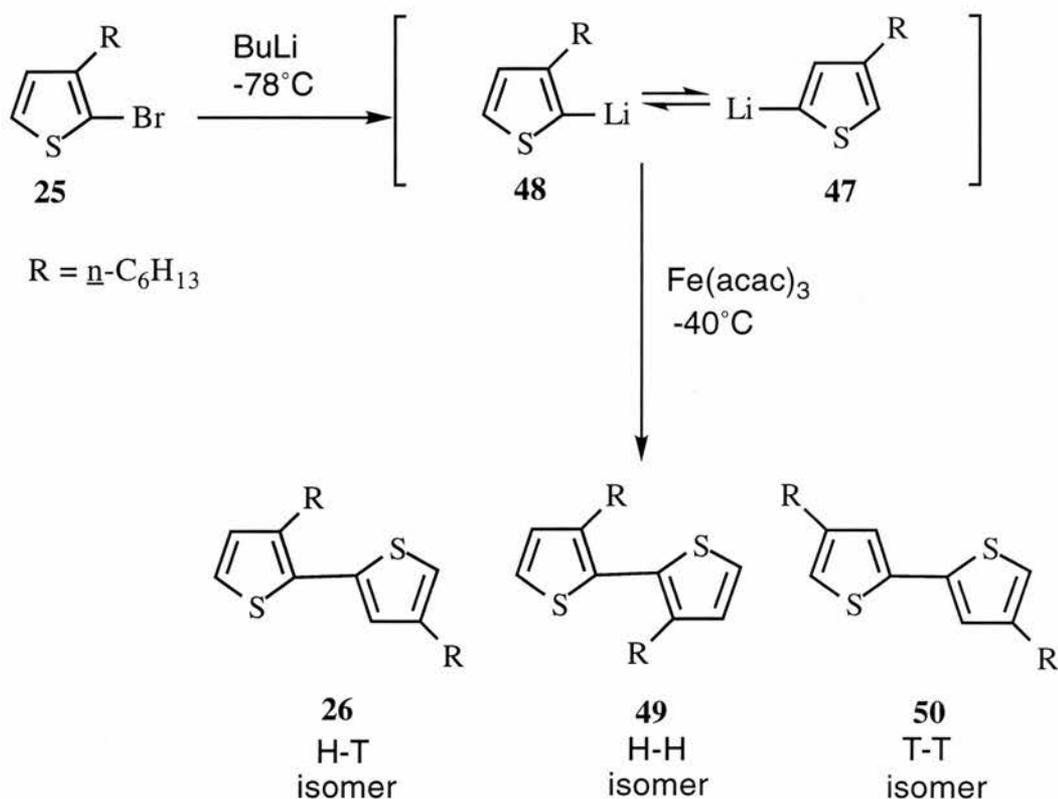


Figure 8

The integrals of the ^1H NMR spectrum suggested a ratio of 1:1 for the head to head and head to tail isomers in addition to signals corresponding to 3-hexylthiophene and 2-bromo-3-hexylthiophene. The signal at 2.75 ppm relating to the α -protons of the head to tail isomer actually showed an overlapping doublet of triplets. This has been attributed to the presence of the tail to tail isomer, since any α -protons attached at the 4-position of dialkylbithiophene have a similar chemical shift. If isomerisation of intermediate **48**, to the more stable **47**, takes place then homo-coupling of **47** can also occur to yield 4,4'-dihexyl-2,2'-bithiophene, **Scheme 10**.



Scheme 10

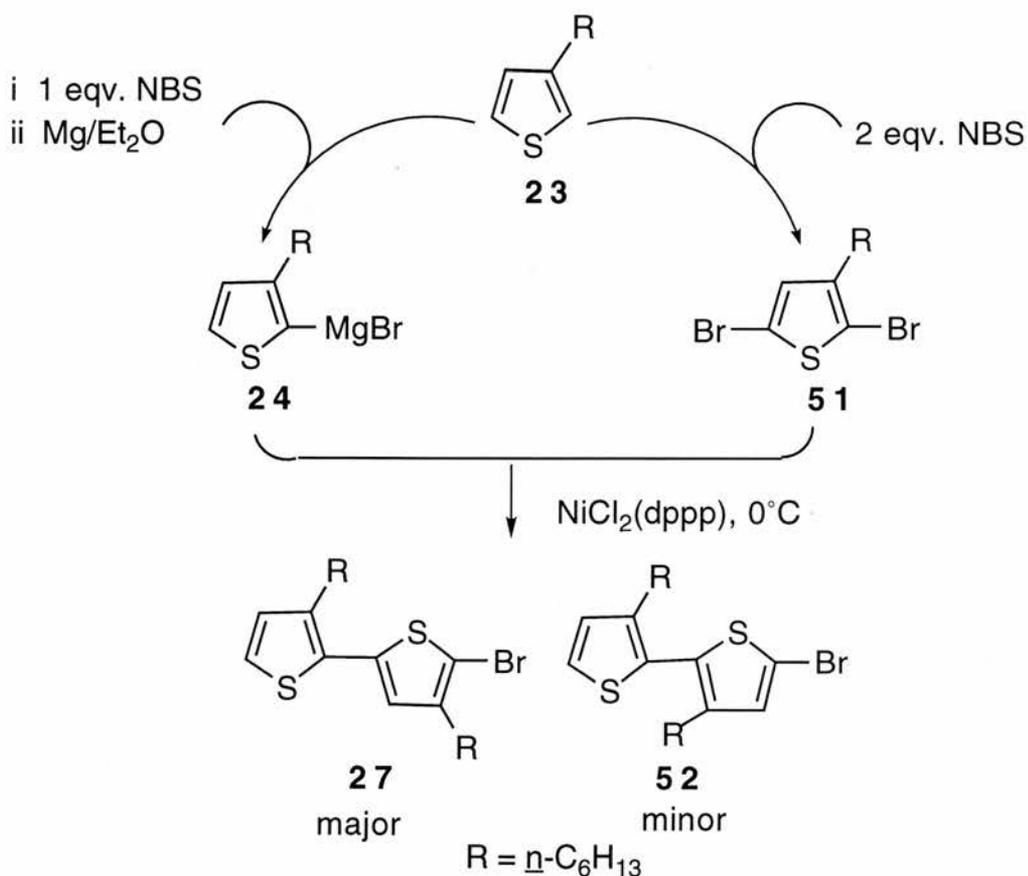
The chemical shift of the α -protons of the tail to tail isomer should be approximately 2.75 ppm. The reaction would appear to have 3 regioisomeric cross-coupled products, in addition to unreacted starting materials and the reduction product 3-hexylthiophene. A separation of the reaction products *via* selective bromination followed by column chromatography was attempted. However, the complete isolation of individual reaction products could not be achieved due to the difficulty involved in estimating the ratio of isomers present. Nevertheless, several reaction products such as 2-bromo-3,4'-dihexyl-2,2'-bithiophene and 3,3'-dihexyl-

2,2'-bithiophene could be identified by ^1H NMR. This method of separation and isolation will be covered in greater detail later in this chapter.

The iron(acetylacetonate) $_3$ catalysed reaction was also repeated at -78°C in order to produce the head to head regioisomer exclusively. The reaction product was found to contain 12% of the head to tail isomer, 20% of the head to head regioisomer and large amounts of unreacted 2-bromo-3-hexylthiophene and 3-hexylthiophene.

Selective Nickel Catalysed Cross-Coupling Reactions

Rather than generate a Grignard reagent *via* a transmetallation reaction we felt Grignard formation would be more efficient if effected directly from the bromide by mixing with magnesium turnings in ether or THF. 2-Bromomagnesium-3-hexylthiophene was added dropwise at 0°C to a solution of 2,5-dibromo-3-hexylthiophene, in ether, in the presence of a nickel(diphenylphosphino)propane catalyst, **Scheme 11**.



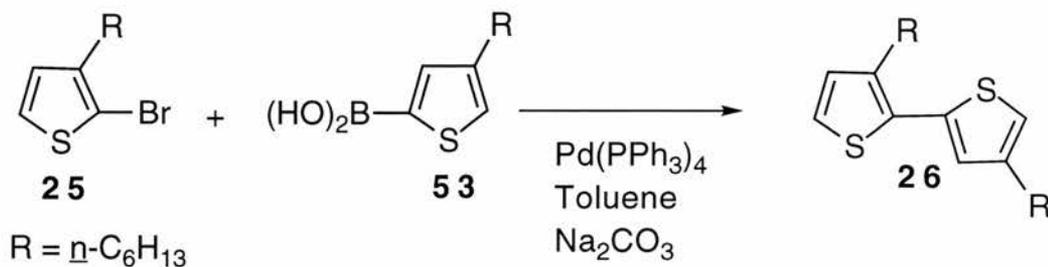
Scheme 11

We postulated that given the steric bulk and electron releasing properties of the adjacent alkyl group, a partially selective reaction at the 5-position of 2,5-dibromo-3-hexylthiophene would take place. The Grignard reagent **24** was formed and added to the dibromide **51** at 0°C over a 2h period. The reaction mixture was then refluxed in diethyl ether/benzene (4:1) for 20h. ¹H NMR analysis indicated mainly unreacted starting materials. A triplet at 2.75ppm suggested that some cross-coupling had occurred. It would appear that Grignard formation took place but did not undergo cross-coupling with the dibromide but was protonated on work up to yield 3-hexylthiophene. Spectroscopy also discounted trimer formation which could occur as a result of further coupling to activated dimers.³¹ This outcome is in agreement with our earlier results where poor cross-coupling yields were observed, despite both components of the coupling reaction being formed.

Attempted Preparation of 3,4'-Dihexyl-2,2'-bithiophene *via* Suzuki Cross-Coupling

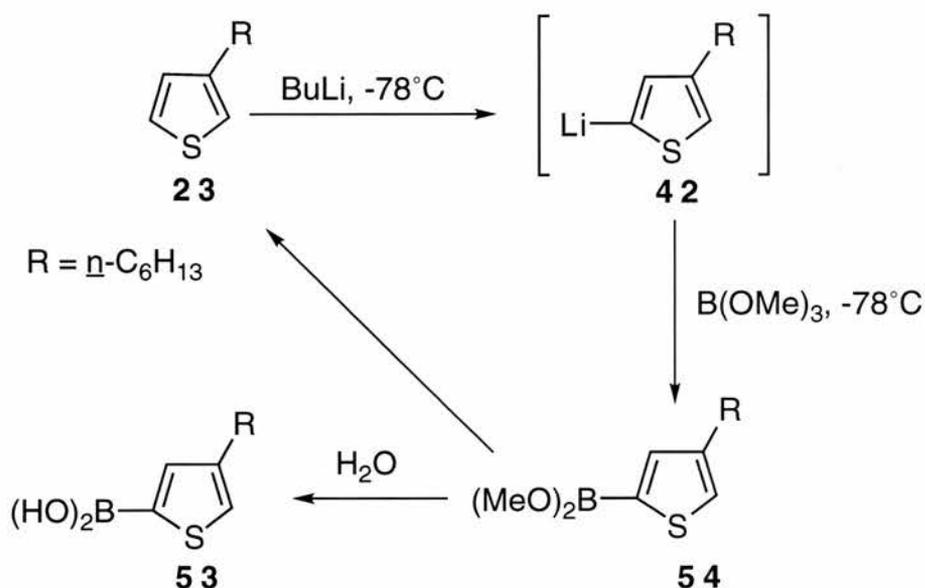
In 1982 Suzuki reported a simple and versatile method for the synthesis of unsymmetrical biaryls *via* the cross-coupling reaction of aryl boronic acids with haloarenes in the presence of a catalytic amount of palladium complex and base.³² Thereafter, many articles reporting the application of coupling reactions in the synthesis of condensed ring systems³³, multiple aryl coupling³⁴, vinyl aryl³⁵ and vinyl-vinyl³⁶ coupling have followed.

We considered the possibility of forming 3,4'-dihexyl-2,2'-bithiophene *via* the cross-coupling reaction between 1-thiophene-3-hexylboronic acid and 2-bromo-3-hexylthiophene, **Scheme 12**.



Scheme 12

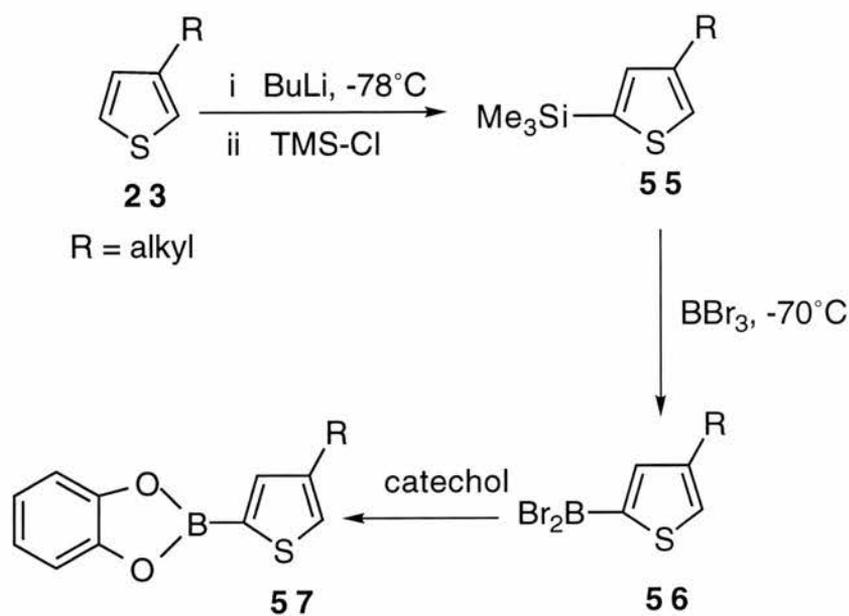
This required the preparation of 1-thiophene-3-hexylboronic acids or esters. 3-Hexylthiophene was lithiated at the 5-position with *n*-butyl lithium at -78°C . This was followed by the addition of trimethylborate also at -78°C . The solution was then allowed to warm to room temperature overnight before being quenched with water, **Scheme 13**.³⁷



Scheme 13

Spectroscopic analysis by ^1H NMR and also GCMS indicated that only a small conversion to the boronic acid had taken place and that the majority of the recovered materials were 3-hexylthiophene and trimethylborate. This can be accounted for by a competitive protodeboronation reaction during aqueous work up as observed by Effenberger and co-workers.³⁸ The reaction was also repeated using tributylborate³⁰ however a similar result was obtained.

Previous experience indicated that a viable route to 1-thiophene-3-alkylboronic acids or esters could be based on a 2-trimethylsilyl-4-alkylthiophene intermediate **55**. This intermediate would then undergo a further reaction with boron tribromide and catechol to afford the catechol ester, **Scheme 14**.



Scheme 14

A solution of 3-methylthiophene in diethyl ether was added to an ethereal solution of *n*-BuLi and TMEDA at -78°C and stirred for 1 hour to allow lithiation. A solution of trimethylsilyl chloride in diethyl ether was then added at -78°C and the solution allowed to warm to room temperature overnight. ^1H NMR spectroscopy of the reaction product showed three methyl peaks, indicative of three different compounds. Comparison of the spectra of 3-methylthiophene and the reaction product indicated that $> 50\%$ of the recovered material corresponded to 3-methylthiophene. The ^1H NMR spectrum of the reaction product also showed three peaks for the trimethylsilyl groups. The aromatic signals comprised a triplet at 7.23ppm and a doublet at 6.9ppm. This did not agree with any plausible substitution pattern and was probably a result of a mixture of reaction products, including the desired 2-trimethylsilyl-4-methylthiophene and presumably 2-trimethylsilyl-3-methylthiophene caused by the difference in steric bulk between hexyl and methyl allowing lithiation to occur at the 2-position.

Given the poor yields observed in this reaction, it was decided that this particular route to the catechol ester **57** was not feasible. If sufficient metallation of the alkylthiophenes occurs then the silylated thiophene should be readily formed and therefore we conclude that insufficient lithiation of 3-methylthiophene was responsible for the poor reaction yield.

Stille coupling

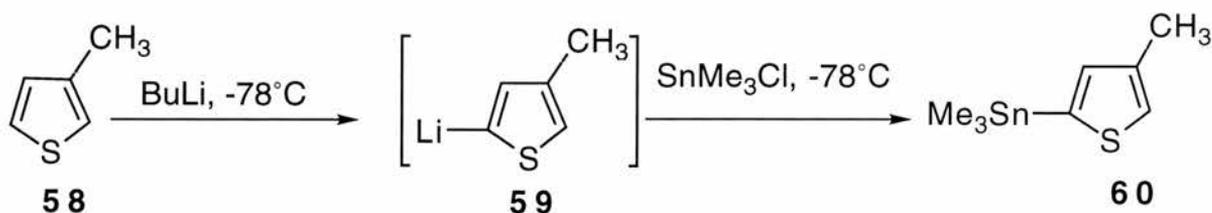
Stille coupling³⁹ is a carbon-carbon bond forming reaction consisting of a palladium catalysed reaction between an organotin reagent and an organic electrophile, **Scheme 15**.



Scheme 15

In this reaction only one of the tin substituents enters into the coupling reaction. This is not a problem if a relatively simple group, for example, methyl, is to be transferred, since tetramethyltin can be used. If the group to be transferred is more expensive or difficult to synthesise, then it would be a distinct advantage to use an organotin reagent which selectively transfers only this group. Fortunately, different groups are transferred with different selectivities from tin, the simple alkyl groups having the slowest transfer rates. Thus, an unsymmetrical organotin reagent containing three simple alkyl groups is chosen; the fourth group which undergoes transfer can be alkynyl, alkenyl, aryl, benzyl or allyl. This route was also appealing in that the organotin reagents are not moisture sensitive and could be isolated and characterised before entering into the coupling reaction.

The attempted synthesis of 2-trimethyltin-4-methylthiophene **60** was carried out in a similar fashion to 2-trimethylsilyl-4-methylthiophene, **Scheme 16**.

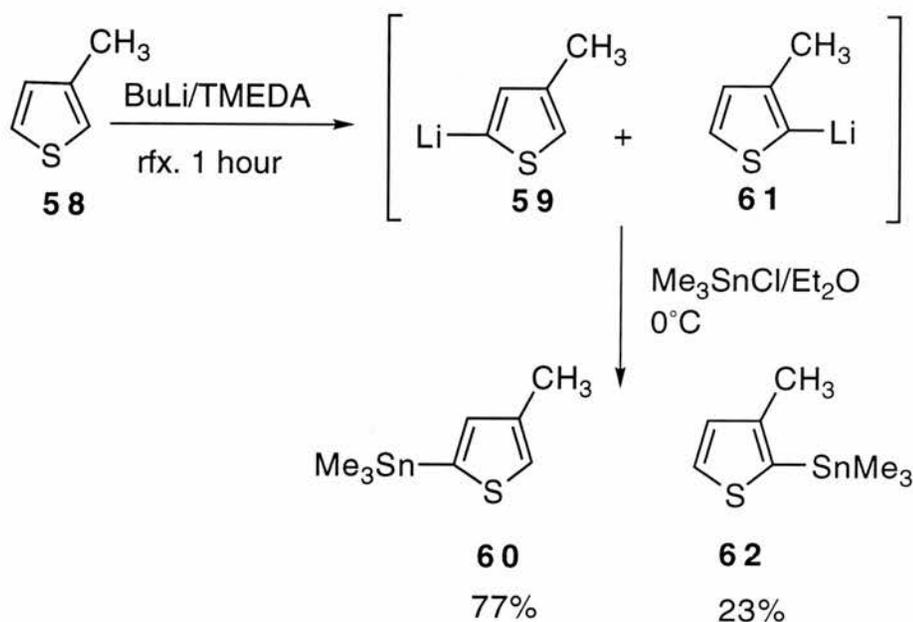


Scheme 16

Again lithiation followed by trapping with trimethyltin chloride was carried out at -78°C. As expected incomplete lithiation of 3-methylthiophene resulted in poor yields of 2-trimethyltin-4-

methylthiophene, although this contrasted with the findings of the experiment in which the lithiate was quenched with D₂O.

It was decided that the low temperatures involved in the lithiation reaction, which are essential in obtaining only the desired regioisomer, should be sacrificed in the quest for higher yielding reactions. The lithiation of 3-methylthiophene with n-BuLi and TMEDA was carried out in refluxing diethyl ether over a 1 hour period. The solution was then cooled to 0°C and a solution of trimethyltin chloride in diethyl ether added. The solution was then stirred at ambient temperature for 2 hours, **Scheme 17**.

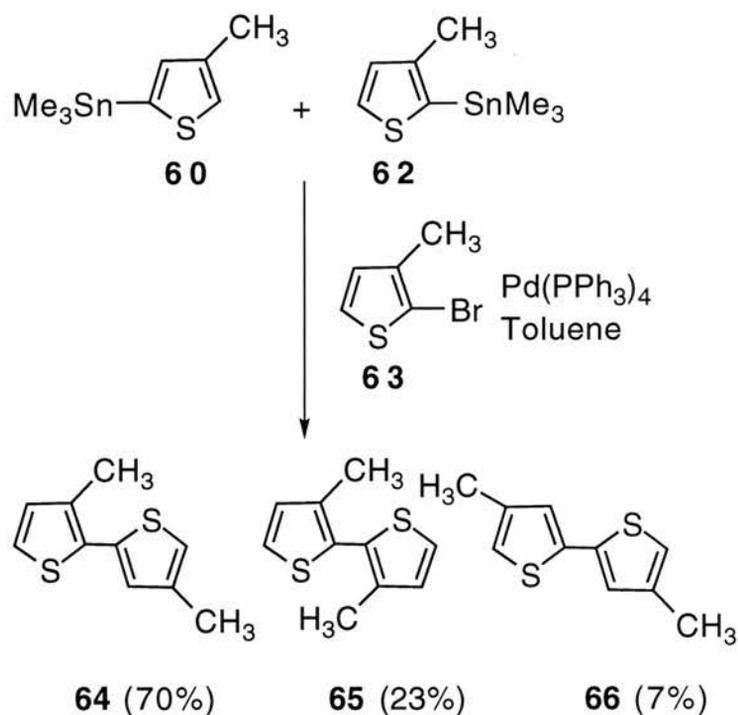


Scheme 17

The reaction product was isolated to reveal the expected mixture of products, 2-trimethyltin-4-methylthiophene **60** and 2-trimethyltin-3-methylthiophene **62**, which occur as a result of lithiation at reflux rather than -78°C and also due to the reduced directing effect of methyl compared to hexyl. The overall reaction yield was approximately 70% with the ratio of **60** to **62** approximately 3:1. These regioisomers could not be separated by distillation or column chromatography on silica gel or alumina powder using a range of solvent combinations. It was decided that the mixture of compounds should be used in a Stille coupling reaction with 2-

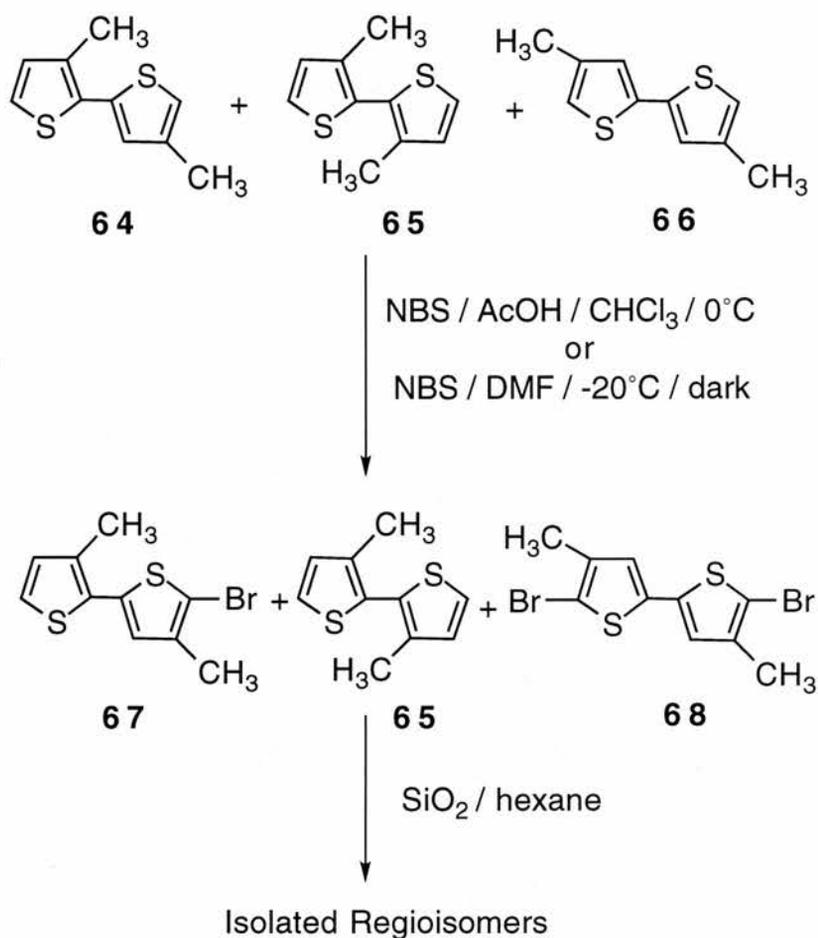
bromo-3-methylthiophene. This reaction afforded an orange oil which was analysed by ^1H NMR spectroscopy and GCMS. GCMS indicated that small amounts of 2-bromo-3-methylthiophene were present in addition to two broad signals both of which had $M^+=194$ amu. ^1H NMR spectrum of the crude reaction product contained five peaks relating to methyl groups, with chemical shifts from 2.17ppm-2.39ppm. From this initial information we deduced that the head to tail product 3,4'-dimethyl-2,2'-bithiophene **64** and head to head product 3,3'-dimethyl-2,2'-bithiophene **65** were the principal reaction products.

Thin layer chromatography on silica gel using various solvent mixtures indicated that these isomers did not separate easily. However using hexane as the eluent we identified three distinct spots (R_f values = 0.4, 0.2 and 0.1). The spots with the lowest R_f values were found to contain minor impurities, whilst ^1H NMR spectra of the fractions with $R_f = 0.4$ still contained 4 signals corresponding to methyl groups. If the head to head and head to tail regioisomers alone are present then we should observe only three methyl signals since those of the head-to-head regioisomer are equivalent. The sample was further analysed by GCMS where it was discovered that the broad signals were now fully resolved, showing three signals with $M^+=194$ amu. The extra signal observed in the ^1H NMR spectra was attributed to the tail to tail isomer, 4,4'-dimethyl-2,2'-bithiophene **66**, **Scheme 18**. This regioisomer occurs as a result of homo-coupling of the thienyl stannanes.⁴⁰



Scheme 18

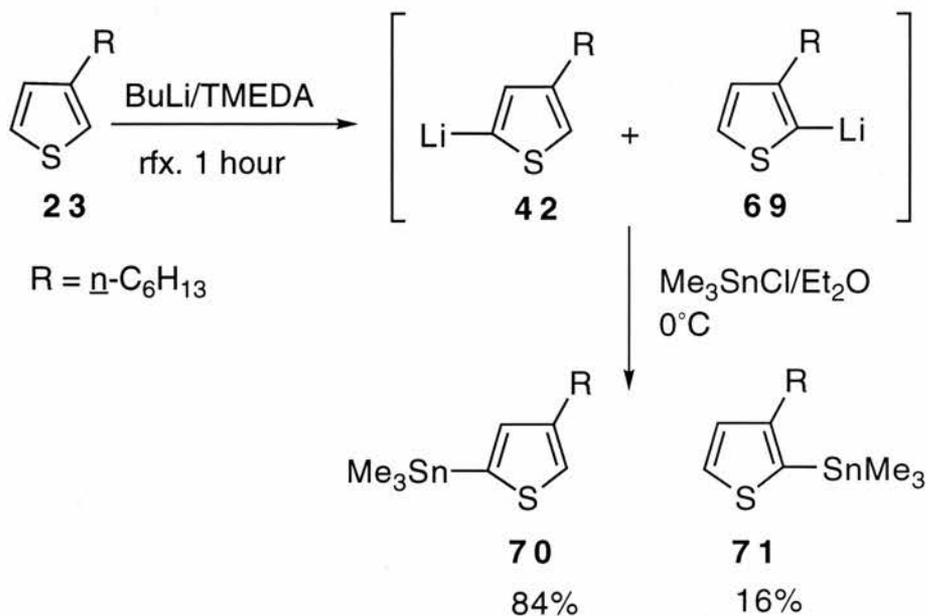
The overall reaction yield was extremely good and afforded approximately 70% of the desired head-to-tail regioisomer. We attempted to separate the three regioisomers **64**, **65** and **66** using conventional separation techniques without success. Separation was made possible by considering the electron releasing effect of the methyl substituents of the regioisomers, which activate the α -positions of each isomer to a different extent. Only one α -position of the head to tail isomer is activated compared to two in the tail to tail isomer and zero in the head to head regioisomer. As mentioned previously, on isolation of 3,4'-dihexyl-2,2'-bithiophene we intended to perform a bromination reaction to afford 5'-bromo-3,4'-dihexyl-2,2'-bithiophene. However, It was felt that the bromination reaction could be incorporated in the separation process. This was achieved by carrying out the bromination reaction with a proportionate amount of N-bromosuccinimide in acetic acid/chloroform at 0°C or at -20°C in dimethylformamide to afford three different substituted compounds **67**, **68** and **69** which could be isolated by column chromatography on silica gel using hexane as the eluent, **Scheme 19**.



Scheme 19

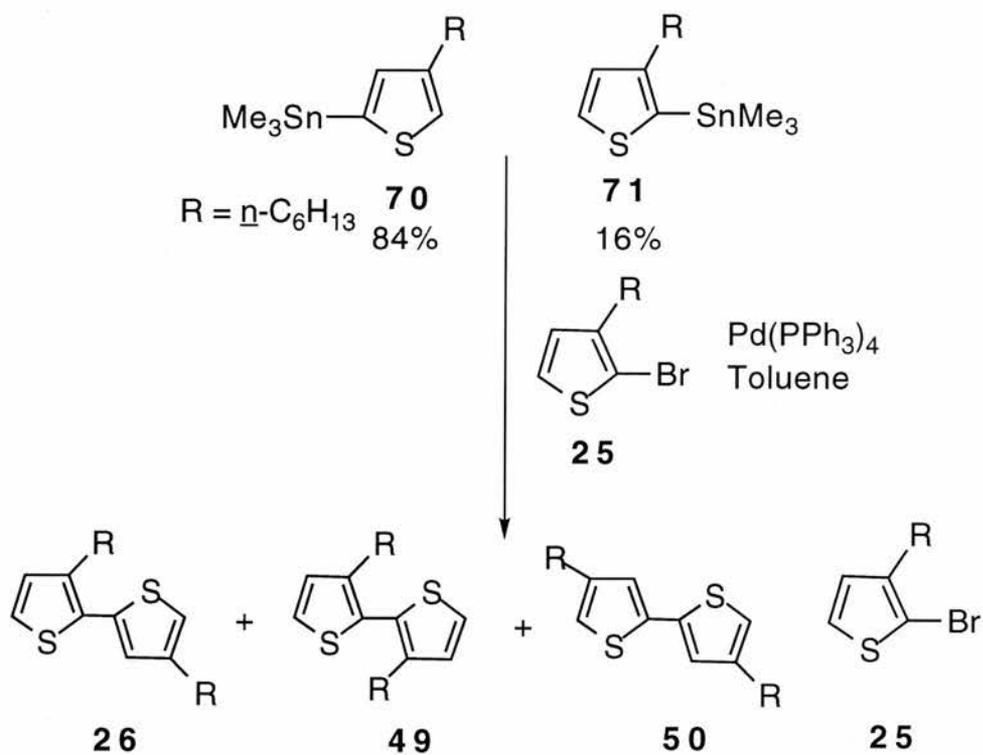
These brominated isomers are light sensitive, gradually changing from a pale yellow liquid to a dark brown oil, before decomposing to a black solid with liberation of HBr, as was found to our cost. The overall combined yield of **60** and **62** was increased from 70% to 95% by using longer reaction times. The yield for the subsequent Stille coupling reaction with 2-bromo-3-methylthiophene was also improved to 85-90%.

The reaction times required to couple the hexyl substituted components are significantly longer and are highly dependent on the quality of catalyst. The steric bulk of the hexyl group also directs lithiation to a greater extent, **Scheme 20**.



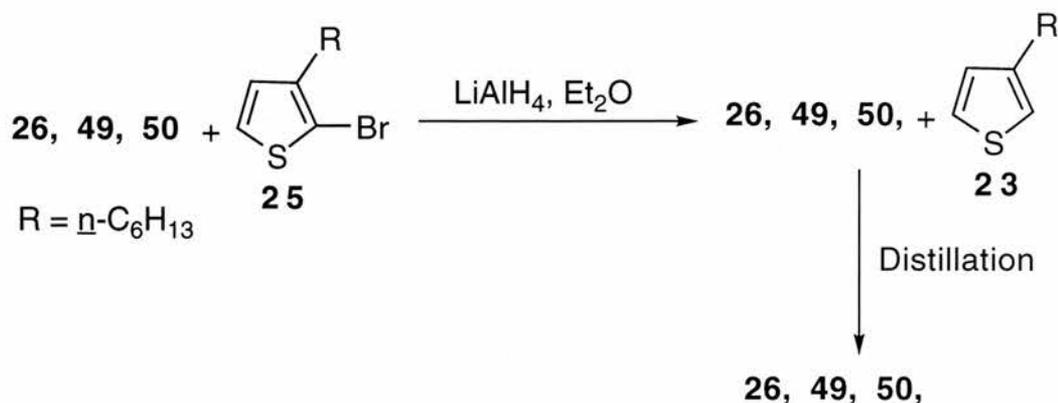
Scheme 20

In the reactions where the catalyst activity was reduced, unreacted 2-bromo-3-hexylthiophene was present in addition to the cross-coupled products, **Scheme 21**.



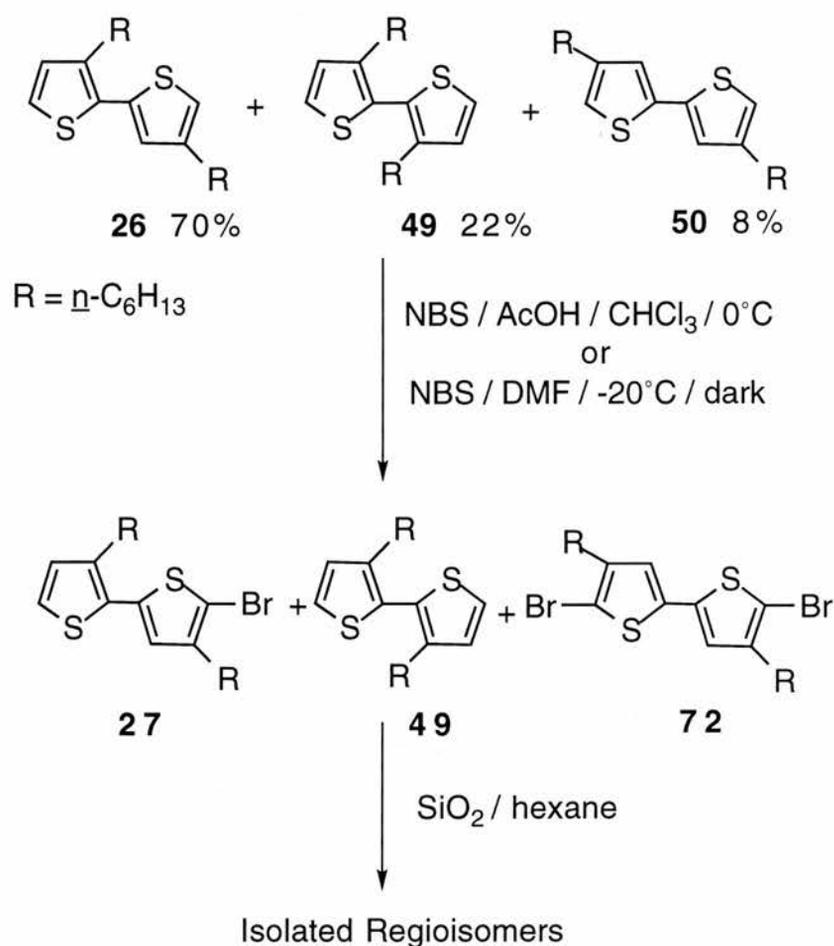
Scheme 21

Unfortunately **25** could not be removed by column chromatography or distillation. The mixture was then purified by reduction of the 2-bromo-3-hexylthiophene **25** to yield 3-hexylthiophene which was then removed by distillation, **Scheme 22**.



Scheme 22

After obtaining the regioisomeric mixture it proved difficult to estimate the ratio of isomers due to overlapping signals. Estimated ratios were evaluated by attempting the reactions on a small scale and analysing the products by GCMS until the correct amount of N-bromosuccinimide was determined, **Scheme 23**. The starting materials could easily be recovered by treatment with lithium aluminium hydride, if multiple halogenation occurred.

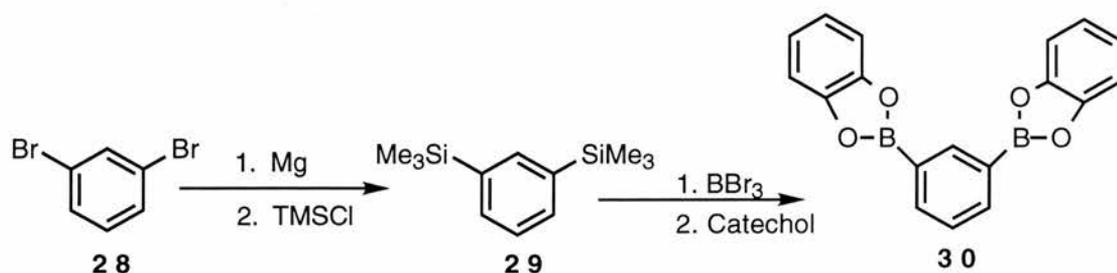


Scheme 23

In conclusion, Stille coupling provides the highest yielding route to 5'-bromo-3,4'-dialkyl-2,2'-bithiophenes. It also allows a synthetic step and separation technique to be combined in an efficient process affording the desired compounds which are easily isolated by column chromatography.

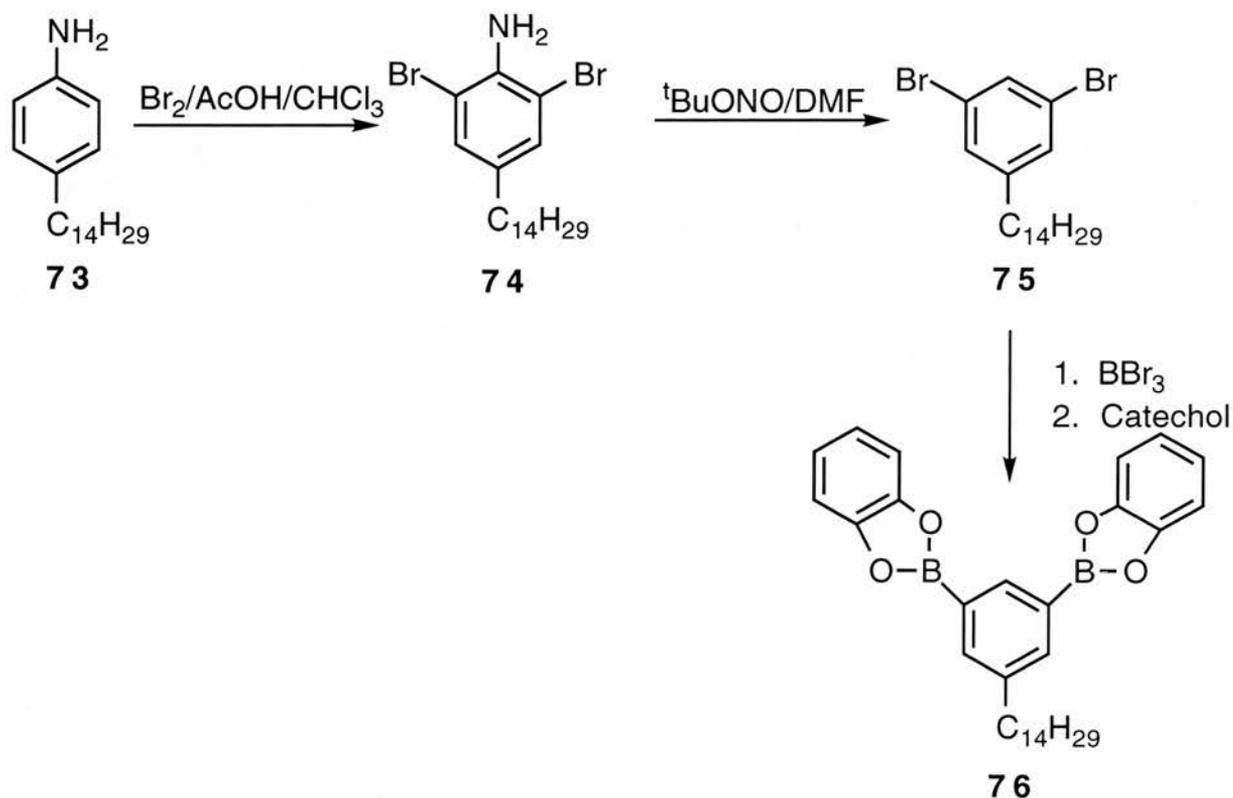
2.4 Synthesis of Ferromagnetic Coupling Unit

The *m*-phenylene component was prepared as shown in **Scheme 24**. Reaction of 2 equivalents of the Grignard reagent of trimethylsilyl chloride with 1,3-dibromobenzene afforded 1,3-bis(trimethylsilyl)benzene in good yield. Further reaction with boron tribromide and catechol resulted in the formation of 1,3-phenylene bis(1,3,2-benzodioxaborole) **30**.



Scheme 24

This route was also viable if a solubilising group was required on the 5- position of the benzene ring, **Scheme 25**.

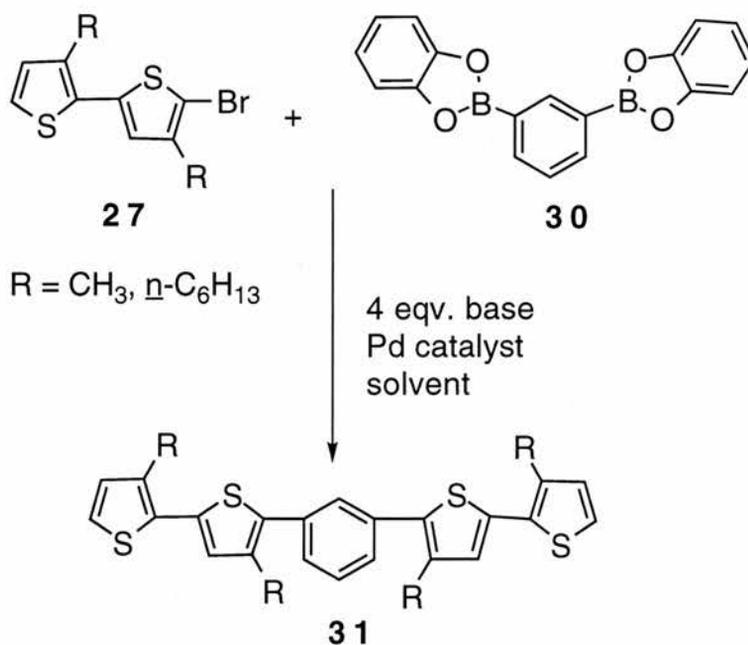


Scheme 25

The commercially available 4-tetradecylaniline provides convenient access to a solubilising alkyl chain and a directing group to provide the desired *meta* functionality.

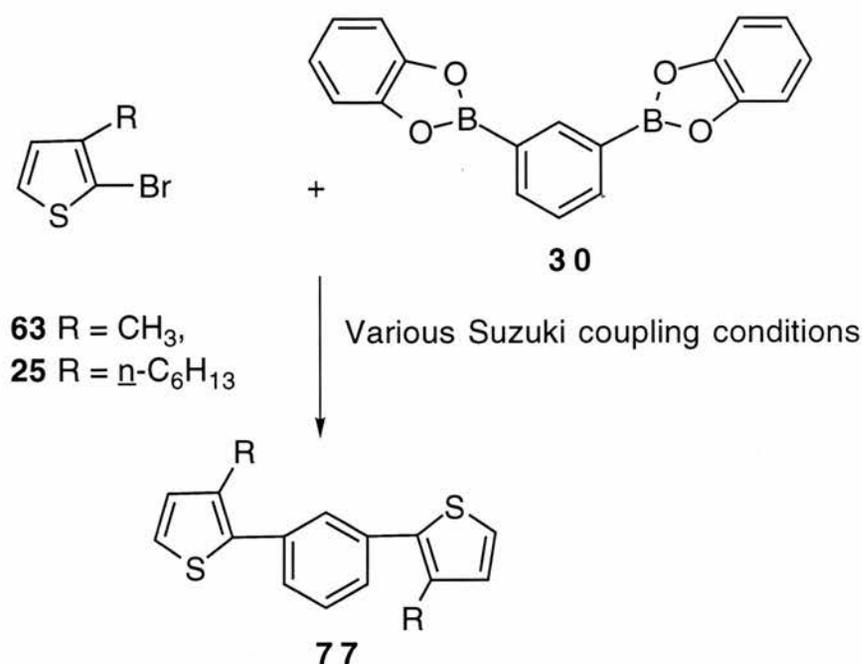
2.5 Suzuki Coupling Studies To Form Target Monomers

We intended to form the target monomers *via* a Suzuki Coupling reaction between 5'-bromo-3,4'-dialkyl-2,2'-bithiophene and 1,3-phenylene bis(1,3,2-benzodioxaborole), **Scheme 26**.



Scheme 26

The standard Pd-catalysed Suzuki coupling reactions employ the use of sodium carbonate as base and benzene or toluene as solvent.²⁰ The Suzuki coupling reaction between **27** and **30** was carried out with 4 equivalents of sodium carbonate and toluene as a reaction solvent but failed to yield the bis-coupled product. Model Suzuki coupling reactions involving 2-bromo-3-alkylthiophenes with 1,3-phenylene bis(1,3,2-benzodioxaborole) utilising a number of different solvent/base combinations were investigated in order to determine the ideal coupling conditions required to form **31**, **Scheme 27**. A summary of these model coupling reactions can be found on page 109.



Scheme 27

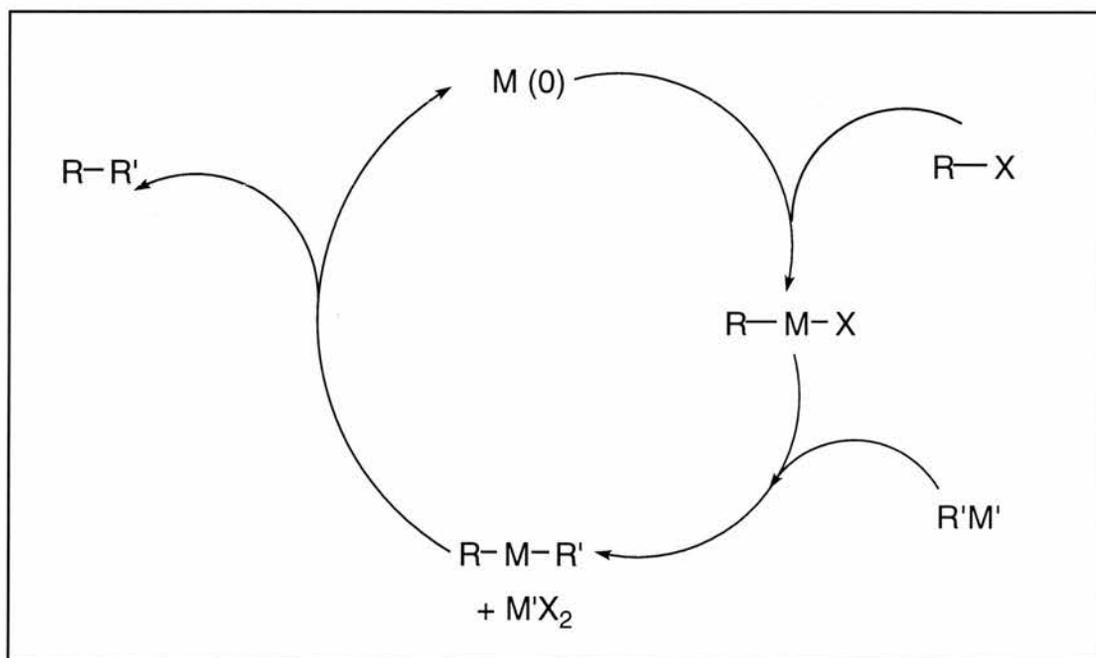
The initial model reaction attempted to couple two equivalents of 2-bromo-3-methylthiophene to the bis boronic ester **30**, again using the standard Suzuki conditions stated previously. A viscous orange oil was obtained in addition to a light brown powder. The presence of the desired coupled product could not be determined by ¹H NMR spectroscopy of the oil in CDCl₃ because the signals of the starting material and the proposed product were similar i.e. equivalent methyl groups and two doublets resulting from the thienyl protons. The peaks corresponding to the phenyl protons of the boronic ester which occur at 8.30 and 8.87 ppm were no longer present. GCMS of the liquid indicated that a large amount of unreacted 2-bromo-3-methylthiophene remained. At a significantly higher GC column temperature a peak with M⁺=174 amu was observed. The isotopes of bromine were not observed and this peak was attributed to 2-phenyl-3-methylthiophene which we assumed occurred as a result of only mono-coupling taking place. Steric hindrance may have prevented the second coupling reaction from occurring.

We then attempted a Suzuki coupling reaction between 2-bromo-3-hexylthiophene and 1,3,2-benzodioxoborole with sodium carbonate and dimethoxyethane in order to suppress any competitive deboronation reactions. Analysis of the reaction product by GCMS again

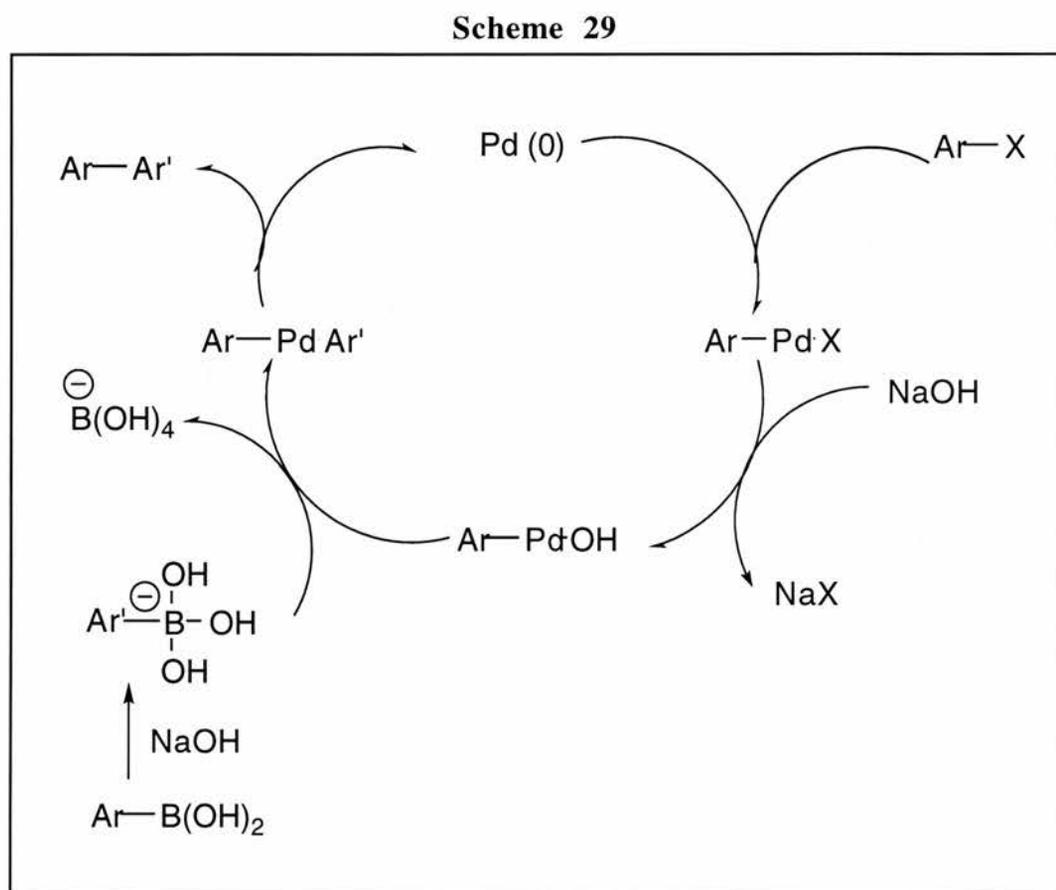
displayed peaks corresponding to 2-bromo-3-hexylthiophene and also the reduction product 3-hexylthiophene. If our assumption that only mono-coupling occurs is correct, we would expect a peak with $M^+=244$ amu, corresponding to 2-phenyl-3-hexylthiophene, which was observed. The 300MHz ^1H NMR spectrum of the reaction product proved to be very similar to that of the previous reaction. Despite using longer reaction times, no bis cross-coupled product could be detected, prompting a consideration of the proposed catalytic cycle for these reactions.

The general catalytic cycle for the cross-coupling of organometallics with organohalides, catalysed by transition metals [usually nickel(0) or palladium(0) species] is widely accepted.⁴¹ These coupling reactions involve the oxidative addition of organohalides to the metal complex to form organometallic halides (R-M-X). This step is followed by transmetalation with main group organometallics ($\text{R}'\text{-M}'$) to provide a diorganometallic complex ($\text{R-M-R}'$), which can undergo a reductive elimination reaction, leading to carbon-carbon bond formation and regeneration of the catalyst, **Scheme 28**.

Scheme 28



Similarly, Suzuki has suggested a catalytic cycle for the cross-coupling of organoboranes with organic halides.⁴² The crucial difference between organoborane cross-coupling and the general catalytic cycle is that, in the former, the oxidative addition is followed by the metathetical displacement of the halide ion from (R-Pd-X) by a basic species to give an organopalladium alkoxide (R-Pd-OR) or organopalladium hydroxide (R-Pd-OH), depending on the base used. These organopalladium alkoxides/hydroxides are believed to be more reactive than organopalladium halides, **Scheme 29**.



As shown in **Scheme 29**, two equivalents of base are required in the catalytic cycle. One is utilised in the formation of boronate, which is consistent with the fact that boronic acids act as acids in the Lewis sense, with the formation of a tetravalent boron atom.^{43,44} The anionic nature of the organic group in organoboronic acids is expected to be enhanced by the formation of an organoborate.⁴⁵ The second equivalent of base is consumed in the metathetical displacement of halide, to form an organopalladium hydroxide. The organopalladium

hydroxide should be more reactive than the organopalladium halide since the Pd-O bond is more polar than the Pd-Br bond, owing to the greater electronegativity of oxygen relative to bromine. As a result, the electrophilicity of the organopalladium hydroxide is stronger than that of the organopalladium bromide, and the electrophilic transmetallation reaction is facilitated. Thus, the transmetallation reaction is favoured by both formation of the aryl boronate and the organopalladium hydroxide. The catalytic cycle clearly explains the failure of attempts to couple organoboronic acids in the absence of base.⁴⁶

A number of factors concerning our model coupling reaction had to be addressed:

- i The mechanism for Suzuki coupling reactions implies that organopalladium halides are displaced by base to form the more reactive organopalladium hydroxides and therefore the use of a stronger base such as sodium methoxide or barium hydroxide may exclude the recovery of the starting halide.
- ii On occasion the reduction product 3-alkylthiophene was observed. It was not clear how this species was formed.
- iii 1,3-phenylene bis(1,3,2-benzodioxaborole) exhibited poor solubility in both toluene and dimethoxyethane and it was felt that an increase in the solubility resulting from the use of tetrahydrofuran could improve the reaction.

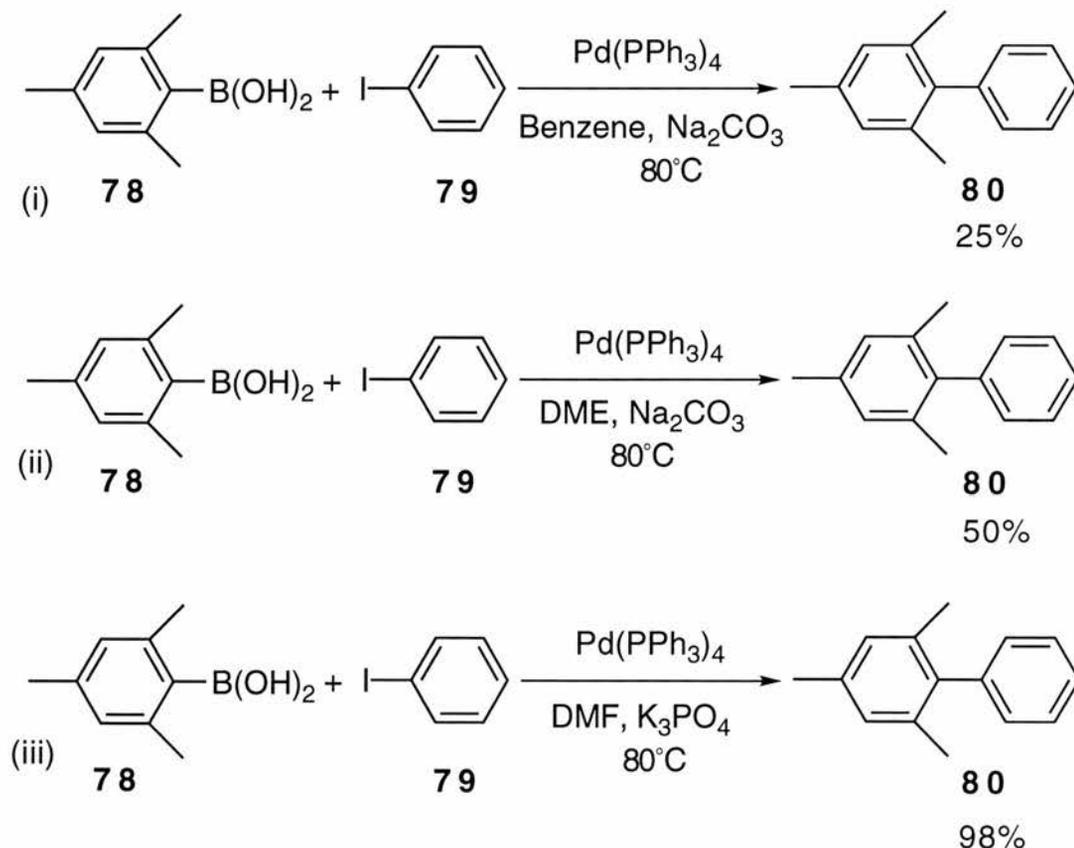
A model coupling reaction between **25**, where R = C₆H₁₃, and **30** was attempted in a 50/50 v/v THF/methanol solution using sodium methoxide as base and a 6% palladium tetrakis(triphenylphosphine) catalyst. Neither GCMS nor ¹H NMR spectroscopy showed any trace of unreacted 2-bromo-3-hexylthiophene vindicating our choice of stronger base. The desired product was not observed, but by-products such as dihexylbithiophene (M⁺=334), which is formed as a result of homo-coupling of 2-bromo-3-hexylthiophene, and also the mono-coupled product, 2-phenyl-3-hexylthiophene, were present in addition to a number of unidentifiable reaction products.

Gronowitz carried out an extensive exploration of the Suzuki coupling reaction of thiophenes and discovered that reaction rates are increased by increasing the ratio of base/halide, by using glycol or catechol boronic esters rather than acids and by using aqueous tetrahydrofuran rather than toluene as a solvent. Increasing the amount of catalyst, as we have, increases the reaction rate but not the reaction yield.^{47,48}

A similar model coupling between **25** and **30** was attempted using THF as the reaction solvent and barium hydroxide as base. This proved to be a 'cleaner' reaction; however, similar by-products to those formed when sodium methoxide was employed as base were obtained.

In examples used by Suzuki, low yielding, sterically hindered cross-coupling reactions involving boronic acids were improved by the use of dibutyl or triethylene glycol boronic esters in conjunction with tribasic potassium phosphate as base in dimethylformamide,

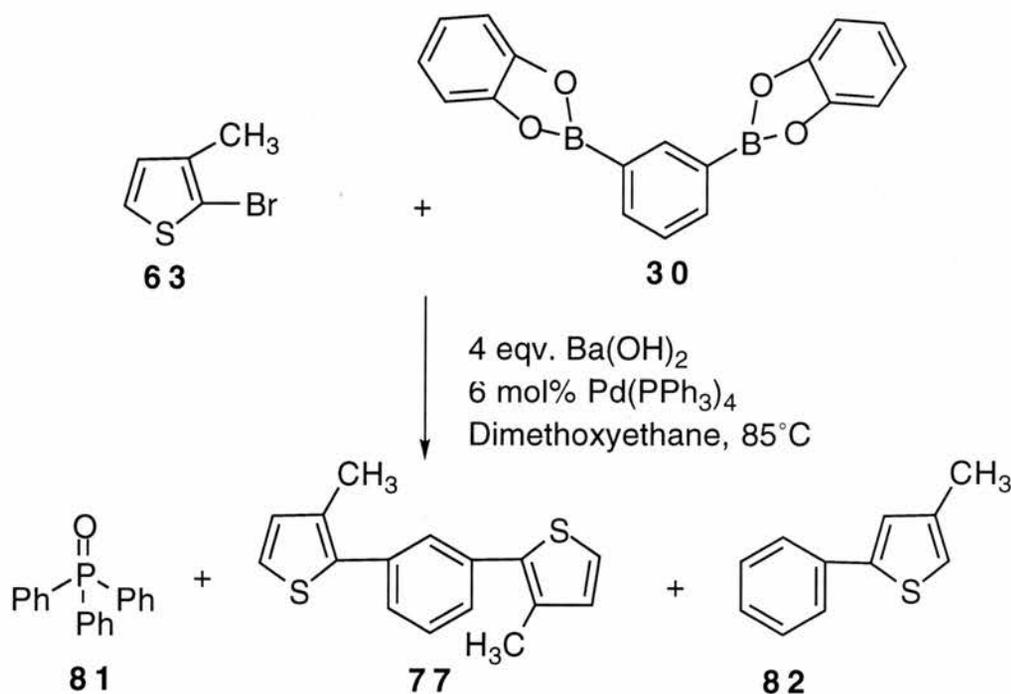
Scheme 30.



Scheme 30

Using the conditions shown in entry iii of **Scheme 30** yielded identical by-products to those observed previously and again failed to afford the desired cross-coupled product. Having almost exhausted the various base/solvent combinations, our attention focused on the method of analysis of the reaction products. ^1H NMR spectroscopy could only be relied upon to distinguish certain starting materials from reaction products and therefore we relied solely on GCMS to identify other reaction products. If the desired cross-coupled product was formed it would contain over 60 atoms and a mass in excess of 400 amu and therefore may be too involatile for observation by GCMS. In order to investigate this, gas chromatograms of all reaction products were obtained at the maximum permitted column temperature (300°C) for 30 minutes, however no peak corresponding to the cross-coupled product was eluted.

A further cross-coupling reaction between 2-bromo-3-methylthiophene and 1,3-phenylene bis(1,3,2-benzodioxaborole) was attempted in 1,2-dimethoxyethane using barium hydroxide as base. Again GCMS analysis showed the expected by-products in addition to a peak with $M^+=270$ corresponding to the desired 1,3-phenylene bis(5-methyl-2-thiophene) **77**. The reaction was then repeated on a larger scale and proceeded to yield 65% of **77**, **Scheme 31**.

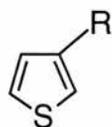


Scheme 31

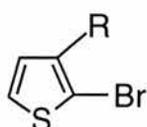
Further investigation showed that aryl exchange can occur allowing ligand bound phenyl groups of the catalyst to enter the cross-coupling cycle, in lieu of the desired aryl halides, thus contaminating the reaction product. This aryl exchange is therefore responsible for the presence of 2-phenyl-3-alkylthiophenes, such as **82**, in our reaction products. TLC of the reaction product on silica gel plates using toluene/ethyl acetate as solvent showed three spots with R_f values = 0.8, 0.3 and 0.1. These components were successfully isolated by column chromatography and identified as 1,3-phenylene bis(5-methyl-2-thiophene) **77**, 3-methyl-2-phenylthiophene **82** and triphenylphosphine oxide **81** respectively. Indeed the majority of the recovered material was found to be the bis coupled product **77**, which was an opaque coloured solid. The Suzuki cross-coupling reaction between 2-bromo-3-hexylthiophene and the bis boronic ester **30** under similar reaction conditions produced identical TLC plates. Column chromatography of the reaction product on silica gel using toluene/ethyl acetate as eluent afforded 1,3-phenylene bis(5-hexyl-2-thiophene) **83** as a brown oil.

Model Suzuki coupling reactions of 2-bromo-3-alkylthiophenes with 1,3-phenylene bis(1,3,2-benzodioxaborole)

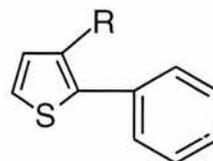
Starting Halide	Base	Catalyst	Solvent	Observed Products
2-bromo-3-hexylthiophene	Na ₂ CO ₃	Pd(PPh ₃) ₄	Toluene	23, 25.
2-bromo-3-hexylthiophene	Na ₂ CO ₃	Pd(PPh ₃) ₄	Dimethoxyethane	23, 25, 82A.
2-bromo-3-methylthiophene	Na ₂ CO ₃	Pd(PPh ₃) ₄	Toluene	63, 82.
2-bromo-3-hexylthiophene	NaOMe	Pd(PPh ₃) ₄	THF/Methanol	23, 26.
2-bromo-3-hexylthiophene	K ₃ PO ₄	Pd(PPh ₃) ₄	Dimethylformamide	23, 26.
2-bromo-3-hexylthiophene	Ba(OH) ₂	Pd(PPh ₃) ₄	Tetrahydrofuran	23, 26.
2-bromo-3-methylthiophene	Ba(OH) ₂	Pd(PPh ₃) ₄	Dimethoxyethane	82, 77.



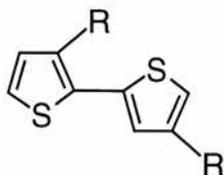
23 R = n-C₆H₁₃
58 R = CH₃



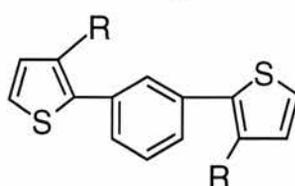
25 R = n-C₆H₁₃
63 R = CH₃



82A R = n-C₆H₁₃
82 R = CH₃

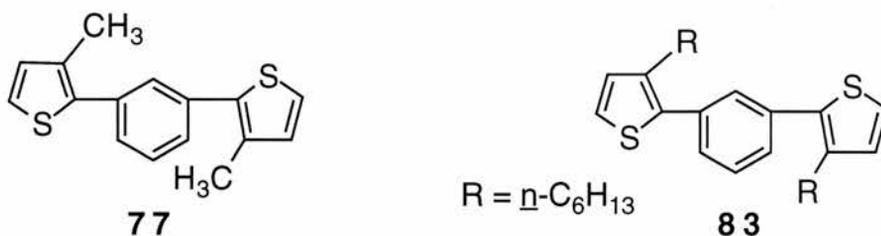


26 R = n-C₆H₁₃
64 R = CH₃



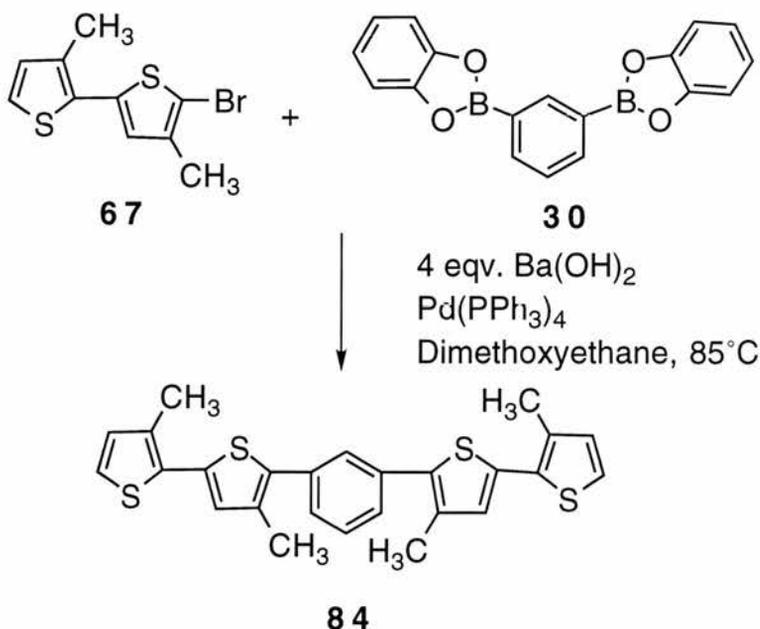
77 R = n-C₆H₁₃
83 R = CH₃

The combination of a stronger base, barium hydroxide and 1,2-dimethoxyethane as a solvent proved successful in coupling the components of our model coupling reactions. The reaction proceeded in yields of 60-70% and the bis-arylthiophene was easily purified by column chromatography. **83** could not be observed by GCMS and therefore we relied on TLC to identify high molecular weight products. We also considered the polymerisation of **77** and **83** since they could serve as interesting materials in their own right



Suzuki Coupling of 5'-Bromo-3,4'-dialkyl-2,2'-bithiophenes with 1,3-Phenylene bis(1,3,2-benzodioxaborole)

Having established the coupling conditions required to produce 1,3-phenylene bis(5-alkyl-2-thiophene) we attempted to couple 5'-bromo-3,4'-dimethyl-2,2'-bithiophenes with 1,3-phenylene (1,3,2-benzodioxaborole), **Scheme 32**.



Scheme 32

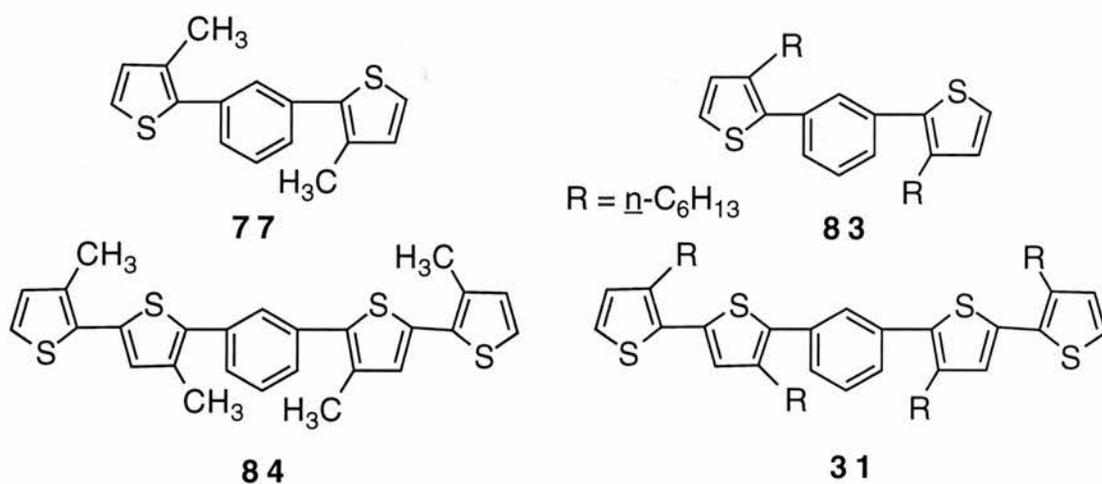
The reaction product was obtained as a dark brown oil. ^1H NMR of the oil in CDCl_3 indicated the presence of the target molecule. Minor signals were present which suggested the formation of other geometric isomers. The brown oil proved soluble in toluene and TLC on silica gel showed three spots with $R_f = 0.8, 0.2$ and 0.1 . Column chromatography on silica gel with toluene/ethyl acetate allowed the isolation of each component. ^1H NMR spectroscopy of the combined fractions corresponding to each individual component revealed that the slower moving fractions contained minor impurities whilst the top component still contained a mixture of isomers. The mixture of isomers was dissolved in pentane where it was discovered that a fraction of the material was insoluble. A comparison of the ^1H NMR spectra of the soluble fraction and the original mixture showed them to be almost identical. However, the insoluble fraction was found to consist solely of the desired 1,3-phenylene bis(5,3'-dimethyl-3,2'-bithiophene). The isolated yield was poor when compared to those of the model coupling reactions, due to the lengthy purification procedure required and the formation of additional regioisomers.

The Suzuki coupling reaction between 5'-bromo-3,4'-dihexyl-2,2'-bithiophene with **30** was also attempted under these conditions. Again a mixture of products was obtained which could only be partially purified by column chromatography. The reaction was repeated and a similar result obtained. The major contamination products produced signals observed by ^1H NMR spectroscopy in the region where we expected the protons of the benzene ring. We then repeated previous Suzuki coupling reactions, producing high yields of 1,3-phenylene bis(5-methyl-2-thiophene) and 1,3-phenylene bis(5-hexyl-2-thiophene). These reactions confirmed the activity of the palladium catalyst. The reaction of 5'-bromo-3,4'-dimethyl-2,2'-bithiophene with 1,3-phenylene bis(1,3,2-benzodioxoborole) was again attempted. On this occasion a 6:1 ratio of dimethoxyethane/water was used as a solvent. Again the crude reaction mixture appeared to contain a mixture of regioisomers. TLC of the crude product showed four small spots and one large spot which was assumed to be the desired product. The reaction mixture was found to be only partially soluble in hexane making chromatographic separation difficult. The product was therefore pre-absorbed onto silica gel using dichloromethane, allowing column chromatography on silica gel with a hexane/dichloromethane solvent mixture, to afford

analytically pure 1,3-phenylene bis(5,3'-dimethyl-3,2'-bithiophene) as a yellow powder in a yield of 65%. Good yields of 1,3-phenylene bis(5,3'-dihexyl-3,2'-bithiophene) were obtained in similar manner. It would appear that the presence of water in the solvent mixture is required in order to produce cleaner reaction products in higher yields. This may be a result of aqueous hydrolysis of the boronic ester to the acid.⁴⁹

2.6 Conclusion

Suzuki coupling conditions have been established allowing the formation of **77**, **83**, **84** and **31**. The coupling reactions have been repeated several times to afford substantial amounts of these monomers for chemical and electrochemical polymerisation.



2.7 Experimental

The majority of ^1H NMR spectra were obtained using a Varian Gemini 200MHz spectrometer. All samples were dissolved in CDCl_3 using Me_4Si as an internal standard. GC/MS work was carried out using a Finnigan Incos 50 quadrupole mass spectrometer interfaced with a Hewlett-Packard HP5890 capillary gas chromatograph fitted with a column coated with methylsilicone as the stationary phase. The majority of temperature profiles used in GCMS involved a ramp from 40°C to 300° at $15^\circ\text{C}/\text{min}$ and a dwell at 300°C for two minutes. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl. Toluene, methylene chloride, trimethylsilyl chloride, dimethylformamide and diisopropylamine were distilled from CaH_2 . All other starting materials were used as received. Chromatographical purification was carried out using silica gel supplied by BDH with a particle size of $40\text{-}63\ \mu\text{m}$. All HCl and NaOH solutions were 2M.

3-Hexylthiophene **23** ($\text{R} = \text{n-C}_6\text{H}_{13}$)

Magnesium turnings (7.2g, 0.30mol), diethyl ether (300cm^3) and 1-bromohexane (36.8g, 0.22mol) were stirred, under nitrogen, in a 500cm^3 three necked flask, fitted with a reflux condenser. After refluxing for 5h, the mixture was transferred via catheter and added dropwise at 0°C to a 1000cm^3 three neck flask containing 3-bromothiophene (36.3g, 0.22mol), $\text{NiCl}_2(\text{dppp})$ (250mg, 0.46mmol) and diethyl ether (200cm^3). The mixture was then refluxed overnight and poured over a mixture of ice (264g) and HCl (72cm^3). After extraction with diethyl ether ($3 \times 100\text{cm}^3$), the mixture was dried over MgSO_4 and the product obtained by fractional distillation ($100\text{-}102^\circ\text{C} / 10\text{mmHg}$) (lit.⁵⁰, $229\text{-}230^\circ\text{C}$) yielding 20.8g (56%) of 3-hexylthiophene. δ_{H} 0.94 (3H, t, CH_3), 1.40 (8H, m, $(\text{CH}_2)_4$), 2.65 (2H, t, $\alpha\text{-CH}_2$), 6.95 (2H, m, H-2, H-4), 7.23 (1H, dd, $J_{4,5}=5.3\text{Hz}$, $J_{2,5}=3.1\text{Hz}$).

2-Bromo-3-hexylthiophene⁵⁰ 25 (R = n-C₆H₁₃)

N-Bromosuccinimide(12.57g, 0.071mol) was added dropwise [in solution in DMF(60cm³)] to a solution of 3-hexylthiophene (11.88g, 0.071mol) in DMF (60cm³) over 4h at -20°C in the dark. The mixture was then stirred for 24h, poured over ice and extracted with CH₂Cl₂ (3x100cm³). The combined organic layers were washed with water and the solution dried over MgSO₄ and evaporated to dryness to afford an orange oil. The remaining DMF was removed by distillation (40-42°C/0.05mmHg) yielding 14.13g (80.2%) 2-bromo-3-hexylthiophene. δ_{H} 0.88 (3H, t, CH₃), 1.35 (8H, m, (CH₂)₄), 2.63 (2H, t, J=4Hz), 6.78 (1H, d, J_{4,5}=5.5Hz, H-4), 7.21 (1H, d, J_{4,5}= 5.5Hz, H-5).

General procedure for regioselective cross-coupling of 3-alkylthiophenes

Into a dry three necked flask was placed dry diisopropylamine in freshly distilled THF. n-Butyllithium (1.6M in hexanes) was added to the solution at room temperature and the solution stirred for 40 min. The solution was cooled to -78°C and 3-alkylthiophene in THF also at -78°C was added via catheter. The temperature was allowed to rise to -40°C whereupon the solution was stirred for 1h. The solution was then cooled to -60°C whereupon MgBr₂.OEt₂ was added. The reaction mixture was then stirred at -60°C for 30 minutes, before being allowed to rise to -10°C over 1h. The reaction mixture was then cooled to -78°C and added via a catheter to a solution containing 2-bromo-3-alkylthiophene and NiCl₂(dppp) (0.5% mol) in THF also at -78°C. The reaction mixture was then left stirring, with temperature rising overnight. The reaction mixture was then poured over ice and the organic layer extracted with CH₂Cl₂, the combined extracts were dried over MgSO₄ and the solvent removed by rotary evaporation to yield the crude product as a dark oil. The head to tail coupled product was identified by ¹H NMR spectroscopy due to the distinct chemical shift of the α -CH₂ hydrogens which resonate at 2.75ppm. ¹H NMR spectroscopy revealed that approximately 20% of the cross-coupled product was present in the reaction mixture.

This reaction was extensively studied, involving many changes to the reactants and the reaction conditions. These reactions are discussed in the results and discussion section and are summarised in a table in Appendix I of this chapter.

3,4'-Dihexyl-2,2'-bithiophene⁵¹ **26** (R = n-C₆H₁₃)

Into a dry three necked flask was placed dry diisopropylamine (1.64 cm³, 12.5mmol) in freshly distilled THF (75cm³). n-Butyllithium (1.6M in hexanes, 7.81cm³, 12.5mmol) was added to the solution at room temperature and the solution stirred for 40 min. The solution was cooled to -78°C and 3-hexylthiophene (2.1g, 12.5mmol) in THF (20cm³) also at -78°C was added via catheter. The temperature was allowed to rise to -40°C whereupon the solution was stirred for 4.5 h. The solution was then cooled to -60°C whereupon MgBr₂.OEt₂ (3.47g, 13.75 mmol) was added. The reaction mixture was then stirred at -60°C for 30 minutes, -40°C for 30 minutes before being allowed to rise to -10°C over 3h. The reaction mixture was then cooled to -78°C and added via a catheter to a solution containing 2-bromo-3-hexylthiophene (3.09g, 12.5mmol) and NiCl₂(dppp) (0.5% mol), in THF (40cm³), also at -78°C. The reaction mixture was then left stirring, with temperature rising overnight. The reaction mixture was then poured over ice and the organic layer extracted with CH₂Cl₂, the combined extracts were dried over MgSO₄ and the solvent removed by rotary evaporation to yield the crude product as a dark oil. Unreacted monomers were then removed by fractional distillation (b.p. 40-45°C/0.05mmHg). The solution was dissolved in hexane and filtered in order to remove long chain oligomers. Further purification was obtained by dry column flash chromatography and also conventional column chromatography using hexane and petroleum ether/ethyl acetate respectively as eluents to yield 0.8g (15%) of **3,4'-dihexyl-2,2'-bithiophene** as a brown liquid; δ_{H} 0.82-1.70 (22H, m, C₅H₁₁), 2.60 (2H, t, J=7.8Hz), 2.75 (2H, t, J=7.6Hz), 6.89 (1H, s), 6.92 (1H, d, J=4.6Hz), 6.95 (1H, s), 7.12(1H, d, J=4.6Hz); δ_{C} 14.1, 22.6, 29.7, 31.0, 31.6, 32.1, 123.8, 124.5, 127.9, 130.8, 131.6, 136.2, 138.0, 139.8; Found: C, 71.51; H 9.23. Calc for C₂₀H₃₀S₂: C, 71.79; H, 9.04%;

GC/MS peak no. m/z (relative intensity): **816**, 334 (M⁺, 23), 263 (15), 193 (83), 179 (20), 160 (20), 147 (23), 134 (10), 97 (15), 55 (32), 43 (100), 29 (94), 18 (15).

5'-Bromo-3,4'-dihexyl-2,2'-bithiophene 27 (R = n-C₆H₁₃)

Into a dry, three necked round bottomed flask, equipped with a pressure equalising dropping funnell, was added 3,4'-dihexyl-2,2'-bithiophene (1.33g, 4.0mmol) in 30 cm³ of freshly dried DMF, under a nitrogen atmosphere. N-bromosuccinimide (0.72g, 4.0mmol) in 20 cm³ of freshly dried DMF was then added dropwise, over 1.5h at -25°C in the dark. The solution was then left stirring overnight, before being poured over ice and extracted with dichloromethane (2x100cm³). The combined organic layers were then washed with brine and dried over MgSO₄. Dichloromethane was then removed by rotary evaporation and the remaining DMF removed by distillation (34-36°C/0.05mmHg). Succinimide salts were removed by dissolution in petroleum ether followed by filtration and concentration to yield 1.62g (98%) 5'-bromo-3,4'-dihexyl-2,2'-bithiophene. δ_{H} 0.90(6H, t, CH₃), 1.33-1.62(16H, m, (CH₂)₄), 2.56(2H, t, J=5.1Hz), 2.71(2H, t, 5.0Hz), 6.78(1H, s, Th-H), 6.91(1H, d, Th-H, J=4.8Hz), 7.16(1H, d, Th-H, J=4.8Hz).

2-Bromo-3-methylthiophene⁵² 63

To a solution of 3-methylthiophene (4.9g, 50mmol) in a mixture of chloroform and acetic acid (50/50 v/v, 20cm³), portions of NBS (9.1g, 51mmol) were added at 0°C over 30 minutes. After stirring for 30 minutes, the solution was diluted with water, extracted with chloroform (2 x 25cm³) and the combined extracts neutralised with KOH and dried over MgSO₄. The solvent was then removed to yield 7.5g (85%) of 2-bromo-3-methylthiophene.

δ_{H} , 2.25 (3H, s), 6.81(1H, d, J_{4,5}=4Hz), 7.18 (1H, d, J_{5,4}=4Hz).

Preparation of 2-lithio-4-hexylthiophene 42 and subsequent reaction with D₂O

Into a dry three necked flask was placed 0.9ml (6.6mmol) of dry diisopropylamine in freshly distilled THF (15cm³). n-Butyllithium (1.6M in hexanes, 4.2cm³, 6.6mmol) was added to the solution at room temperature and the solution stirred for 40 minutes. The solution was cooled to -78°C and 3-hexylthiophene (1.0g, 6.6mmol) in THF (10 cm³) also at -78°C was added *via* catheter. The temperature was allowed to rise to -40°C whereupon the solution was stirred for 90 min. D₂O(262μl, 14.5mmol) in THF was added *via* catheter. The reaction mixture was then allowed to stir for 30 minutes before being extracted with CH₂Cl₂. The solvent was then removed by rotary evaporation to afford an orange/brown liquid. δ_{H} 0.94 (t, 3H, CH₃), 1.40 [m, 8H, (CH₂)₄], 2.65 (t, 2H, α -CH₂), 6.95 (m, 2H, H-2, H-4), 7.23 (dd, 1H, J_{4,5}=5.3Hz, J_{2,5}=3.1Hz). The relative intensity of the peak at 7.23, when compared with 3-hexylthiophene, indicated that the hydrogen at position -5 had almost completely been replaced by deuterium. ²D NMR 76.8 MHz (CHCl₃) δ_{D} 7.2ppm (s)

Attempted cross-coupling reaction using Fe(acac)₃

To a solution of 2-bromo-3-hexylthiophene (4.95g, 20mmol) in THF (150cm³), n-butyllithium (1.6M in hexanes, 14 cm³, 22.5 mmol) was added dropwise via syringe/septum cap over 15 min under a nitrogen atmosphere at -78°C. After stirring for 20 min at -78°C the mixture was warmed to -40°C and Fe(acac)₃ (7.06g, 20mmol) was added in portions over 30 min. The reaction was then stirred at -40°C for 2 h, and diluted with water (150mL), neutralised with HCl, and extracted with dichloromethane. The extracts were washed with brine and the solvent evaporated. The product was chromatographed on silica gel with hexane (3.2 cm x 8 cm) as the eluent to afford an orange oil which was distilled to remove 3-hexylthiophene (b.p. 96-98°C/10 Torr) yielding a mixture of both 3,3'-dihexyl-2,2'-bithiophene, 3,4'-dihexyl-2, 2'-bithiophene and 4,4'-dihexyl-2,2'-bithiophene. These regioisomers could not be isolated by a selective bromination reaction followed by column chromatography on silica gel.

A similar reaction was performed where $\text{Fe}(\text{acac})_3$ was added at -78°C rather than -40°C . From the chemical shifts of the $\alpha\text{-CH}_2$ groups on the hexyl chain present in the ^1H NMR spectrum of the crude mixture, the products were assigned as 68% 2-bromo-3-hexylthiophene ($\delta_{\text{H}} \alpha\text{-CH}_2 = 2.63\text{ppm}$), 20% of the head-to-head isomer ($\delta_{\text{H}} \alpha\text{-CH}_2 = 2.50\text{ppm}$) and 12% of the head-to-tail isomer ($\delta_{\text{H}} \alpha\text{-CH}_2 = 2.75\text{ppm}$).

2,5-Dibromo-3-hexylthiophene⁵² 51

Into a dry three necked round bottomed flask was placed 2-bromo-3-hexylthiophene (1.0g, 4mmol) in freshly dried dimethylformamide (30cm^3). N-bromosuccinimide (0.72g, 4mmol) dissolved in dry DMF was then added dropwise over 1.5h, at -25°C , in the dark. The reaction mixture was then left stirring overnight, before being poured over ice and extracted into dichloromethane. The combined organic extracts were then dried over MgSO_4 and dichloromethane removed by rotary evaporation. DMF was then removed by distillation ($34\text{-}36^\circ\text{C}/0.1\text{mmHg}$). Succinimide salts were then removed by dissolution in petroleum ether, followed by filtration. The solution was then concentrated to yield 2,5-dibromo-3-hexylthiophene (1.1g, 84%) as an orange liquid. δ_{H} 0.89(CH_3 , t, 3H, $J=1.7\text{Hz}$), 1.30-1.70(8H, m, $(\text{CH}_2)_4$), 2.52(2H, t, αCH_2 , $J=7.5\text{Hz}$), 6.78(1H, s).

Attempted Kumada reaction of 2-bromo-3-hexylthiophene 25 with 2,5-dibromo-3-hexylthiophene 51.

Into a dry three-necked round bottomed flask, equipped with a reflux condenser, was placed 2-bromo-3-hexylthiophene (0.68g, 2.75mmol) and dry magnesium turnings (0.072g, 3.0mmol) in 15cm^3 of freshly dried diethyl ether. The Grignard reaction was then activated by the addition of a few drops of 1,2-dibromoethane. The solution was then refluxed under nitrogen for 3 h. The resultant Grignard reagent was then transferred to a dropping funnel, via catheter, and added dropwise to a solution of 2,5-dibromo-3-hexylthiophene (0.90, 2.75mmol) and $\text{NiCl}_2(\text{dppp})$ (0.027g, 0.5% mol) in diethyl ether/benzene (4:1) and stirred under reflux for 20

h. The solution was then poured over ice and extracted into dichloromethane. The combined organic extracts were washed with brine and dried over MgSO_4 . The solution was concentrated to yield 1.54g of an orange oil. GC/MS **peak no.** m/z (relative intensity): **401**, 168 (10), 111 (17), 97 (100), 53 (15), 45 (32), 39 (24), 27 (27), 18 (10), **3-hexylthiophene**. **512**, 248 (2), 246 (2), 175 (20), 162 (1), 151 (1), 143 (1), 133 (1), 123 (2), 117 (1), 110 (8), 97 (100), 69 (10), 45 (25), 39 (24), 29 (28), 27 (30), 10 (10), **2-bromo-3-hexylthiophene**. **613**, 326 (4), 269 (1), 255 (8), 245 (1), 211 (1), 203 (1), 197 (1), 188 (2), 175 (55), 162 (1), 151 (1), 137 (8), 123 (9), 109 (12), 95 (27), 81(12), 69 (30), 51 (21), 41 (90), 29 (100), 18 (13), **2,5-dibromo-3-hexylthiophene**. Partial ^1H NMR, **2,5-dibromo-3-hexylthiophene** δ_{H} 2.52(2H, t, $J=7.6\text{Hz}$), 6.78(1H, s, Th-H), **3-hexylthiophene** δ_{H} 2.65(2H, t, $J=7.8\text{Hz}$), **1,2-dibromoethane** δ_{H} 3.66(4H, s). Repetition of this experiment removed all traces of 1,2-dibromoethane and 2-bromo-3-hexylthiophene but failed to produce the desired 3,4'-dihexyl-2,2'-bithiophene.

Attempted preparation of 1-thiophene-3-hexylboronic acid 53

To a solution of 3-hexylthiophene (2.0g, 11.8mmol) in 30cm^3 of diethyl ether at -78°C was added 1.6M n-butyllithium (7.94cm^3 , 12.7mmol). The solution was stirred at -78°C for 2 h before being transferred via catheter to a flask containing tributyl borate (9.6cm^3 , 35.7mmol) also at -78°C . The flask was then slowly allowed to warm to room temperature overnight. The solution was diluted with water and the layers separated. The aqueous layer was washed twice with diethyl ether (20cm^3) and the combined organic layers dried over MgSO_4 . The solvent was removed by evaporation to afford 7.2g of an orange liquid. δ_{H} 0.70-0.95(27 \dagger , m), 1.20-1.60(36H \dagger , m), 2.62(2H, t, $J=7.4\text{Hz}$), 3.60(9H \dagger , t), 3.80(9H \dagger , t), 6.95(2H, t), 7.23(1H, m). ^1H NMR data indicated that the excess material recovered from the reaction was mostly starting materials. \dagger Integrals in comparison to those of 3-hexylthiophene.

Further attempted preparation of 1-thiophene-3-hexylboronic acid

53

A solution of 1.6M n-butyllithium (4.3cm³, 7mmol) in hexanes was added to a solution of 3-hexylthiophene (1.01g, 6mmol) at -78°C in freshly distilled diethyl ether. The solution was then allowed to warm to -40°C and stirred at this temperature for 1h. The reaction mixture was cooled to -78°C and transferred via catheter to a flask containing trimethylborate (2.1cm³, 18.5mmol) in diethyl ether at -70°C. The reaction mixture was then allowed to warm to room temperature overnight before being quenched with aqueous HCl (100cm³). The solution was extracted with ether, dried over MgSO₄, and the solvent removed by rotary evaporation to yield a solid and an orange liquid. The solid recovered was found to be excess trimethyl borate whilst ¹H NMR spectroscopy indicated that only a small amount of 3-hexylthiophene had been converted to the boronic acid with the majority of the liquid being unreacted 3-hexylthiophene.

Attempted preparation of 2-trimethylsilyl-4-methylthiophene

55

Into a dry three-necked round bottomed flask equipped with a septum inlet and magnetic stirring bar was added TMEDA(3.76cm³, 25mmol), via syringe/septum cap. To the solution was added 40cm³ of freshly dried THF followed by 1.6M n-butyllithium (15.7cm³, 25mmol). The solution was then stirred at room temperature for 45 minutes before being cooled to -78°C. 3-Methylthiophene (2.45g, 25mmol) in 10cm³ of THF was then added via catheter. The solution was then allowed to warm to -40°C and stirred at this temperature for 3h, before being cooled to -78°C whereupon trimethylsilylchloride (3.2cm³, 25mmol) in 10cm³ of freshly dried THF, also at -78°C, was added via catheter. The reaction mixture was stirred overnight and the temperature allowed to rise to room temperature. The mixture was then diluted with water and extracted with diethyl ether. The combined extracts were washed with brine and dried over MgSO₄ before being concentrated to yield (2.90g) of an orange liquid. Partial ¹H NMR, namely peaks at 7.20ppm and 6.90ppm, in the ratio of 1:2 indicated that the required lithiation

and substitution had occurred in low yield, rendering the planned route to the boronic acid unfeasible.

Attempted preparation of 2-trimethylstannyl-4-methylthiophene 60

Into a dry three-necked round bottomed flask equipped with a septum inlet and magnetic stirring bar was added TMEDA (3.76 cm³, 25 mmol), via syringe/septum cap. To the solution was added 40 cm³ of freshly dried THF followed by 1.6 M n-butyllithium (15.7 cm³, 25 mmol). The solution was then stirred at room temperature for 45 minutes before being cooled to -78 °C. 3-Methylthiophene (2.45 g, 25 mmol) in 10 cm³ of THF was then added via catheter. The solution was then allowed to warm to -40 °C and stirred at this temperature for 3 h, before being cooled to -78 °C whereupon freshly dried trimethylstannyl chloride (3.2 cm³, 25 mmol) in 10 cm³ of THF, also at -78 °C, was added via catheter. The reaction mixture was stirred overnight and the temperature allowed to rise to room temperature. The mixture was then diluted with water and extracted with diethyl ether. The combined extracts were washed with brine and dried over MgSO₄ before being concentrated to yield a dark orange solution. Partial ¹H NMR data again indicated a poor percentage conversion to 2-trimethylstannyl-4-methylthiophene.

2-Trimethylstannyl-4-methylthiophene 60

To a solution of 3-methylthiophene (3.30 g, 33 mmol) and TMEDA (5.6 cm³, 36 mmol) in 60 cm³ of freshly dried diethyl ether was added 1.6 M n-butyllithium (23 cm³, 36 mmol). The solution was then refluxed for 3 h. The solution was then cooled to 0 °C and trimethylstannyl chloride (7.30 g, 37 mmol), in 30 cm³ of freshly dried diethyl ether, added via catheter. The solution was stirred under reflux for a further 16 h before being quenched with saturated ammonium chloride. The organic layer was separated and the aqueous layer extracted with diethyl ether. The combined organic layers were washed with brine and dried over MgSO₄, before being concentrated to yield 8.38 g (95%) of an orange oil as a mixture of 2 and 5

substituted 3-methylthiophene in a ratio of 1:4. **2-trimethylstannyl-4-methylthiophene** (major product) δ_{H} 0.38(9H, s, $[\text{CH}_3]_3$), 2.41(3H, s, CH_3), 7.09(1H, s, Th-H), 7.24(1H, s, Th-H). **2-trimethylstannyl-3-methylthiophene** δ_{H} 0.60(9H, s, $[\text{CH}_3]_3$), 2.46(3H, s, CH_3), 7.12(1H, d, Th-H, $J=5\text{Hz}$), 7.59(1H, d, Th-H, $J=5\text{Hz}$).

Stille coupling reaction of 2-bromo-3-methylthiophene 63 with trimethylstannyl-4-methylthiophene 60

To a solution of the 80:20 mixture of trimethylstannyl-3-methylthiophene isomers (8.0g, 29mmol) in 50cm³ of dry toluene was added a solution of 2-bromo-3-methylthiophene (5.15g, 29mmol) and Pd(PPh₃)₄ (1.0g, 0.87mmol) in 50cm³ of dry toluene, via catheter. The solution was stirred under reflux until TLC indicated the disappearance of the halide. The reaction mixture was quenched with HCl and neutralised with saturated sodium hydrogen carbonate solution. The organic layer was then separated and the aqueous layer extracted with toluene. The combined extracts were then dried over MgSO₄ and concentrated to yield 4.13g (74%) of a dark brown liquid. GC/MS, **peak no**, m/z (relative intensity): **255**: 97 (100), 69 (25), 53 (30), 45 (50), 18 (75), **3-methylthiophene. 487**, 194 (63), 179 (38), 161 (20), 134 (35), 110 (35), 51 (41), 45 (100), 39 (62), 27 (33), 18 (45), **dimethyl-2,2'-bithiophene. 540**, 194 (63), 179 (38), 161 (20), 134 (35), 110 (35), 51 (41), 45 (100), 39 (62), 27 (33), 18 (45), **dimethyl-2,2'-bithiophene. 558**, 194 (63), 179 (38), 161 (20), 134 (35), 110 (35), 51 (41), 45 (100), 39 (62), 27 (33), 18 (45), **dimethyl-2,2'-bithiophene**. Partial ¹H NMR, δ_{H} 2.19(6H, s, CH_3), 2.28(6H, s, CH_3), 2.32 (3H, s, CH_3), 2.42(3H, s, CH_3). Combining the results of GCMS and ¹H NMR data and also comparing known chemical shifts of 3,3'-dimethylbithiophene indicated a mixture of head-to-tail, head-to-head and tail-to-tail isomers in a ratio of 70%, 16% and 10% respectively.

Selective bromination of a mixture of dimethylbithiophenes

To a mixture of dimethylbithiophenes (3.83g, 20mmol) in a mixture of chloroform and acetic acid (50.50 v/v, 30cm³), proportionate amounts of NBS (3.0g, 17mmol) were added at 0°C over 30 minutes. After stirring for 30 minutes, the mixture was diluted with water, extracted into chloroform and the combined organic layers dried over MgSO₄. The solvent was removed to yield 4.4g (86%) of a mixture of brominated dimethylbithiophenes. TLC of the reaction mixture showed three spots, which were isolated on silica gel (20cm x 3cm), using hexane as the eluent. Analysis of the three spots gave the following compounds. **5,5'-dibromo-4,4'-dimethyl-2,2'-bithiophene** (minor product). GC/MS, **peak no.**, m/z (relative intensity), **779**, 354 (20), 352 (40), 350 (20), 273 (50), 271 (55), 229 (20), 227 (20), 194 (63), 179 (40), 161 (18), 147 (14), 134 (28), 110 (20), 97 (21), 69 (32), 51 (32), 45 (100), 39 (60), 27 (32). ¹H NMR, δ_H 2.20(6H, s, CH₃), 6.78 (2H, s, Th-H). **5-bromo-3,4'-dimethyl-2,2'-bithiophene** (major product), GC/MS, **peak no.**, m/z (relative intensity), **668**, 274 (40), 272 (55), 194 (63), 179 (40), 161 (18), 147 (14), 134 (28), 110 (20), 97 (21), 69 (32), 51 (32), 45 (100), 39 (60), 27 (32) (Found: M⁺, 271.9324. C₁₀H₉S₂Br requires 271.9329); ¹H NMR, δ_H 2.22(3H, s, CH₃), 2.39(3H, s, CH₃), 6.84 (1H, s, Th-H), 6.88(1H, d, Th-H), 7.14 (1H, d, Th-H). **3,3'-dimethyl-2,2'-bithiophene** (minor product), GC/MS, **peak no.**, m/z (relative intensity), **500**, 194 (63), 179 (40), 161 (18), 147 (14), 134 (28), 110 (20), 97 (21), 69 (32), 51 (32), 45 (100), 39 (60), 27 (32). ¹H NMR, δ_H 2.19(6H, s, CH₃), 6.95(2H, d, Th-H, J=4.2Hz), 7.19(2H, d, Th-H, J=4.2Hz).

2-Trimethylstannyl-4-hexylthiophene 70

To a solution of 3-hexylthiophene (1.0g, 6mmol) and TMEDA (1.0cm³, 6.6mmol) in 30cm³ of freshly dried diethyl ether was added 1.6M n-butyllithium (4.1cm³, 6.6mmol). The solution was refluxed for 3h. The solution was cooled to 0°C and trimethylstannylchloride (1.31g, 6.6mmol) in 30cm³ of freshly dried diethyl ether added via catheter. The solution was

stirred under reflux for a further 16 h before being quenched with saturated ammonium chloride. The organic layer was separated and the aqueous layer extracted with diethyl ether. The combined organic layers were washed with brine and dried over MgSO_4 , before being concentrated to yield 1.94g (90%) of an orange oil as a mixture of 2- and 5- substituted 3-hexylthiophene in a ratio of 1:4. **2-trimethylstannyl-4-hexylthiophene** (major product) δ_{H} 0.38(9H, s, $[\text{CH}_3]_3$), 0.90-1.70(11H, m, hexyl chain), 2.65(2H, t, CH_2), 7.03(1H, s, Th-H), 7.21(1H, s, Th-H). **2-trimethylstannyl-3-hexylthiophene** δ_{H} 0.60(9H, s, $[\text{CH}_3]_3$), 0.90-1.70(11H, m, hexyl chain) 2.60(2H, t, CH_2), 7.14(1H, d, Th-H, $J=5\text{Hz}$), 7.60(1H, d, Th-H, $J=5\text{Hz}$).

Stille coupling reaction of 2-bromo-3-hexylthiophene 25 with trimethylstannyl-3-hexylthiophene 70.

A solution of the 80:20 mixture of trimethylstannyl-3-hexylthiophene compounds (12.9g, 39mmol) in 50cm^3 of dry toluene, was added to a solution of 2-bromo-3-hexylthiophene (9.6g, 36mmol) and $\text{Pd}(\text{PPh}_3)_4$ (1.35g, 1.17mmol) in 50cm^3 of dry toluene, *via* catheter. The solution was stirred under reflux until TLC indicated the disappearance of the halide. The reaction mixture was then quenched with HCl and neutralised with saturated sodium hydrogen carbonate solution. The organic layer was separated and the aqueous layer extracted with toluene. The combined extracts were dried over MgSO_4 and concentrated to yield 13.9g of a dark brown liquid. This liquid was found to contain unreacted starting materials in addition to the desired product. 3-Hexylthiophene was removed by distillation ($60^\circ\text{C}/10\text{mmHg}$). 2-bromo-3-hexylthiophene could not be removed by distillation or by column chromatography. The mixture was diluted with dry diethyl ether and added dropwise, under nitrogen, to a solution of LiAlH_4 /diethyl ether. This reduced 2-bromo-3-hexylthiophene to 3-hexylthiophene, which was removed by distillation ($60^\circ\text{C}/10\text{mmHg}$) to yield a mixture of H-T ($\delta_{\text{H}} \alpha\text{-CH}_2 = 2.50\text{ppm}$, 2H and 2.75ppm , 2H), H-H ($\delta_{\text{H}} \alpha\text{-CH}_2 = 2.50\text{ppm}$, 4H) and T-T ($\delta_{\text{H}} \alpha\text{-CH}_2 = 2.70\text{ppm}$, 4H) dihexylbithiophenes 6.0g (61%) in the ratio of 70%, 20% and 10% respectively. GCMS, **peak no.**, m/z (relative intensity) : **816**, 334 (23), 263 (15), 193

(83), 179 (20), 160 (20), 147 (23), 134 (10), 97 (15), 55 (32), 43 (100), 29 (94), 18 (15). **891**, 334 (23), 263 (15), 193 (83), 179 (20), 160 (20), 147 (23), 134 (10), 97 (15), 55 (32), 43 (100), 29 (94), 18 (15). **951**, 334 (23), 263 (15), 193 (83), 179 (20), 160 (20), 147 (23), 134 (10), 97 (15), 55 (32), 43 (100), 29 (94), 18 (15). Partial ^1H NMR showed overlapping triplets corresponding to the $\alpha\text{-CH}_2$ groups of the alkyl chains. From these signals the above estimate of the percentage composition of each isomer was made.

Selective bromination of a mixture of dihexylbithiophenes

To a mixture of dihexylbithiophenes (3.83g, 20mmol) in a mixture of chloroform and acetic acid (50.50 v/v, 30cm³), proportionate amounts of NBS (3.0g, 17mmol) were added at 0°C over 30 minutes. After stirring for 30 minutes, the mixture was diluted with water, extracted into chloroform and the combined organic layers dried over MgSO₄. The solvent was removed to yield 4.4g (86%) of a mixture of brominated dihexylbithiophenes. TLC of the reaction mixture showed three spots, which were isolated on silica gel (20cm x 3cm), using hexane as the eluent. Analysis of the three spots gave the following compounds. **5,5'-dibromo-4,4'-dihexyl-2,2'-bithiophene** (minor product R_f= 0.3). δ_{H} 0.90(6H, s, CH₃), 1.33-1.62(16H, m, (CH₂)₄), 2.56(4H, t, J=5.1Hz), 6.92(2H, s, Th-H); δ_{C} 112.6, 127.8, 134.6, 138.0. **5'-bromo-3,4'-dihexyl-2,2'-bithiophene** (major product R_f= 0.37) δ_{H} 0.90(6H, s, CH₃), 1.33-1.62(16H, m, (CH₂)₄), 2.56(2H, t, J=5.1Hz), 2.71(2H, t, 5.0Hz), 6.78(1H, s, Th-H), 6.91(1H, d, Th-H, J=4.8Hz), 7.16(1H, d, Th-H, J=4.8Hz); δ_{C} 14.1, 22.6, 29.7, 31.1, 31.8, 32.0, 110.9, 124.5, 127.9, 130.8, 131.6, 136.3, 138.0, 139.8; Found: C, 57.96; H 7.16. Calc for C₂₀H₂₉S₂Br: C, 58.10; H, 7.07%. **3,3'-dihexyl-2,2'-bithiophene** (minor product R_f= 0.45) 0.90(6H, t J=1.7Hz, CH₃), 1.33-1.62(16H, m, (CH₂)₄), 2.50(4H, t, J=7.0Hz), 6.96(2H, d, J=5Hz), 7.22(2H, d, J=5Hz); δ_{C} 14.0, 22.6, 29.6, 31.1, 31.7, 124.5, 127.8, 132.4, 138.0.

A number of these bromination reactions were carried out in order to establish the number of equivalents of NBS required to effect a successful selective bromination of

dialkylbithiophenes. All unsuccessful bromination reaction products were returned to starting materials by reduction with LiAlH_4 in diethyl ether.

1,3-Bis(trimethylsilyl)benzene 29

Magnesium turnings (4.64g, 0.19mol), THF (30cm³) and trimethylsilyl chloride (23.57g, 0.22mol) were stirred in a three neck flask fitted with a reflux condenser and an addition funnel. The Grignard reaction was initiated by the addition of a few drops of 1,2-dibromoethane. 1,3-Dibromobenzene (20g, 0.085mol) dissolved in THF (50cm³) was added over a 1h period. The resulting solution was refluxed under nitrogen for 24 h. The mixture was cooled, added to hexane (150cm³) and washed with saturated NH_4Cl solution (100cm³). The aqueous layer was further extracted with hexane (2 x 50cm³) and the combined organic extracts were passed through 5 cm of silica gel. Concentration yielded (20.3g) of crude product which was further purified by fractional distillation (70-72°C / 0.1mmHg) to yield 17.14g (89.9%) 1,3-bis(trimethylsilyl)benzene (lit.⁵³, 112°C/0.22mmHg). δ_{H} 0.27 (18H, s, 2(CH₃)₃), 7.36 (1H, s, H-4), 7.54 (2H, d, H-3, H-5), 7.70 (1H, s, H-2); m/z (relative intensity) 223(9), 207(66), 96(18), 73(100), 45(60).

1,3-Phenylene-bis(1,3,2-benzodioxoborole) 30

To a dry 100cm³ three-necked flask fitted with a reflux condenser was added 1,3-bis(trimethylsilyl)benzene (1.1g, 5 mmol) in dry CH_2Cl_2 (15cm³) and the solution cooled to -78°C. A solution of BBr_3 (1.0M in CH_2Cl_2 , 10.0 cm³, 10 mmol) was slowly added and the solution stirred until it reached room temperature. The resulting pale yellow suspension was refluxed under nitrogen for 24 h. The dark brown solution was cooled in an ice bath and catechol (1.g, 1mmol) added in one portion. The white suspension was then stirred at room temperature for 24 h and filtered to give a fine white powder. This product was further purified by recrystallisation from chloroform to yield 0.48g (31%) of 1,3-phenylene-bis(1,3,2-benzodioxoborole), m.p. 212-214°C. δ_{H} 7.16 (4H, dd, J=3.4Hz, 2.4 Hz), 7.36 (4H, dd,

J=3.4Hz, 2.4Hz), 7.65 (1H, t, J=8.0Hz), 8.30 (2H, d, J=8Hz), 8.87 (1H, s); m/z (relative intensity) 314 (65), 157(10), 136(10), 69(6), 62(63), 45(100). Found: C, 68.91; H 3.89. Calc for C₁₈H₁₂B₂O₄: C, 68.87; H, 3.85%.

General procedure for Suzuki coupling reactions

A flask equipped with a reflux condenser, a septum inlet and a magnetic stirring bar, was charged with Pd(PPh₃)₄ (3% mol), 1,3-phenylene-bis(1,3,2-benzodioxoborole) (1mmol) and Ba(OH)₂ (4mmol). The flask was then evacuated and flushed with nitrogen, and charged with 1,2-dimethoxyethane (15cm³), and haloarene (2mmol), through the septum inlet with a syringe. The mixture was stirred under reflux for >20 h. The product was extracted with toluene, washed with brine, and dried over MgSO₄. The product was then isolated by silica gel column chromatography using toluene as eluant.

Experimental conditions and observed reaction products for model Suzuki reactions between 2-bromo-3-alkylthiophenes with 1,3-phenylene bis(1,3,2-benzodioxoborole) are discussed in the results and discussion section section of chapter 2 and are summarised in a table on page 109.

1,3-Phenylene bis(5-methyl-2-thiophene) 77

To a dry round bottomed three necked flask equipped with a reflux condenser, septum inlet and magnetic stirring bar were added 1,3-phenylene-bis(1,3,2-benzodioxoborole) (0.78g, 2.50mmol), tetrakis(triphenylphosphine)palladium (0.07g, 6%/mol) and Ba(OH)₂·(H₂O)₈ (3.15g, 10mmol) under nitrogen. Dimethoxyethane (10cm³) was then added and 2-bromo-3-methylthiophene (0.88g, 5mmol). The mixture was warmed to reflux temperature and refluxed for 48 h. The product was extracted into toluene, washed with brine and dried over MgSO₄. The product was obtained by removal of the solvent by rotary evaporation, to yield a viscous orange oil. GCMS of the crude mixture showed the following products. **2-phenyl-3-methylthiophene, peak no., m/z (relative intensity) : 483, 174(100), 147(10), 141(21), 129(29), 121(15), 115(29), 102(8), 97(48), 85(15), 77(35), 51(35), 45(65).**

Triphenylphosphine 765, 262(42), 183(100), 170(4), 152(20), 108(90), 51(40). **1,3-Phenylene bis(5-methyl-2-thiophene) 820**, 270(100), 255(10), 235(10), 221(39), 208(15), 184(16), 171(53), 134(32), 111(31), 97(73), 45(92). **Triphenylphosphine oxide 931**, 278 (5), 277(55), 199(40), 183(30), 152(28), 77(100), 51(80), 18(80). These products were isolated by column chromatography on silica gel using toluene/ethyl acetate to yield the desired **1,3-Phenylene bis(5-methyl-2-thiophene)** as an opaque solid. δ_{H} 2.38(6H, s, [CH₃]₂), 6.95(2H, d, J=5Hz, Th-H), 7.23(2H, d, J=5Hz), 7.42(3H, bs, Ph-H), 7.57(1H, s, Ph-H). δ_{C} 15.0, 123.6, 127.7, 128.7, 129.5, 131.1, 133.4, 135.0, 137.5; m/z (relative intensity) 270(100), 255(10), 235(10), 221(39), 208(15), 184(16), 171(53), 134(32), 111(31), 97(73), 45(92) (Found: M⁺, 270.0529 C₁₆H₁₄S₂ requires 270.4066); Found: C, 71.20; H 5.30. Calc for C₁₆H₁₄S₂: C, 71.07; H, 5.22%;

1,3-Phenylene bis(5-hexyl-2-thiophene) 83

1,3 phenylene bis(1,3,2-benzodioxaborole) (1.58g, 5.0mmol) was added to a dry three necked round bottomed flask, under nitrogen, equipped with a septum inlet and magnetic stirring bar. Tetrakis(triphenylphosphine) palladium (0.7g, 0.61mmol) and barium hydroxide hexahydrate (6.37g, 20.2mmol) were then added followed by 1,2-dimethoxyethane (15cm³). 2-Bromo-3-hexylthiophene (2.5g, 10.1mmol) was added and the solution stirred at 85°C for 72h. The reaction mixture was allowed to cool and extracted with toluene, washed with brine and dried over MgSO₄. The solvent was then removed by rotary evaporation to yield a crude brown oil. The following products could be identified by GCMS, **peak no.**, m/z (relative intensity) : **3-hexylthiophene 390**, 168(11), 111(13), 97(100), 84(7), 77(5), 53(18), 45(30), 39(24), 27(24), 18(30). **2-Phenyl-3-hexylthiophene 656**, 244(8), 173(57), 129(21), 115(11), 45(38), 28(25), 18(100). **Dihexylbithiophene 808**, 334(2), 263(2), 207(1), 193(13), 171(2), 160(2), 147(5), 134(4), 123(1), 111(1), 97(3), 55(12), 43(12), 28(21), 18(100). Although 1,3-phenylene bis(5-hexyl-2-thiophene) could not be detected by GCMS, TLC of the crude reaction product was very similar to that of 1,3-phenylene bis(5-methyl-2-thiophene). Flash column chromatography on silica gel with toluene/ethyl acetate afforded pure **1,3-**

phenylene bis(5-hexyl-2-thiophene). δ_{H} 0.89(6H, t, CH_3), 1.30-1.42(8H, m, $2[\text{CH}_2]_2$), 1.55-1.68(8H, m, $2[\text{CH}_2]_2$), 2.70(4H, t, $J=6\text{Hz}$, 2CH_2), 7.00ppm(2H, d, $J=4\text{Hz}$, Th-H), 7.22(2H, d, $J=4\text{Hz}$, 2H), 7.42(3H,bs, Ph-H), 7.56(1H, s, Ph-H). δ_{C} 14.1, 22.6, 29.2, 29.7, 31.0, 31.6, 123.8, 128.3, 128.4, 128.6, 132.0, 132.2, 135.1, 138.9. Found: C, 76.23; H 8.37. Calc for $\text{C}_{26}\text{H}_{34}\text{S}_2$: C, 76.04; H, 8.35%;

Attempted Suzuki coupling reaction between 1,3-phenylene bis(1,3,2-benzodioxoborole) 30 and 5'-bromo-3,4'-dimethyl-2,2'-bithiophene 67

Into a dry round-bottomed flask equipped with a reflux condenser, nitrogen inlet, magnetic stirrer bar and septum inlet, were placed 1,3-phenylene bis(1,3,2-benzodioxoborole) (0.22g, 0.71mmol), barium hydroxide hexahydrate(0.90g, 2.86mmol) and $\text{Pd}(\text{PPh}_3)_4$ (0.1g, 0.08mmol). To the flask was added dimethoxyethane (15cm^3), followed by 5'-bromo-3,4'-dimethyl-2,2'-bithiophene (0.39g, 1.43mmol) and the solution stirred at reflux for 90h. The solution was diluted with water and extracted into toluene. The combined extracts were washed with brine and dried over MgSO_4 to yield a dark brown oil. ^1H NMR of the crude product indicated the presence of the desired 1,3-phenylene bis(5,3'-dimethyl-3,2'-bithiophene) in addition to other geometric isomers and side products of the cross-coupling reaction. TLC of the reaction mixture showed three spots which were isolated by column chromatography on silica gel with hexane. The majority of the isolated material was confined to a single spot, the other fractions containing minor impurities which could not be characterised. ^1H NMR of the isolated material again showed a mixture of regioisomers which could be separated by dissolving the oil in pentane since only 1,3-phenylene bis(5,3'-dimethyl-3,2'-bithiophene) was found to be insoluble in pentane. **1,3-phenylene bis(5,3'-dimethyl-3,2'-bithiophene)** δ_{H} 2.40(6H, s, CH_3), 2.46(6H, s, CH_3), 6.90(2H, d, $J=5.8\text{Hz}$), 7.03(2H, s, Th-H), 7.15(2H, d, $J=5.8\text{Hz}$), 7.46(3H, s), 7.62(1H, s).

Attempted Suzuki coupling reaction between 1,3-phenylene bis(1,3,2-benzodioxaborole) 30 and 5'-bromo-3,4'-dihexyl-2,2'-bithiophene 27

Into a dry round-bottomed flask equipped with a reflux condenser, nitrogen inlet, magnetic stirrer bar and septum inlet, were placed 1,3-phenylene bis(1,3,2-benzodioxaborole) (0.15g, 0.48mmol), barium hydroxide hexahydrate(0.61g, 1.94mmol) and Pd(PPh₃)₄ (0.07g, 0.06mmol). To the flask was added dimethoxyethane (15cm³), followed by 5'-bromo-3,4'-dihexyl-2,2'-bithiophene (0.40g, 0.97mmol) and the solution stirred at reflux for 90h. The solution was then diluted with water and extracted into toluene. The combined extracts were washed with brine and dried over MgSO₄ to yield a dark brown oil. ¹H NMR of the crude mixture indicated the presence of the desired product in addition to other geometric isomers and side products of the cross-coupling reaction. Column chromatography resulted in a much cleaner product in which the proton signals corresponding to 1,3-phenylene bis(5,3'-dihexyl-3,2'-bithiophene) could clearly be observed by ¹H NMR in addition to many other signals in the region of 7.4-7.8ppm corresponding to those of the boronic ester. The desired product could not be obtained in its pure form by further chromatography or by extraction with various solvents. This reaction was repeated under similar conditions with fresh catalyst however identical results were obtained.

1,3-Phenylene bis(5,3'-dimethyl-3,2'-bithiophene) 84

1,3-Phenylene-bis(1,3,2-benzodioxaborole) (0.26g, 0.82mmol) was added to a dry three necked round bottomed flask, under nitrogen, equipped with a septum inlet and magnetic stirring bar. Tetrakis(triphenylphosphine) palladium (0.1g, 0.1mmol) and barium hydroxide hexahydrate (1.04g, 3.3mmol) were added followed by 1,2-dimethoxyethane(15cm³) and H₂O(3cm³). 5'-Bromo-3,4'-dimethyl-2,2'-bithiophene (0.45g, 1.65mmol) was added and the solution stirred at 85°C for 90h. The reaction mixture was allowed to cool and was extracted with toluene, washed with brine and dried over MgSO₄. The solvent was removed by rotary

evaporation to yield a crude brown oil. The brown oil was absorbed onto silica gel using hexane/dichloromethane and flash column chromatography performed on silica gel using hexane as eluent to afford pure **1,3-phenylene bis(5,3'-dimethyl-3,2'-bithiophene)** as a yellow powder, m.p.>300°C. δ_{H} 2.40(6H, s, 2CH₃), 2.46(6H, s, 2CH₃), 6.89(2H, d, J = 5.8Hz, Th-H), 7.00(2H, s, Th-H), 7.15 (2H, d, J = 5.8Hz), (7.48(3H, bs, Ph-H), 7.62(1H, s, Ph-H). δ_{C} 15.70, 15.97, 123.61, 128.10, 129.32, 129.57, 129.98, 131.1, 131.94, 133.4, 134.31, 136.5; Found: C, 67.30; H 4.62. Calc for C₂₆H₂₂S₄: C, 67.49; H, 4.62%.

1,3-Phenylene bis(5,3'-dihexyl-3,2'-bithiophene) 31

1,3 Phenylene bis(1,3,2-benzodioxaborole) (0.34g, 1.1mmol) was added to a dry three necked round bottomed flask, under nitrogen, equipped with a septum inlet and magnetic stirring bar. Tetrakis(triphenylphosphine) palladium (0.15g, 0.13mmol) and barium hydroxide hexahydrate (1.73g, 5.5mmol) were added followed by 1,2-dimethoxyethane(15cm³) and H₂O(3cm³). 5'-bromo-3,4'-dimethyl-2,2'-bithiophene.(0.45g, 1.65mmol) was added and the solution stirred at 85°C for 90h. The reaction mixture was allowed to cool and extracted with toluene, washed with brine and dried over MgSO₄. The solvent was removed by rotary evaporation to yield a crude brown oil. The brown oil was absorbed onto silica gel using hexane and flash column chromatography performed on silica gel using hexane as eluent to afford **1,3-phenylene bis(5,3'-dihexyl-3,2'-bithiophene)** as a brown oil. δ_{H} 0.89(12H, t, 4CH₃), 1.30-1.42(16H, m, 4[CH₂]₂), 1.55-1.68(16H, m, 4[CH₂]₂), 2.70(4H, t, J=6Hz, 2CH₂), 2.78(4H, t, 2CH₂), 6.95(2H, d, J=4Hz, Th-H) 7.00ppm(2H, s, Th-H), 7.22(2H, d, J=4Hz, Th-H), 7.42(3H,bs, Ph-H), 7.56(1H, s, Ph-H). δ_{C} 14.0, 22.5, 29.2, 29.6, 30.9, 31.6, 123.5, 128.1, 128.4, 128.8, 129.9, 130.1, 134.6, 134.8, 137.3, 139.2; Found: C, 74.54; H 8.36. Calc for C₄₆H₆₂S₄: C, 74.34; H, 8.41%.

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Appendix I

Summary of Nickel Catalysed Cross-Coupling Reactions of 3-Alkylthiophenes

<u>STARTING MATERIAL</u>	<u>METALATION CONDITIONS</u>	<u>COUPLING CONDITIONS</u>	<u>VARIANT</u>	<u>PERCENTAGE COUPLING</u>
1. 3-Hexylthiophene	1. LDA in THF at -78°C 2. MgBr ₂ .OEt ₂ at -60°C 3. -60°C → -5°C 40 min	Add to 2-bromo-3-hexylthiophene in presence of NiCl ₂ (dppp) at -78°C	N / A	~ 20%
2. 3-Hexylthiophene	1. LDA in THF at -78°C 2. MgBr ₂ .OEt ₂ at -60°C 3. -60°C → -5°C 2h	Add to 2-bromo-3-hexylthiophene in presence of PdCl ₂ (dppf) at -78°C	Catalyst	~ 17%
3. 3-Hexylthiophene	1. LDA in THF at -78°C 2. MgBr ₂ .OEt ₂ at -60°C 3. -60°C → -5°C 1.5h	Add to 2-bromo-3-hexylthiophene in presence of NiCl ₂ (dppp) at -78°C	Fresh MgBr ₂ .OEt ₂	~ 20%
4. 3-Hexylthiophene	1. LDA in THF at -78°C 2. MgBr ₂ .OEt ₂ at -60°C 3. -60°C → -5°C 1.5h	Add to 2-bromo-3-hexylthiophene in presence of NiCl ₂ (dppp) at -30°C	Temperature of coupling reaction	~ 22%
5. 3-Hexylthiophene	1. LDA in THF at -78°C 2. MgBr ₂ .OEt ₂ at -60°C 3. -60°C → -5°C 1.5h	Add to 2-bromo-3-hexylthiophene in presence of NiCl ₂ (dppp) at -30°C	Addition of a further 0.5% mole of catalyst after 12h	~ 22% i

6. 3-Hexylthiophene	1. LDA in THF at -78°C 2. MgBr ₂ .OEt ₂ at -60°C 3. -60°C → -5°C 1.5h	Add to 2-bromo-3-hexylthiophene in presence of NiCl ₂ (dppp) dropwise over 1h at 0°C	1. Purified 2-bromo-3-hexyl thiophene 2. Addition conditions	0%
7. 3-Hexylthiophene	1. LDA in THF at -78°C 2. MgBr ₂ .OEt ₂ at -60°C 3. -60°C → -5°C 1.5h	Add to 2-bromo-3-hexylthiophene in presence of NiCl ₂ (dppp) dropwise over 1h at 0°C	1. Purified 2-bromo-3-hexyl thiophene 2. Addition conditions 3. Fresh NiCl ₂ (dppp)	0%
8. 3-Hexylthiophene	1. LDA in THF at -78°C 2. MgBr ₂ .OEt ₂ at -60°C 3. -60°C → -5°C 1.5h	Add to 2-bromo-3-hexylthiophene in presence of NiCl ₂ (dppp) dropwise over 1h at -78°C	1. Lithiation allowed to take place over 1.5-2h rather than 40 min.	21%
9. 3-Hexylthiophene	1. LDA in THF at -78°C 2. MgBr ₂ .OEt ₂ at -60°C 3. -60°C → -5°C 1.5h	Add to 2-bromo-3-hexylthiophene in presence of NiCl ₂ (dppp) dropwise over 1h at 0°C	1. Grignard formation over 2h rather than 1h.	20%
10. 3-Hexylthiophene	1. LDA in THF at -78°C 2. MgBr ₂ .OEt ₂ at -60°C 3. -60°C → -5°C 1.5h	Add to 2-bromo-3-hexylthiophene in presence of NiCl ₂ (dppp) dropwise over 1h at -78°C	4 Eqv of magnesium bromide etherate used 2h allowed for metallation	0%

11. 3-Methylthiophene	<ol style="list-style-type: none"> 1. LDA in THF at -78°C 2. $\text{MgBr}_2 \cdot \text{OEt}_2$ at -60°C 3. $-60^{\circ}\text{C} \rightarrow -5^{\circ}\text{C}$ 1.5 h 	Add to 2-bromo-3-methylthiophene in presence of $\text{NiCl}_2(\text{dppp})$ at -78°C	Side chain	~ 10%
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Chapter Three

Alternative Monomer Units

3.0 Alternative Monomer Units

3.1 Introduction Part 1

McConnell's theory on intermolecular magnetic interactions claimed that exchange interaction between two aromatic radicals could be ferromagnetic when the product of spin densities at two interacting sites on different molecules are negative in sign.¹ This was beautifully illustrated by Izuoka who synthesised three isomers of bis(phenylmethylene)[2,2]paracyclophane, in which two isomers satisfied McConnell's model and exhibited high spin coupling whereas anti-ferromagnetic coupling was observed in the third isomer, which had a positive spin density product.² This was the first experiment which proved McConnell's hypothesis.

We have explained that ferromagnetic alignment may be achieved by appropriate coupling *via* a benzene moiety³ and have synthesised target monomers **77**, **83**, **84** and **31** based on the ability of *m*-phenylene to act as a ferromagnetic coupling unit.

Studies have shown that *o*- and *p*-benzoquinodimethane are ground state singlets and therefore exhibit anti-ferromagnetic coupling, **Figure 1**.³

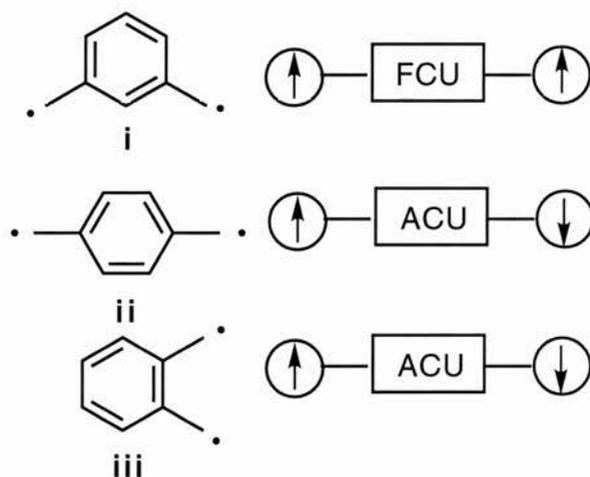
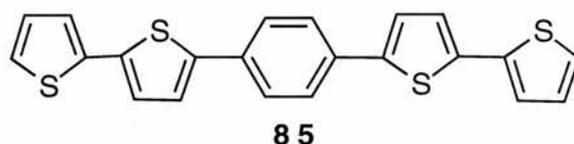


Figure 1

We can determine the nature of the coupling simply by counting the number of atomic centres between the sites with unpaired electrons. If this number is odd, as in **i**, then ferromagnetic coupling occurs. If the number is even, as in **ii** and **iii**, then the unit acts as an anti-ferromagnetic coupling unit.

We attempted to synthesise a monomer similar to **31** and **84** which would display anti-ferromagnetic rather than ferromagnetic coupling. This should have contrasting magnetic properties to **31** and **84**, especially since anti-ferromagnetic coupling units tend to be more effective compared to their ferromagnetic counterparts, and would tend to corroborate the underlying theory. We decided to synthesise **85**, which we felt would be accessible through the Suzuki coupling reaction between 5-bromo-2,2'-bithiophene and 1,4-phenylene(1,3,2-benzodioxaborole).



To facilitate a short order synthesis of **85**, the bithiophene unit was not functionalised with alkyl solubilising groups. A clear contrast of the spin-coupling involved in **85** compared to the *m*-phenylene derivative is shown in **Figure 2**.

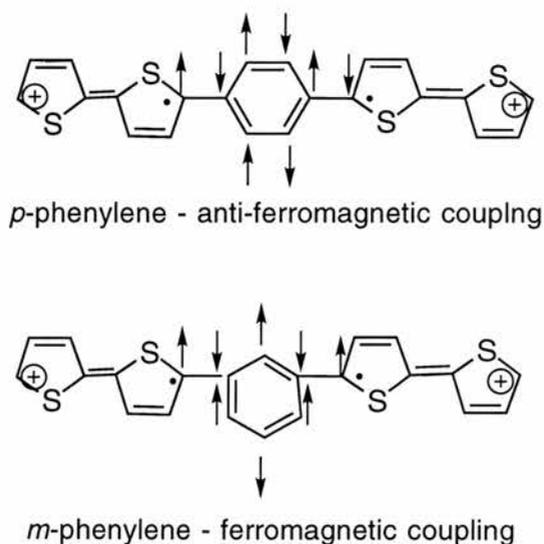
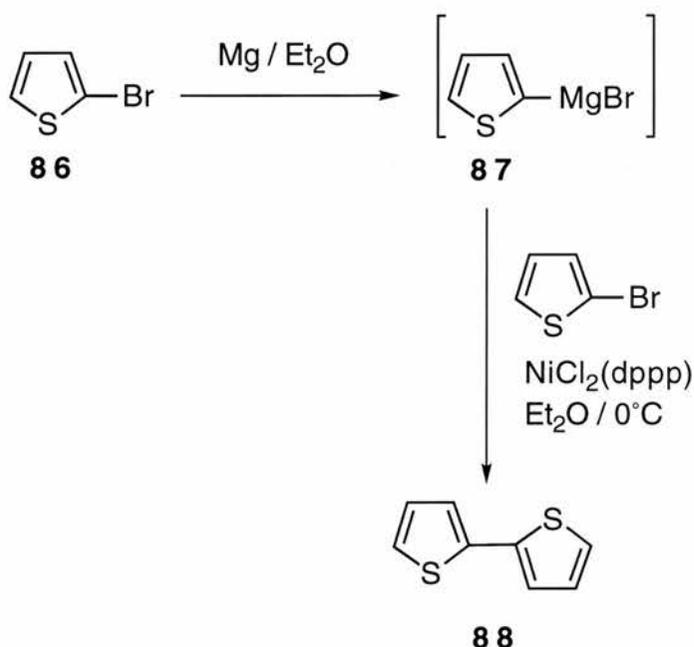


Figure 2

3.2 Synthesis of 1,4-phenylene bis(3,2'-bithiophene) 85

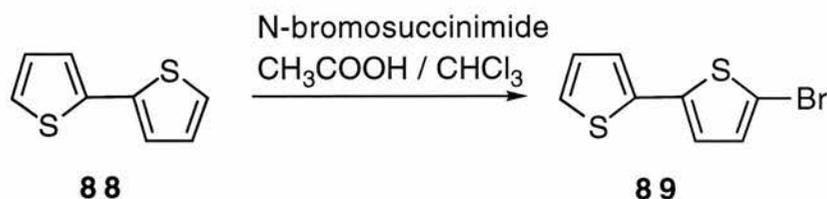
Having established synthetic routes towards **77**, **83**, **84** and **31**, utilising nickel and palladium catalysed coupling reactions, we adopted a similar approach in the synthesis of **85**. The bithiophene unit was formed in good yield by the nickel catalysed homo-coupling reaction of 2-bromothiophene **86**, **Scheme 1**.



Scheme 1

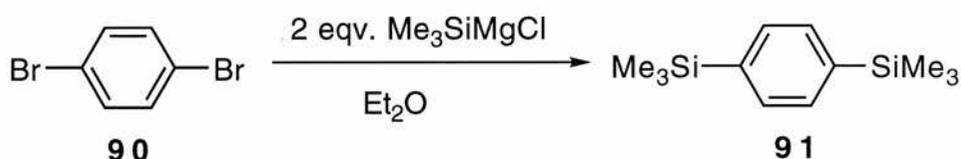
The yield for this reaction proved to be significantly higher (87% compared to 22%) than the previous attempts to couple 5-bromomagnesio-3-hexylthiophene with 2-bromo-3-hexylthiophene under similar conditions. Although the 5-bromomagnesio-3-hexylthiophene was generally formed *via* the lithiate, rather than direct insertion of magnesium, attempts to couple alkyl substituted thiophenes in this manner proved to be very low yielding. These poor yields would appear to be associated with the presence of alkyl chains at the β -position. The steric hindrance which these groups provide has been noted by Barbarella *et. al.* who confirmed that the Kumada reaction results in very poor yields for thiophenes with long β -alkyl chains.⁴

2,2'-Bithiophene **88** was brominated using *N*-bromosuccinimide in acetic acid/chloroform, (Scheme 2), to afford 5'-bromo-2,2'-bithiophene **89** which could then take part in a Suzuki coupling reaction with 1,4-phenylene bis(1,3,2-benzodioxaborole).



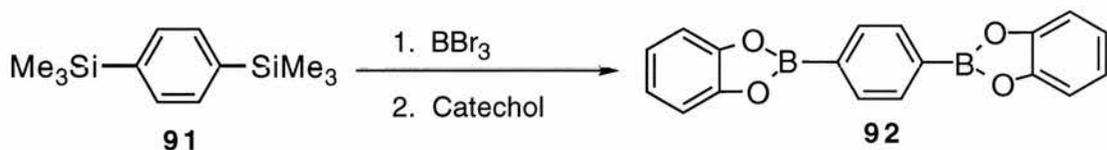
Scheme 2

We attempted to form 1,4-phenylene(1,3,2-benzodioxaborole) in a similar fashion to the 1,3-substituted derivative. This involved the reaction of two equivalents of trimethylsilylmagnesium chloride with 1,4-dibromobenzene **90** to yield 1,4-bis(trimethylsilyl)benzene **91** as a white powder, Scheme 3.



Scheme 3

Bis-silane **91** was then subjected to a reaction with boron tribromide in dichloromethane at -70°C followed by the addition of catechol, in an attempt to form the 1,4-bis boronic ester **92**, Scheme 4.

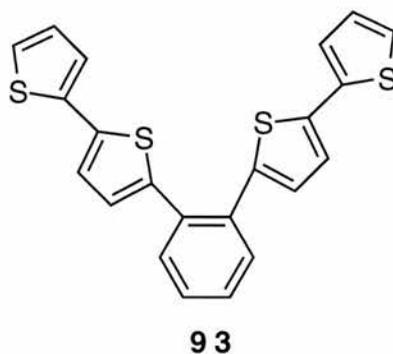


Scheme 4

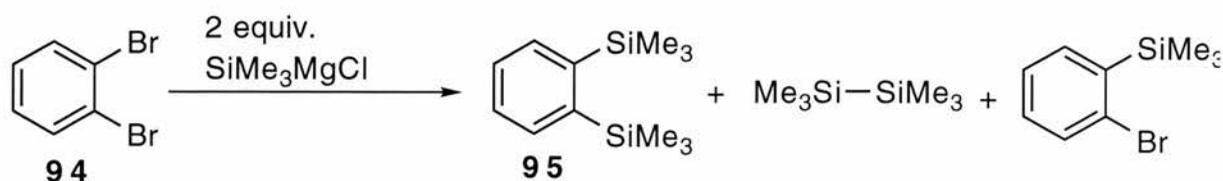
A small amount of a fine white powder was formed which was recrystallised from chloroform. ¹H NMR analysis of the reaction product in DMSO showed similarities when compared to *m*-

substituted bis boronic ester **30**. The aromatic hydrogens of catechol borane were present, but the signal corresponding to the hydrogens of the *p*-phenylene unit, which are equivalent, showed a unresolved multiplet, suggesting an incomplete or side reaction had taken place. 1,3-Bis(trimethylsilyl)benzene was reformed and the reaction repeated. Again a fine white powder was recovered and the ^1H NMR spectrum of the crude product was identical to that obtained previously. TLC of the powder on silica gel and aluminium oxide using a variety of solvents as eluents suggested that the components of the reaction mixture could not be isolated by column chromatography.

We also intended to form **93** by Suzuki coupling methodology, this would require the synthesis of a 1,2-bis boronic ester.

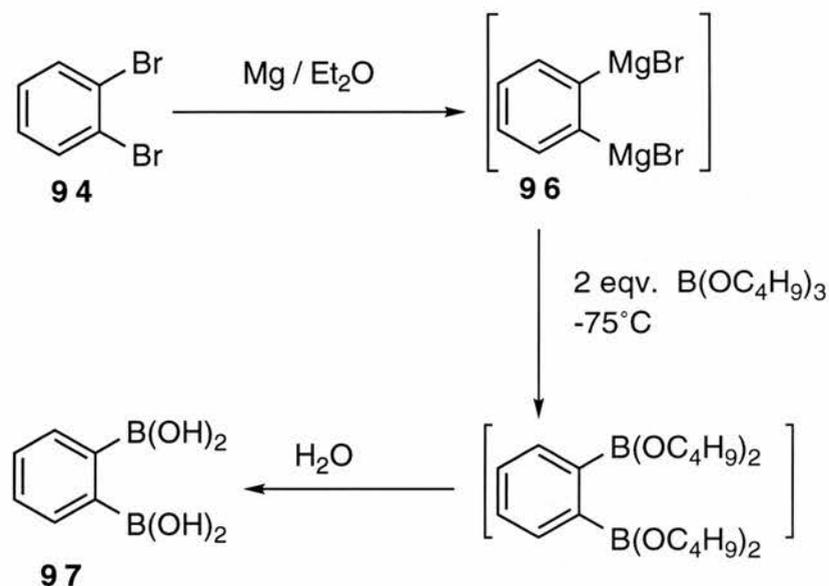


Several attempts were made to form the intermediate 1,2-bis(trimethylsilyl)benzene **95** by reaction of 1,2-dibromobenzene **94** with the Grignard of trimethylsilyl chloride. These were only partially successful since the reaction consistently produced side products such as 1-bromo-2-trimethylsilyl(benzene), hexamethyldisilane and trimethylsilylbenzene in addition to unreacted 1,2-dibromobenzene and the desired 1,2-bistrimethylsilylbenzene, **Scheme 5**.



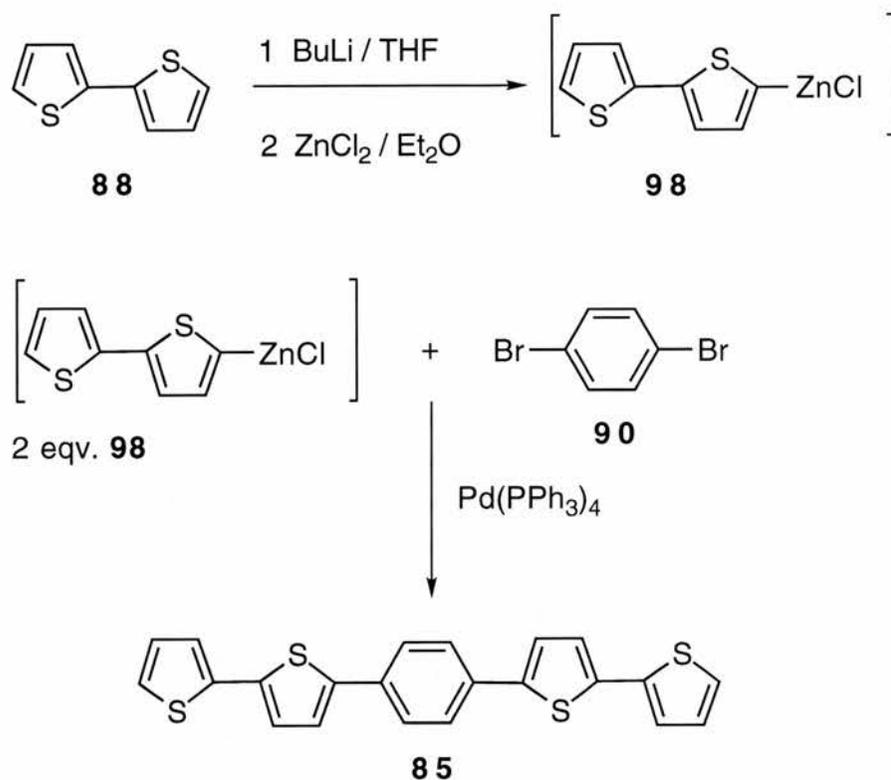
Scheme 5

We also attempted to form the 1,2-bis boronic ester **97** directly from 1,2-dibromobenzene by forming the Grignard intermediate **96** and allowing it to react with tributylborate, **Scheme 6**.



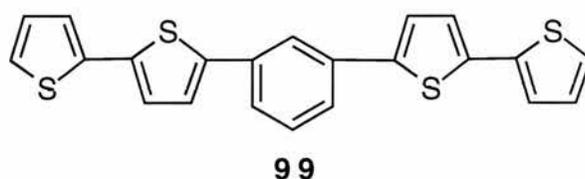
Scheme 6

The white solid recovered was only sparingly soluble in DMSO however and mass spectroscopy confirmed that only starting materials had been recovered. A successful synthesis of **85** was achieved by the zinc mediated coupling of bithiophene **88** with 1,4-dibromobenzene **90**, **Scheme 7**.



Scheme 7

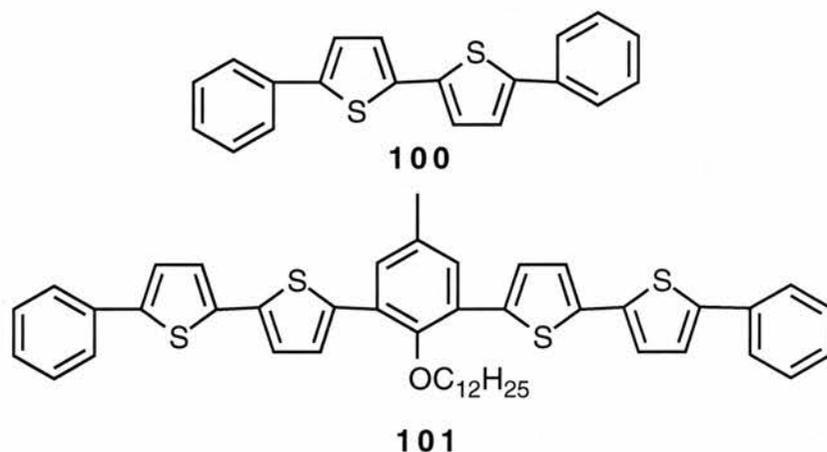
Bithiophene was formed as before and was lithiated using butyl lithium/THF at -60°C. Transmetalation with zinc chloride gave the zinc derivative **98**, of which two equivalents were used in coupling to 1,4-dibromobenzene **90** to afford 1,4-phenylene bis(3,2'-bithiophene) **85** as a yellow solid. This yellow powder was extremely insoluble and therefore difficult to characterise. This was not due solely to the absence of the alkyl solubilising groups since **99** has been found to be soluble in common organic solvents.



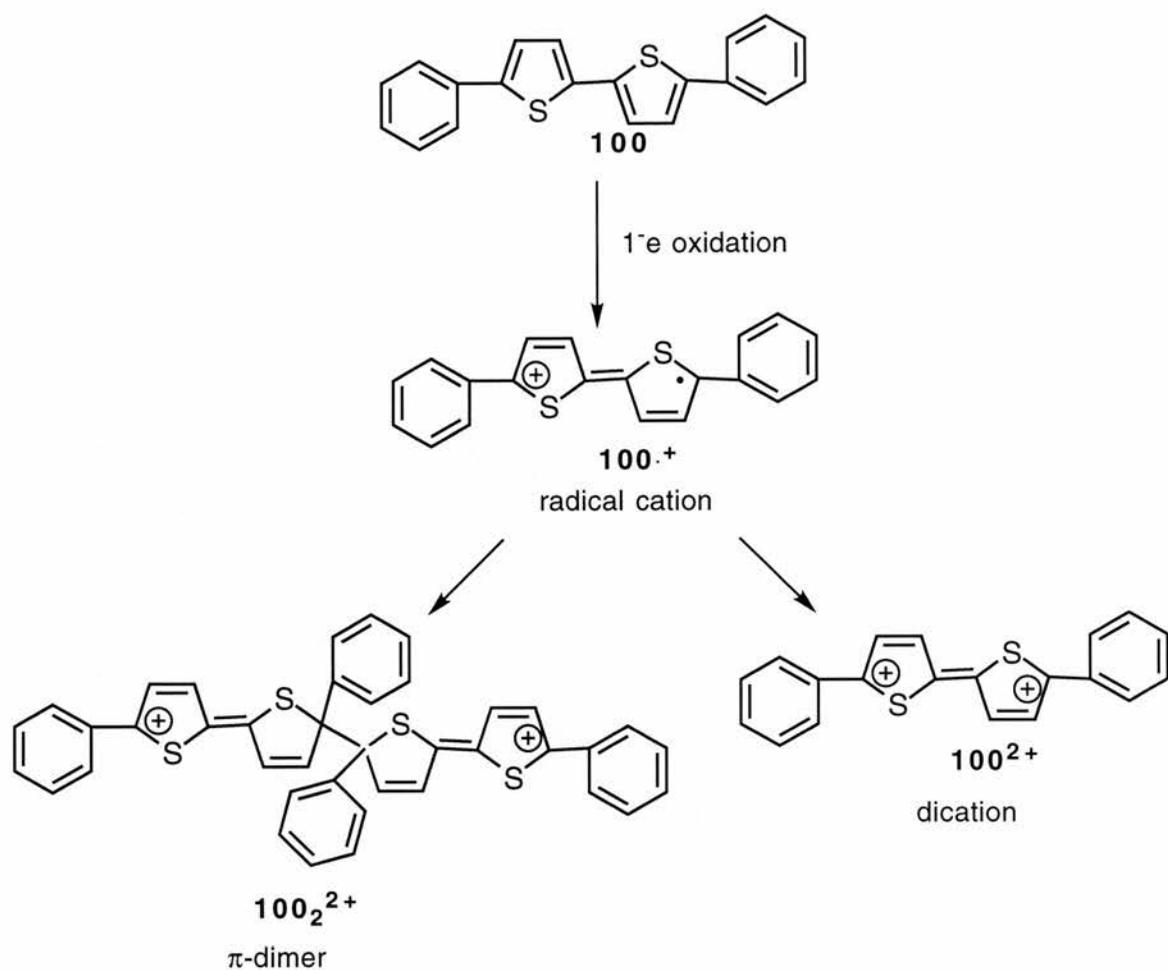
We feel the difference in solubility must be related to the conformation of the monomer units.

3.3 Introduction Part 2

As mentioned previously Janssen and others have suggested that cation radicals of oligothiophenes can form diamagnetic π -dimers in the solid state and in solution at low temperatures.^{5,6,7} Obviously π -dimerisation and the associated anti-ferromagnetic pairing of unpaired electrons would be detrimental to obtaining high spin molecules. In order to assess the effect of π -dimerisation Janssen studied model oligomers such as **100** and **101**.⁸



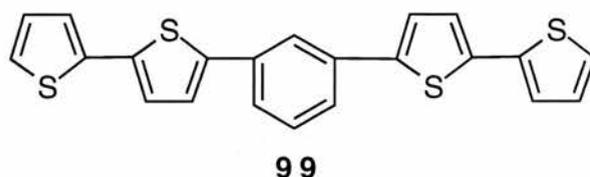
Janssen restricted the π -conjugated segments to two heterocyclic rings to maximise the electron density at the carbon atoms directly connected to the central 1,3-phenylene unit upon doping. Cyclic voltammetry showed that **100** undergoes two reversible one electron oxidation's to the radical cation **100**^{•+} followed by further oxidation to the dication **100**²⁺. The cyclic voltamogram of **101** reveals two partially resolved one electron oxidation waves. Comparison with the CV of **100** suggested that the wave represented the process **101** \rightarrow **101**^{•+} \rightarrow **101**²⁺. In contrast to **100**, **101** cannot be oxidised reversibly beyond the dication radical. Electronic absorption spectroscopy and ESR spectroscopy were used to follow the chemical oxidations of **100** and **101**. These revealed that upon lowering the temperature both **100** and **101** undergo reversible π -dimerisation as shown in **Scheme 8**.



Scheme 8

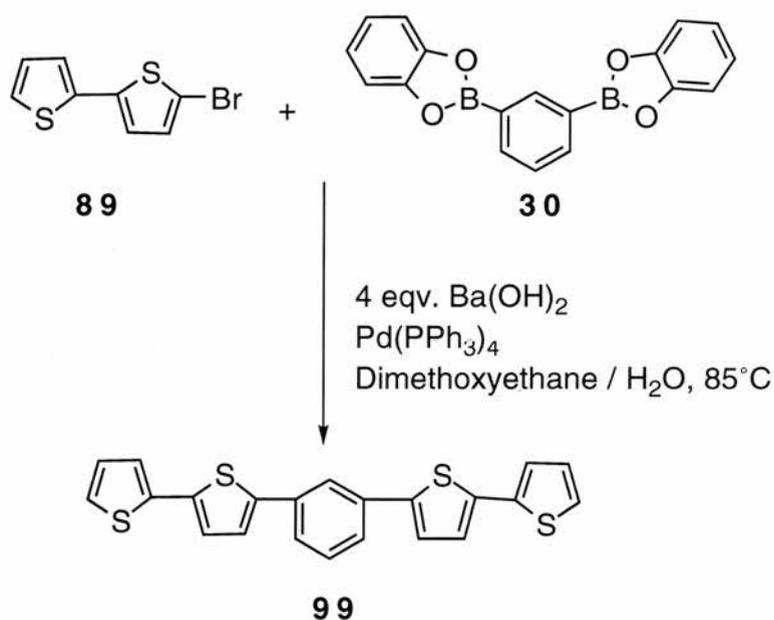
Janssen concluded that due to the strong tendency to form π -dimers it would not be possible to obtain high spin molecules based on dopable π -conjugated segments containing thiophene. Clearly radical cation stability varies according to conjugation length and we would therefore expect the degree of π -dimerisation to vary accordingly. Generally the cationic state of oligothiophenes with a shorter conjugation lengths are highly reactive and couple immediately and reversibly. However, it has been reported that a stable cationic state exists in quaterthiophene⁹ and that the cation has almost the same spatial extent as theoretically predicted.¹⁰ Moreover this size is almost half the theoretically predicted spatial extent of the bipolaron and, hence, makes the bipolaron state unstable.

We have addressed the problem of π -dimerisation in monomers **77**, **83**, **84** and **31** by incorporating bulky alkyl chains attached to the quaterthiophene unit. These should prevent dimerisation due to steric factors. In order to determine the effectiveness of the alkyl substituents we chose to synthesise **99** which should have a lower spin concentration than **31**, if π -dimerisation occurs.



3.4 Synthesis of 1,3-Phenylene bis(3,2'-bithiophene) **99**

2,2'-Bithiophene **88** was again formed by the nickel catalysed homo-coupling of 2-bromothiophene. Bromination with N-bromosuccinimide in chloroform/acetic acid, as described previously afforded 5-bromo-2,2'-bithiophene **89**, facilitating a Suzuki coupling reaction with 1,3-phenylene-bis(1,3,2-benzodioxaborole), which was formed as described in chapter 2, **Scheme 9**.



Scheme 9

(0.25g, 0.46mmol) at 0°C. The solution was stirred at this temperature for 45 min. before being refluxed overnight whereupon it had turned dark orange in colour. The solution was then poured over ice and extracted with dichloromethane. The combined extracts were then dried over MgSO₄ and the solvent removed by rotary evaporation, to yield a green/brown solid 3.96g (87%).m.p. 32-33°C (lit., m.p. 32-33°C¹¹); δ_{H} 7.00-7.05(2H, m), 7.20-7.25(4H, m); δ_{C} 123.69, 124.25, 127.66, 137.33; GCMS, **peak no.**, m/z (relative intensity): **447**, 166(100), 134(27), 127(12), 121(70), 108(18), 102(6), 90(13), 77(25), 69(50), 63(25), 58(30), 51(19), 45(75), 39(2).

5-Bromo-2,2'-bithiophene 89

2,2'-Bithiophene (2.80, 16.85mmol) was dissolved in 40cm³ of a 50/50 v/v solution of chloroform and acetic acid at 0°C. To this was added N-bromosuccinimide (3.0g, 16.85mmol) portion wise over a 1h period at 0°C. The solution was then left to stir for a further 1h before being quenched with water and extracted into chloroform. The combined extracts were washed with saturated NaHCO₃ and dried over MgSO₄ before being concentrated in vacuo to yield the crude product. Column chromatography on silica gel using hexane as eluent removed trace amounts of 5,5'-dibromo-2,2'-bithiophene and 2,2'-bithiophene to afford 3.40g (82%) of the title compound as a colourless solid; m.p. 31°C (lit.,¹² 30-33°C); δ_{H} 6.91-7.01(2H, m), 7.12(1H, m), 7.20-7.26(m, 2H); GCMS, **peak no.**, m/z (relative intensity): **569**, 246(30), 244(30), 165(40), 121(100), 82(28), 69(43), 63(23), 57(17), 50(12), 45(50), 39(13).

1,4-Bis(trimethylsilyl)benzene 91

Into a three necked flask was placed dry magnesium turnings (1.75g, 71.62mmol) in freshly dried ether followed by the addition of freshly distilled trimethylsilyl chloride (10.3cm³, 81.37mmol) under a nitrogen atmosphere. As soon as the Grignard reaction was initiated, 1,4-dibromobenzene (7.5g, 31.8mmol) was added dropwise over 1h and the solution refluxed under nitrogen for 36h. During this period all Mg turnings were incorporated in the reaction

and a white solid formed. The solution was allowed to cool and the white solid dissolved by the addition of sat. NH_4Cl . The organic layer was isolated and extracted with hexane and the combined extracts dried (MgSO_4) and the solvent removed under reduced pressure to yield the title compound as a yellow/white powder 6.20g (88%); m.p. 90-92°C; (lit. m.p. 95.5 - 96.5°C)¹³ δ_{H} 0.30[18H, s, $\text{Si}(\text{CH}_3)_3$], 7.54(4H, s, Ph-H).

Attempted preparation of 1,4-phenylene (1,3,2-benzodioxaborole) 92

1,4-Bis(trimethylsilyl)benzene (3.0g, 13.54mmol) was dissolved in freshly distilled dichloromethane (50cm³) and 1.0M boron tribromide in dichloromethane (27.1cm³, 27.1mmol) added at -70°C. The solution was allowed to warm to room temperature, before being refluxed overnight. The solution was then cooled on an ice bath and catechol (2.98, 27.1mmol) added at 0°C. The solution was then stirred at room temperature for 48h before being filtered to yield a fine white powder, which was recrystallised from chloroform. m.p. 302-306°C; δ_{H} 6.48(s), 6.55(4H, dd, J=3.4Hz, 2.4Hz), 6.72(4H, dd, J=3.4Hz, 2.4Hz), 7.43(s), 7.46(s), 7.68(d, J=4.0Hz), 7.74(s). The hydrogens of the catechol borane were present, however, the multiple signals in the aromatic region indicate a significant amount of impurities. These could not be removed by column chromatography. The reaction was repeated but a similar ¹H NMR spectrum was obtained.

Attempted preparation of 1,2-bis(trimethylsilyl)benzene 95

The Grignard reagent of trimethylsilyl chloride was formed by the reaction of trimethylsilyl chloride (5.37cm³, 42.37mmol) with magnesium turnings (1.10g, 45.20mmol) in diethyl ether. As soon as the reaction was initiated 1,2-dibromobenzene (4.0g, 16.95mmol) in diethyl ether was added dropwise and the solution refluxed for 48h. The solution was left to cool whereupon two layers, an orange liquid and a grey solid, were formed. The solution was diluted with sat. NH_4Cl which dissolved the solid layer. The solution was extracted with

hexane and the combined organic extracts dried over MgSO_4 . The solution was filtered and the solvent removed by rotary evaporation to yield a pale orange liquid 1.9g; GCMS, **peak no.**, **m/z** (relative intensity): **hexamethyldisilane 119**, 147(100), 131(9), 117(3), 103(5), 87(4), 73(40), 66(33), 59(21), 52(15), 45(23), 43(17), 41(10), 29(10); **trimethylsilylbenzene 243**, 150(10), 135(100), 119(5), 105(14), 91(5), 79(6), 67(7), 53(17), 43(40), 29(7); **1,2-bis(trimethylsilyl)benzene 420**, 222(8), 207(100), 191(5), 175(4), 161(4), 145(4), 133(4), 119(5), 105(5), 96(40), 82(15), 73(78), 45(32); **1-bromo-2-trimethylsilylbenzene 600**, 228(4), 226(20), 211(100), 195(13), 181(10), 165(14), 152(10), 106(28), 73(14), 53(20), 43(47). The reaction was repeated allowing complete formation of trimethylsilylmagnesium chloride before the addition of 1,2-dibromobenzene but identical by-products were observed. No attempts were made to isolate the desired 1,2-bis(trimethylsilyl)benzene from the reaction mixture.

Attempted preparation of 1,2-phenylene bis(boronic acid) 97

To a 500cm³ three necked round bottomed flask equipped with a reflux condenser, nitrogen inlet and dropping funnel was placed tributyl borate (11.7g, 50.8mmol) in freshly dried ether and the solution cooled to -75°C. The Grignard of 1,2-dibromobenzene was prepared in the usual fashion to afford a red/orange solution which was transferred via catheter to the dropping funnel. The 1,2-bis(bromomagnesio)benzene was added to the tributyl borate dropwise, with rapid stirring and the temperature monitored to ensure it remained below -70°C. A red solid was formed on addition as was a white/yellow precipitate, both of which dissolved upon further addition. The orange solution was stirred at -75°C for 2h and was then allowed to warm to 10°C overnight. The reaction mixture was poured over ice cold 10% sulphuric acid before being transferred to a separating funnel, where the organic layer was separated and the aqueous layer extracted with 4 x 100cm³ portions of ether. The combined organic fractions were concentrated to yield a dark brown liquid to which 50cm³ of distilled water was added. The water was then removed as an azeotrope until no smell of butanol could be detected. The remaining solution was acidified and made up to 60cm³ by adding distilled water. Without

removing the precipitated solid, the liquid was heated until the precipitate dissolved and a heavy brown oil appeared. The hot solution was poured through a fluted filter paper and the oil further extracted with 3 x 40cm³ portions of boiling water. The aqueous fractions were concentrated by rotary evaporation to yield a white solid (m.p. 180-184°C) which was dried under vacuum. This solid was only sparingly soluble in DMSO but was soluble in D₂O. ¹H NMR spectroscopy showed broad singlets at 4.0ppm and 9.0ppm and also a small aromatic signal. Low resolution mass spectroscopy showed a peak with m⁺= 234 amu and a fragmentation pattern which indicated that we recovered 1,2-dibromobenzene.

Preparation of 1,4-phenylene bis(3,2'-bithiophene) 85

A solution of 2,2'-bithiophene (3.0g, 18.1mmol) in freshly dried THF (50cm³) was introduced to a flask equipped with a condenser, a dropping funnel and a nitrogen inlet. The solution was cooled to -60°C and a solution of 1.6M n-butyl lithium introduced (12.4cm³, 19.91mmol). The solution was then stirred at -60°C for 1h, before a solution of zinc chloride (1.0M in diethyl ether) (19.91 cm³, 19.9mmol) was added also at -60°C. The solution was then stirred allowing the temperature to rise slowly to room temperature. A solution of 1,4-dibromobenzene (2.13g, 9.05mmol) in dry THF (25cm³) containing tetrakis(triphenylphosphine) palladium (0.2g, 0.17mmol) was then added dropwise over several hours resulting in a bright yellow reaction mixture. The solution was stirred for 48 hours and the THF removed by rotary evaporation and the residue redissolved in dichloromethane (100cm³). The solution was then filtered to remove an insoluble yellow solid which was dried under vacuum. The solution was washed with distilled water and the aqueous layer extracted with dichloromethane. The combined organic fractions were then dried over MgSO₄ and the solvent removed by rotary evaporation. Spectroscopic analysis of the reaction mixture suggested unreacted 2,2'-bithiophene and 1,4-dibromobenzene. The precipitated product was very involatile and proved to be insoluble in common organic solvents however analysis by I.R spectroscopy and solid state ¹³C NMR spectroscopy in addition to low resolution mass spectroscopy and a positive DEI accurate mass result confirmed that the

desired 1,4-phenylene bis(3,2'-bithiophene) had been formed. I.R (cm^{-1}) (1637, 1494, 1457, 1427, 1413, C=C stretch), (882, 834, C-H stretch of benzene ring), (800, C-H stretch of 2,5-disubstituted thiophene), (689, C-H stretch of 2-substituted thiophene); δ_{C} 124.0, 128.1, 132.3, 136.2, 137.9, 142.0; m/z 406 (M^+ , 100%), 330 (8), 322 (13), 277 (7), 203 (50), 127 (38), 121(22), 45(32), 39(46) (Found: M^+ , 405.9979 $\text{C}_{22}\text{H}_{14}\text{S}_4$ requires 405.9978).

1,3-Phenylene-bis(1,3,2-benzodioxaborole) 30

To a dry 100 cm^3 three-necked flask fitted with a reflux condenser was added 1,3-bis(trimethylsilyl)benzene (1.1g, 5 mmol) in dry CH_2Cl_2 (15 cm^3) and the solution cooled to -78°C . A solution of BBr_3 (1.0M in CH_2Cl_2 , 10.0 cm^3 , 10 mmol) was slowly added and the solution stirred until it reached room temperature. The resulting pale yellow suspension was then refluxed under nitrogen for 24 h. The dark brown solution was cooled in an ice bath and catechol (1.g, 1mmol) added in one portion. The white suspension was then stirred at room temperature for 24 h and filtered to give a fine white powder. This product was further purified by recrystallisation from chloroform to yield 1,3-phenylene-bis(1,3,2-benzodioxaborole) 0.48g (31%), m.p. 212-214 $^\circ\text{C}$. δ_{H} 7.16 (4H, dd, $J=3.4\text{Hz}$, 2.4 Hz), 7.36 (4H, dd, $J=3.4\text{Hz}$, 2.4Hz), 7.65 (1H, t, $J=8.0\text{Hz}$), 8.30 (2H, d, $J=8\text{Hz}$), 8.87 (1H, s); m/z (relative intensity) 314 (65), 157(10), 136(10), 69(6), 62(63), 45(100). Found: C, 68.91; H 3.89. Calc for $\text{C}_{18}\text{H}_{12}\text{B}_2\text{O}_4$: C, 68.87; H, 3.85%.

1,3-Phenylene-bis(3,2'-bithiophene) 99

1,3-Phenylene bis(1,3,2-benzodioxaborole) (0.77g, 2.44mmol) was added to a dry three necked round bottomed flask, under nitrogen, equipped with a septum inlet and magnetic stirring bar. Tetrakis(triphenylphosphine) palladium (0.35g, 0.3mmol) and barium hydroxide hexahydrate (3.08g, 9.8mmol) were then added followed by 1,2-dimethoxyethane (15 cm^3)

and H₂O (3cm³). 5-Bromo-2,2'-bithiophene (1.2g, 1.65mmol) was added and the solution stirred at 85°C for 90h. The reaction mixture was allowed to cool and extracted with toluene, washed with brine and dried over MgSO₄. The solvent was then removed by rotary evaporation to yield a crude brown oil. The brown oil was absorbed onto silica gel using hexane/dichloromethane and flash column chromatography performed on silica gel using hexane as eluent to afford pure 1,3-phenylene bis(3,2'-bithiophene) as a yellow powder 0.78g (79%), m.p.>300°C. δ_{H} 7.05(2H, dd $J = 5.0, 4.0\text{Hz}$, Th-H), 7.18(2H, d, $J = 4.0\text{Hz}$, Th-H), 7.23(2H, dd $J = 4.0, 1.0\text{Hz}$, Th-H), 7.26(2H, dd $J = 5.0, 1.0\text{Hz}$, Th-H), 7.29(2H, d $J = 4.0\text{Hz}$, Th-H), 7.52(3H, s, Ph-H), 7.80(1H, s, Ph-H); δ_{C} 124.9, 125.4, 126.2, 127.8, 128.4, 135.0, 137.8, 138.1, 144.0; I.R, I.R (cm⁻¹) (1634, 1496, 1453, 1427, 1413, C=C stretch), (875, Ph-H), (790, Ph-H), (785, C-H of 2,5-substituted thiophene), (705, 2-substituted thiophene), (690, Ph-H); m/z 406 (M⁺, 100%), 330 (8), 322 (13), 277 (7), 203 (50), 127 (38), 121(22), 45(32), 39(46) (Found: M⁺, 405.9976 C₂₂H₁₄S₄ requires 405.9978).

3.6 References

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Chapter Four

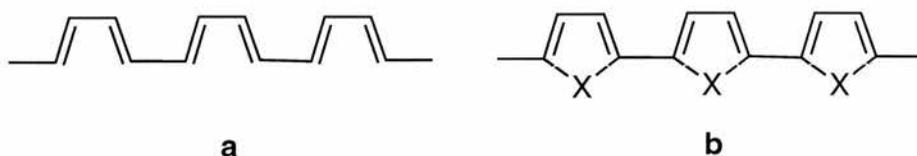
Polymerisation and Characterisation of Potential Organic Ferromagnets

Chapter 4 Polymerisation and Characterisation of Potential Organic Ferromagnets

4.0 Introduction

Conducting polymers have been extensively studied due to their multiple potential applications extending from bulk utilisation such as antistatic coatings, to sophisticated molecular devices such as organic electronic components, or selective modified electrodes and sensors. The lightness of weight, processability and resistance against corrosion of organic polymers have led, in many applications, to the replacement of metals or to the creation of materials with unique properties.

The modern era of conducting polymers began in the late 1970's when Heeger and MacDiarmid discovered that polyacetylene $(CH)_X$ synthesised by Shirakawa's method¹ could undergo a 12 orders of magnitude increase in conductivity upon charge-transfer oxidative doping.² The essential structural characteristic of conducting polymers is their conjugated π system extending over a large number of recurrent monomer units. This characteristic feature results in low-dimensional materials with a high anisotropy of conductivity which is greatest along the chain direction. Polyheterocycles **b** can be viewed as an sp^2p_X carbon chain in which the structure is analogous to that of *cis* $(CH)_X$ **a** and is stabilised by the heteroatom.



These polyheterocycles differ from polyacetylene in three main respects:

- i Their non-degenerate ground state which is related to their two limiting mesomeric forms i.e. aromatic and quinoid.

- ii High environmental stability.
- iii Structural versatility which allows the modulation of electronic and electrochemical properties.

An important step in the development of conjugated polyheterocycles occurred in 1979 when it was shown that highly conducting and homogeneous free standing films of polypyrrole could be produced by oxidative electropolymerisation of pyrrole.³ This electrochemical polymerisation was rapidly extended to other aromatic compounds including thiophene which quickly became the subject of considerable interest. This attention stemmed from the fact that polythiophene, unlike other conducting polymers, was not oxygen or moisture sensitive. The development of a stable polymer which could be reversibly doped and undoped under very rough conditions represented a very attractive goal considering the large area of potential applications.

The performance of a conducting polymer has been shown to depend on the doping level, the regularity, and the homogeneity of the chain structure. In this respect polythiophene and its derivatives appeared as good candidates exhibiting high chemical and electrochemical stability in both doped and undoped states, a reversible doping level in the range 25-50 %⁴ compared to 6-20 % for polyacetylene and polyparaphenylene⁵ and a highly regular polymeric backbone obtained by varying the nature of the dopant or the structure of the monomer.

Synthesis of Polythiophenes

Polythiophenes are essentially prepared by either chemical or electrochemical methods.

Chemical Synthesis

Thiophene, furan and selenophene have been polymerised with a variety of initiators such as sulphuric acid⁶ or Ziegler catalysts.⁷ However, experimental data has shown that with an

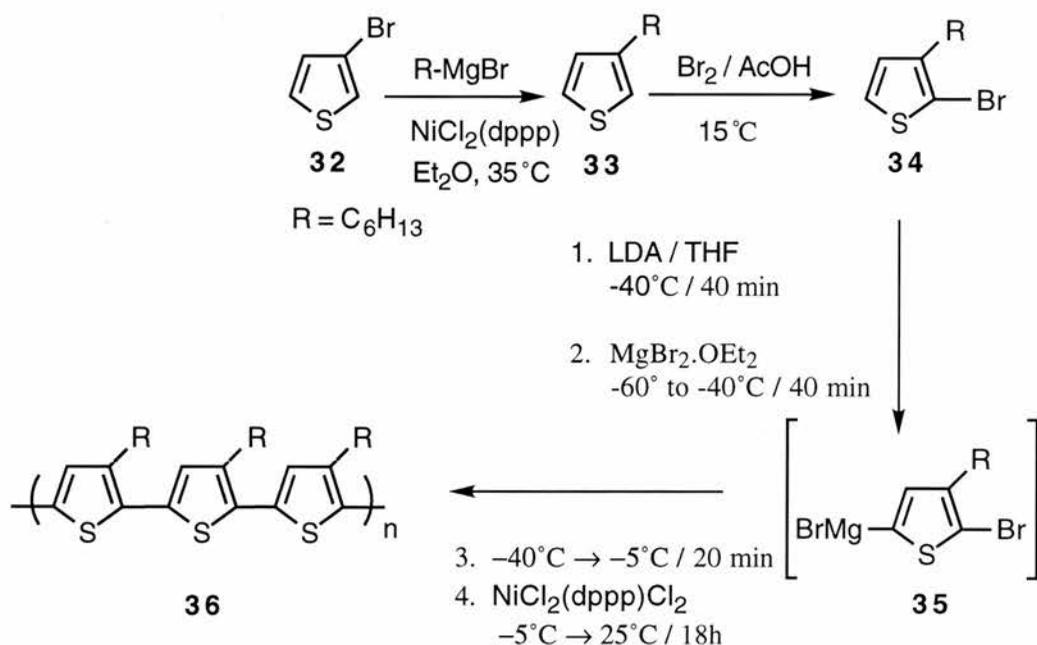
acidic promoter, polythiophene consists of alternating thiophene and tetrahydrothiophene units.⁸

The most common method of polymerising thiophenes involves the dropwise addition of monomer to a solution of iron trichloride in chloroform.⁹ This method can result in the polymer growing as an aggregate of thick particles, within which monomer, oxidant and hydrogen chloride are retained. A more uniform polymerisation can be obtained by adding, drop by drop, a solution of iron trichloride in nitromethane to a solution of the monomer in carbon tetrachloride. Using this method, solid iron trichloride (the active state of the oxidant) gradually precipitates and reacts due to its insolubility in carbon tetrachloride¹⁰, resulting in the formation of polymer in its doped state, as a fine powder. The oxidative coupling route, which can also be carried out using MoCl_5 , RuCl_3 and NOPF_6 , produces polymers with higher molecular weights than other methods (M_w up to 250000) with a relatively high degree of stereoregularity (80% head-to-tail, 20% head-to-head) for poly(3-alkylthiophenes). The resulting polymers contain residual iron(III) salts which can only be reduced in concentration by rigorous purification. Contamination of our polymers by paramagnetic iron species would contribute to the observed magnetism and therefore iron trichloride catalysed polymerisation was unsuitable for our purposes.

Many of the methods used in preparing thiophene oligomers have also been utilised in polymer formation. Thus mixtures of several thiophene oligomers have been obtained by reaction of 2-iodothiophene with copper bronze.¹¹ Quaterthiophene and sexithiophene have been synthesised by coupling α -lithiated thiophenes in the presence of cupric chloride or organoboranes.¹² The synthesis of polythiophene by oxidative coupling of bis-lithiated thiophene derivatives has also been reported.¹³ Grignard coupling of 2,5-dihalothiophenes in the presence of transition metal catalysts has been extensively employed in the synthesis of polythiophenes. Polycondensation of 2,5-dibromothiophene using 2,2'-bipyridinenickel dichloride or nickel acetylacetonate as a catalyst was reported in 1981.¹⁴ Kossmehl and Chatzitheodorou have also synthesised polyheterocycles by bringing together the appropriate

monomer and the complex AsF_5 .¹⁵ The generated polymers are generally black and insoluble and their compositions depend on the reaction time and also the AsF_5 pressure.

Various groups recognised that the ability to design and control conjugated π architectures was essential in creating new advanced materials.¹⁶ As mentioned previously the standard synthetic methods applied to prepare polyalkylthiophenes generated an array of defects at the 2,5-positions on the thiophene ring. The resultant structures contained a large number of thiophene rings which were twisted far out of conjugation due to steric interaction between alkyl chains. A structurally homogeneous head-to-tail arrangement would therefore improve the materials' electronic and optical properties. McCullough *et. al.* developed a synthetic route that allowed complete regiochemical control to produce structurally homogeneous poly(3-alkylthiophenes). The polymerisation is carried out in a one flask reaction consisting of metallation of 2-bromo-3-alkylthiophene selectively at the 5-position, followed by trapping the 2-bromo-3-alkyl-5-lithiothiophene with magnesium bromide etherate to afford **35**. Subsequent treatment of **35**, in situ with $\text{NiCl}_2(\text{dppp})$ leads to regiochemically defined head to tail coupled poly(3-alkylthiophenes), **Scheme 1**.



Scheme 1

This route to structurally homogeneous poly(3-alkylthiophenes) compares well with electrochemical methods which generally lead to the most extensively conjugated and most conductive polythiophenes.

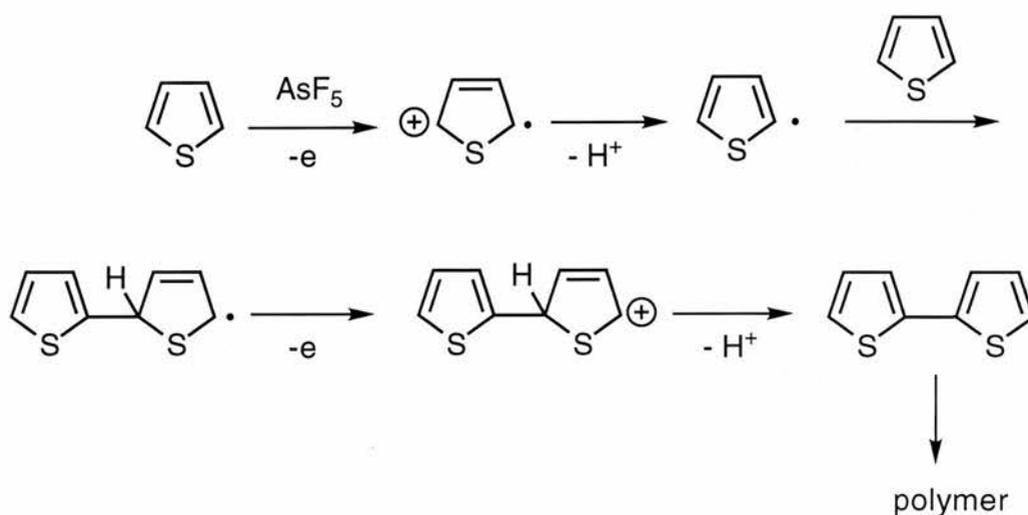
Electrochemical Synthesis

Cathodic route: In addition to the oxidative anodic electropolymerisation of the monomer which is the most convenient and most widely used method, polythiophene can also be prepared by a cathodic route involving the electroreduction of a (2-bromo-5-thienyl)triphenylnickel bromide in acetonitrile.¹⁷ This method was initially proposed for the synthesis of poly(p-phenylene) but has been extended to polythiophene.¹⁸ The major drawback of this method is that the polymer is produced in its neutral insulating form which leads rapidly to a passivation of the electrode and limits attainable film thickness to $\approx 100\text{nm}$. This technique is however applicable to electrode materials which are subject to anodic corrosion such as small band gap semiconductors.¹⁹

Anodic route: Compared to other chemical and electrochemical syntheses of conducting poly(heterocycles), the anodic electropolymerisation of the monomer presents several distinct advantages such as the absence of catalyst, direct grafting of the doped conducting polymer onto the electrode surface (which is of particular interest for many electrochemical applications) and also the ability to control the film thickness through the deposition charge. A principal advantage of the electrochemical synthesis is that impurities due to the supporting salt or secondary electrochemical reactions have never been detected. In contrast, structural defects and/or impurities are generally observed with the chemical path i.e. Ni or Mg in catalysis reactions and AsO_6 or As_3O_4 impurities in the AsF_5 synthesis.

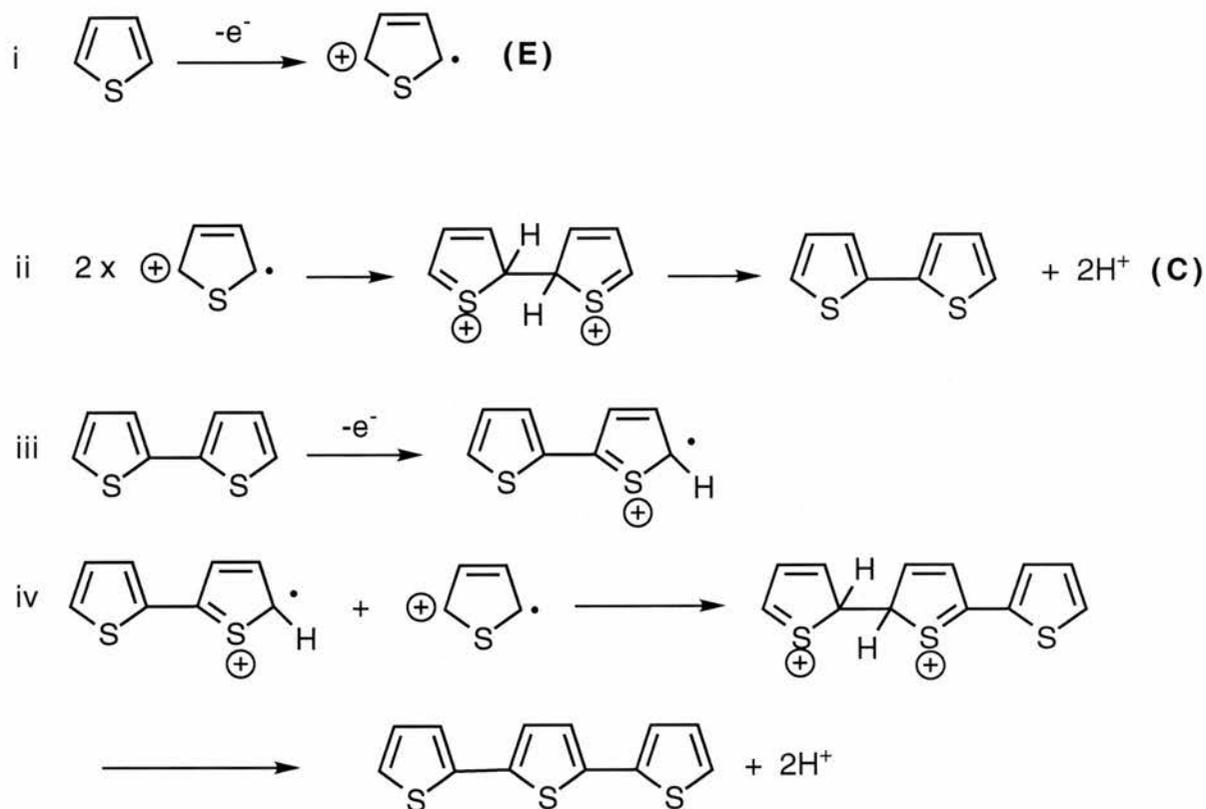
Polymerisation Mechanisms

As mentioned previously the mechanism proposed for the catalysis reaction involves the formation of a magnesium compound and the decomposition of nickel complexes to zero valent nickel.²⁰ Kossmehl and Chatzitheodorou have proposed the mechanisms shown in **Scheme 2** to account for polymerisation using the AsF_5 complex.



Scheme 2

The electrochemical formation of conducting polymers presents some similarities with the electrodeposition of metals, since it proceeds via a nucleation and phase growth mechanism. The major difference lies in the fact that the charged species which are precursors of the deposited material must be initially produced by oxidation of the neutral monomer at the anode surface. The consequence of this is that various electrochemical and chemical follow up reactions are possible making the elucidation of the electropolymerisation mechanism a very complex problem. An important aspect of the electropolymerisation of thiophene is that it proceeds by transferring 2.07-2.50 electrons per monomer unit.²¹ Oxidation of the monomer requires 2 electrons per molecule while the excess of charge corresponds to the reversible oxidation or doping of the polymer.



Scheme 3

Scheme 3 represents the mechanism proposed for the electropolymerisation of heterocycles, in this case thiophene.²² The first electrochemical step (E) consists of the oxidation of the monomer to its radical cation. Since the electron transfer reaction is faster than diffusion of the monomer from the bulk solution, it follows that a high concentration of radicals is continuously maintained near the electrode surface. The second step involves the coupling of two radicals to produce a dihydro dication dimer which leads to a dimer after loss of two protons and rearomatisation. This rearomatisation constitutes the driving force of the chemical step (C). Due to the applied potential, the dimer, which is more easily oxidised than the monomer, is converted to its radical form, and undergoes a further coupling with a monomeric radical. Electropolymerisation proceeds through successive electrochemical and chemical steps according to a general E(CE)_n scheme, where E denotes an electrochemical step, and C a chemical step. The growing oligomer chains will eventually become insoluble in the reaction

medium and precipitate onto the electrode surface. On the basis of theoretical calculations, deprotonation has been proposed as the rate-limiting step in the electropolymerisation of thiophenes.²³ This hypothesis is however contradicted by the absence of any isotope effect on the electropolymerisation rate of [2,5-²H₂] thiophene.²⁴

The exact role of oligomers in both the initial steps and the propagation of the electropolymerisation has also been a point of debate. On the basis of the delay observed between the rise of the current level and the onset of ellipsometric signals, it has been concluded that the formation of oligomers in solution precedes the polymer deposition.²⁵ Recent probe beam deflection (PBD) experiments have confirmed the oligomer mechanism.²⁶

A contrasting view has been expressed by Pletcher *et al.* who proposed that the initial step involved the absorption of thiophene on the electrode surface.²⁷ These observations appear difficult to reconcile with the hypothesis of the formation of oligomers in solution, since it is difficult to understand why, once absorbed, the monomer leaves the electrode surface to form oligomers in solution which reprecipitate onto the electrode. However NEXAFS experiments have shown that monomer absorption does occur and that the polymeric chains are well ordered up to a thickness of $10^2 - 2 \times 10^3$ Å, regardless of the polymer and the anion used. When the film thickness is increased to 0.5 - 1 µm the surface is no longer homogenous and defects appear, depending now on the polymer and the anion.

Perhaps the major argument against oligomer formation as the main reaction pathway towards the polymer, is provided by the considerable deterioration of the mechanical, electrical, electrochemical and optical properties of the polymer observed when oligomers are used as the substrate for electropolymerisation instead of the monomer.²⁸ If oligomer formation was actually a necessary step between the monomer and polymer, the same polymer should be obtained with both types of precursors.

Thus, although oligomers have been detected in the synthesis medium and extracted from polymer films²⁹, these results do not constitute an unequivocal proof that the electropolymerisation proceeds via oligomers since the observed oligomers may well result from side reactions competitive to the production of the polymer chain.

Effects of Electrosynthesis Conditions

The electropolymerisation of five membered heterocycles involves many experimental variables such as the solvent, concentration of reagents, temperature, cell geometry, nature and shape of the electrodes and applied electrical conditions. As a consequence electrosynthesis conditions determine to a large extent the structure and properties of the resulting polymer.

The solvent of the electrolytic medium exerts a strong effect on the structure and properties of polythiophene films. The solvent must have a high dielectric constant to ensure the ionic conductivity of the electrolytic medium and also good electrochemical resistance against decomposition at the potentials required to oxidise the thiophene ring ($\approx 1.4 - 2.3\text{V}$).

The most conductive polythiophenes have been prepared in rigorously anhydrous aprotic solvents of high dielectric constants and low nucleophilicity such as acetonitrile, benzonitrile, nitrobenzene and propylene carbonate. Polythiophenes are generally electrogenerated in the presence of small anions derived from strong acids such as ClO_4^- , PF_6^- , BF_4^- and AsF_6^- , associated with lithium or tetraalkylammonium cations. The nature of the anion strongly affects the morphology³⁰, and electrochemical properties.³¹

The anode material is a critical consideration since the physiochemical properties of its surface determine the nature and strength of the bond between the polymer and the electrode which affects the polymerisation process and the properties of the resulting polymer. Polythiophenes are generally grown on noble metals such as platinum and gold or on optically transparent electrodes such as tin oxide or indium tin oxide coated glass. However, polythiophenes have

also been deposited on other surfaces such as titanium or iron. Until now, the most conductive polymers have been obtained on bulk platinum, presumably because thiophene absorbs more efficiently on platinum and also because platinum presents a large number of potentially active sites thus leading to a high density of initial nucleation sites. The applied electrical conditions also exert considerable effects on the structure and properties of electrogenerated polythiophenes.

Polythiophenes have also been deposited by potentiostatic and galvanostatic conditions and also through recurrent potential sweeps or current pulses. The most homogeneous and conducting films are generally obtained by galvanostatic growth at potentials $\approx 0.5\text{V}$ more positive than the oxidation potential of the monomer. The role of this overpotential has not been fully elucidated; however, it has been suggested that it allows the instantaneous creation of a large number of initial nucleation sites, which improves the compactness and thus the conductivity of the polymer.

As mentioned previously the polymers obtained from bithiophene or terthiophene differ markedly from those obtained from thiophene. The lower conductivities observed in poly(bithiophene) and poly(terthiophene) are related to a decrease in the average length of the conjugated π system in the polymer. This is due to an increase in the stability of the corresponding radical cation, which causes a decrease in polymerisability. The increase in the stability of the radical cation of oligomeric species also explains the detrimental mechanical, optical and electrical properties experienced in polymers prepared from oligomers.

Physicochemical and Electronic Properties

Conductivity

The ultraviolet-visible absorption spectra of polythiophene and its derivatives are generally characterised by an intense broad band with a maximum which varies with the length of polymeric chain. The length of the chain is related to the structure of the monomer and the synthesis method, as shown below.

Compound	λ_{\max} (nm)
Chemical poly(2,5-thiophene) [†]	418
Chemical poly(2,4-thiophene)	240
Chemical poly(2,5-thiophene) [‡]	480
Electrochemical poly(2,5-thiophene)	480

[†] FeCl₃ catalysed reaction [‡] Mg, Ni catalysed reaction

The maximum absorption at 480 nm is characteristic of long conjugated polymeric chains. This maximum can shift to 418 nm if synthesised chemically by a method which can result in impurities and structural defects.

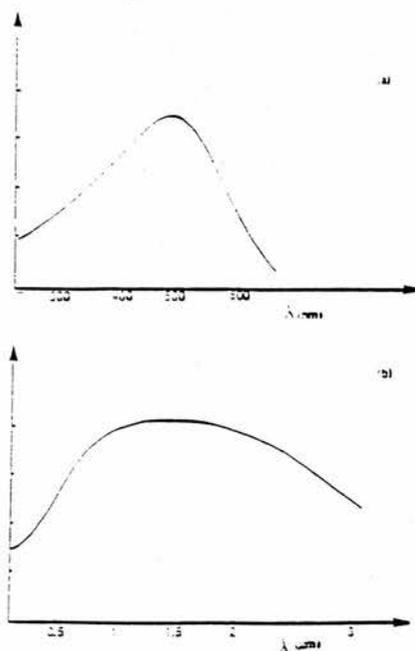


Figure 1 Visible absorption spectrum of poly(methylthiophene) (PMeT) at a Pt electrode (a) undoped state (b) doped with ClO₄⁻.

Polyheterocycles can be doped with either a donor or acceptor group. Electrochemical or chemical doping leads to an important modification of the UV absorption spectra. The 400 nm-500 nm band disappears yielding a new band extending from 650 nm-2000 nm characteristic of the appearance of free carriers.

Electron Spin Resonance Spectroscopy of Polyradicals

Spin-spin dipolar interactions in solid state polyradicals lead to a broadening of the EPR lines compared with solution spectra. In favourable cases the degree of broadening can be calculated from known or estimated spin densities and the distance the spins are apart. Exchange interactions (J) can be larger than the dipolar interactions by up to two orders of magnitude. When this occurs, the exchange narrowing of linewidths can approach those of the monomer radicals in solution. If the observed linewidth of the solid polyradical is the same as that for the polymer in a dilute solution, or in a dispersed solid, then it is reasonable to assume that the intrachain exchange interactions are important. As the temperature is lowered the dipole-dipole linewidth increases, while the exchange-narrowed linewidth is unchanged.

The metallic behaviour of polythiophenes have been confirmed by ESR spectroscopy. The g -value obtained with several polythiophene derivatives is equal to 2.0027, which is similar to the value obtained with polyacetylene (2.0028) and polypyrrole (2.0028). The deviation Δg of the g factor from the free electron spin (g_e) value arises from spin-orbit coupling of the excited state to the electronic ground states,

$$\Delta g = \lambda / D$$

where λ is the spin-orbit coupling and D is the energy difference between the ground and the excited states.

$$\lambda = 382 \text{ cm}^{-1} \text{ for p electrons of S.}$$

$$\lambda = 28 \text{ cm}^{-1} \text{ for p electrons of C.}$$

$$\lambda = 76 \text{ cm}^{-1} \text{ for p electrons of N.}$$

so the Δg value should change with the nature of the polymer studied if the heteroatom orbitals are involved in the conduction process. The Δg independence shows that the conduction for these polymers occurs along the carbon chains, **Figure 2**.

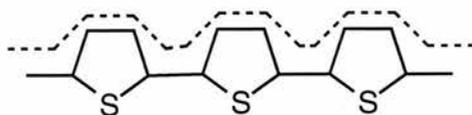
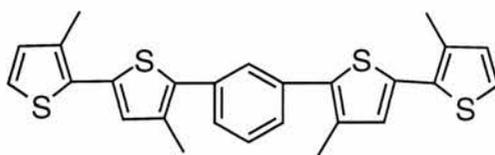


Figure 2

4.1 Investigation of the Chemical Polymerisation of 1,3-Phenylene bis(thienyl) Derivatives

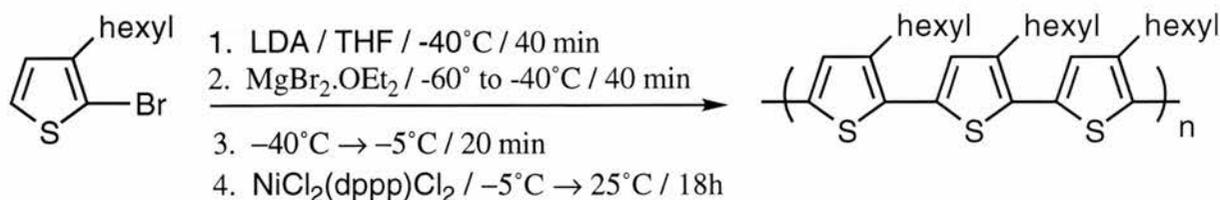
We intended to polymerise 1,3-phenylene bis(thienyl) derivatives such as **84** by chemical and electrochemical methods.



84

We dismissed the popular FeCl_3 catalysed chemical polymerisation route because of the difficulty in removing residual iron, however the method of McCullough *et al.*, detailed in chapter 2, which produces structurally homogenous head-to-tail coupled thiophenes was considered.

The problems encountered in forming 3,4'-dialkyl-2,2'-bithiophenes *via* a similar route to McCullough prompted us to attempt the polymerisation of 3-hexylthiophene before sacrificing 1,3-phenylene bis (5,3'-dimethyl-3,2'-bithiophene), **Scheme 4**.

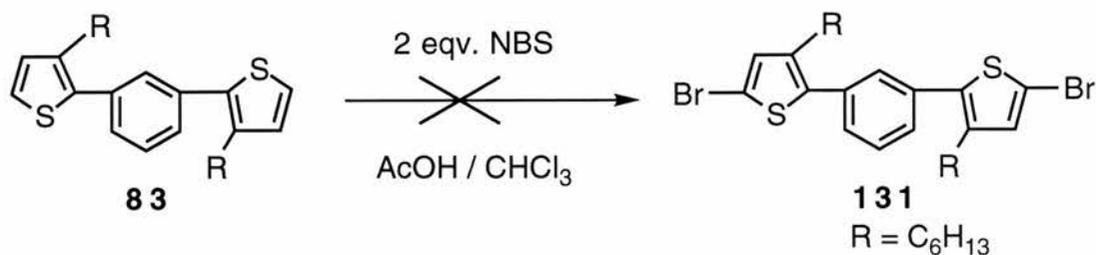


Scheme 4

The reaction yielded only starting materials and the reduction product 3-hexylthiophene. ^1H NMR spectroscopy of poly(3-hexylthiophene) should display a singlet at 6.98ppm however the doublet signals of 2-bromo-3-hexylthiophene were clearly visible.

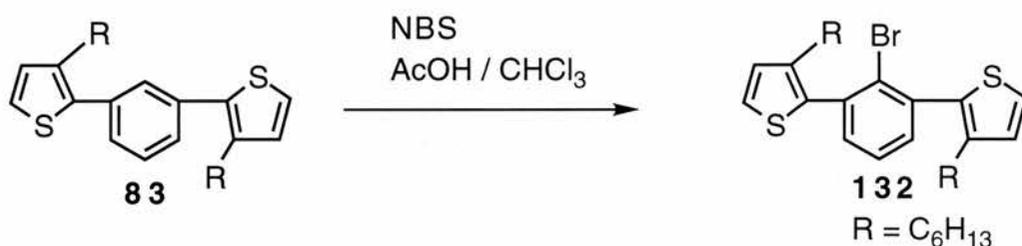
The reaction was repeated using n-butyl lithium rather than lithium diisopropylamide as the metallating agent. The ^1H NMR spectrum was more complex but displayed a triplet at 2.75 ppm which corresponds to the α -protons of a hexyl chain resulting from a head-to-tail coupling. GCMS analysis suggested the formation of 5-butyl or 2-butyl- 3-hexylthiophene and 2,5-dibutyl-3-hexylthiophene in addition to 3-hexylthiophene, 2-bromo-3-hexylthiophene and, ironically, dihexylbithiophene, which the ^1H NMR information showed was present as the head-to-tail regioisomer. We may possibly have formed H-T poly(3-hexylthiophene) which would not be detected by GCMS. Due to the large number of side products and low yields observed when sterically hindered alkyl groups are attached to the thiophene ring, we felt this method of polymerisation would not be satisfactory for our requirements.

Another problem associated with the potential McCullough polymerisation of 1,3-phenylene bis(5,3'-dialkyl-3,2'-bithiophene) involved the bromination reaction to produce the reaction precursor. On investigating the synthesis of 1,3-phenylene bis(5,3'-dialkyl-3,2'-bithiophene) from 1,3-phenylene bis(5-hexyl-2-thiophene) we attempted the reaction shown in **Scheme 5**.



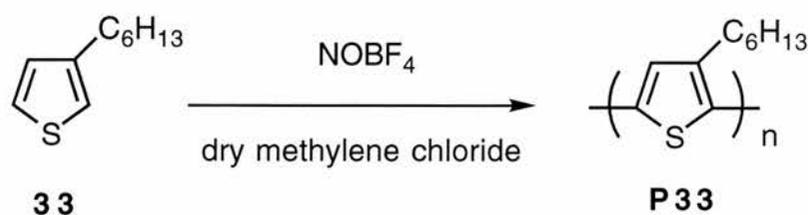
Scheme 5

On analysing the reaction product by ^1H NMR spectroscopy we found that substitution actually occurred at the 2-position of the benzene ring despite the steric hindrance provided by the hexyl group, **Scheme 6**. This is easily recognised by ^1H NMR spectroscopy due to the disappearance of the signal at 7.5 ppm.



Scheme 6

We were then forced to consider oxidative coupling methods which, unlike the McCullough route, yield the polymers in their doped state. Again 3-hexylthiophene was used as a model as we attempted a polymerisation using nitrosonium tetrafluoroborate (NOBF_4) in dry methylene chloride, **Scheme 7**.

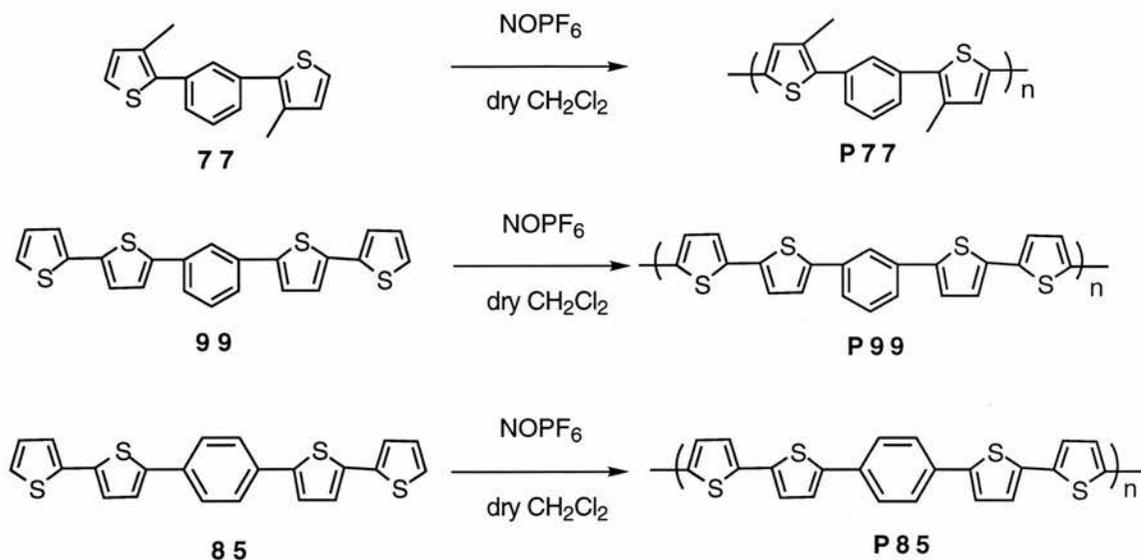


Scheme 7

A solution of 3-hexylthiophene in methylene chloride was added dropwise to a solution of the oxidant under a nitrogen atmosphere. The solution rapidly changed from clear to orange, red then blue/black. After stirring for 18h the solution was poured into methanol (500cm³) however no precipitate was formed. The methanol was removed by rotary evaporation to yield a black solid which was exhaustively washed with methanol and purified by soxhlet extraction with methanol followed by chloroform, to yield a thick black powder. We attempted to dedope the polymer by stirring in ammonium hydroxide solution but the powder remained insoluble in common organic solvents preventing characterisation.

We also attempted to polymerise 3-methylthiophene (0.4g) using 2.5 equivalents of nitrosonium hexafluorophosphate (NOPF₆). Identical colour changes were observed; however, after stirring for 15 hours a black precipitate was isolated by filtration (0.8g). After washing with methanol, and purification by soxhlet extraction, the mass of the recovered materials decreased to 0.16g. Stirring of the insoluble powder in hydrazine hexahydrate for 72h failed to yield the neutral polymer.

The fact that we could not dedope the resultant powders consequently prevented us from ensuring that the correct products had been formed. The NOPF₆ catalysed reactions seemed most encouraging due to the fact that a precipitate was formed and the colour change reflected increased conjugation. However, the small amounts of recovered material corresponded to yields of approximately 25-30%. We therefore carried out polymerisation reactions on the most abundant monomers available, as shown in **Scheme 8**.

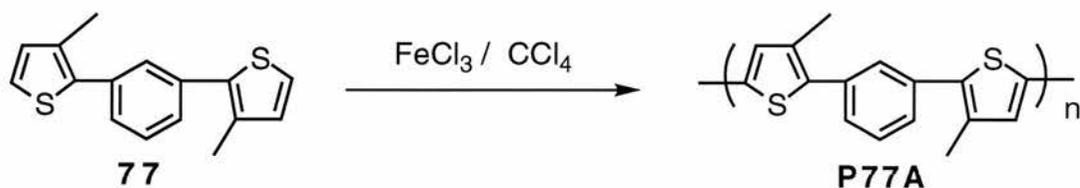


Scheme 8

These reactions were carried out and the polymers purified in a similar manner to those described previously and the resultant black polymers stored for magnetic characterisation.

Additional Polymerisations

In a separate investigation we successfully synthesised poly(3-hexylthiophene) using iron trichloride and attempted to polymerise 1,3-phenylene bis (5-methyl-2-thiophene) in a similar fashion, **Scheme 9**.

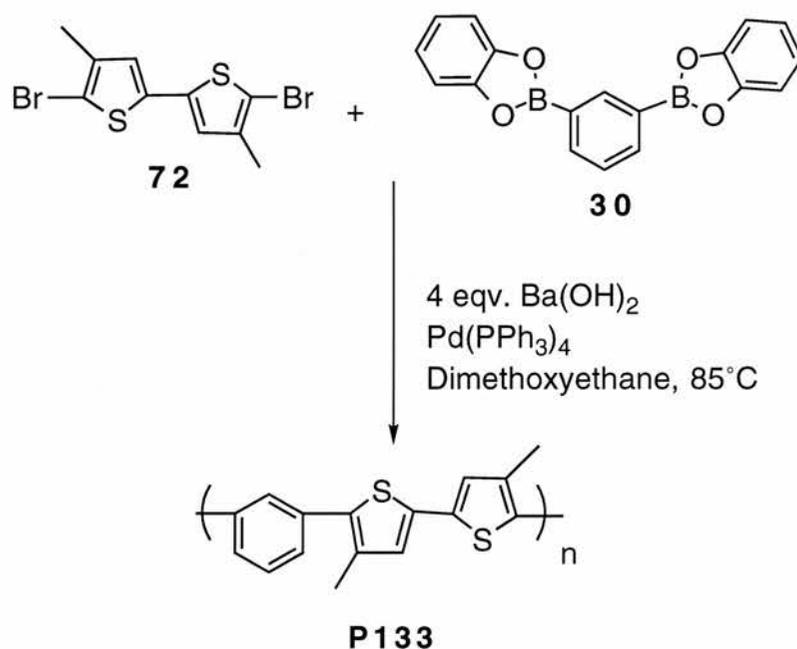


Scheme 9

The reaction produced a thick brown/green powder which was washed with methanol, CHCl₃, diethyl ether and distilled water and stirred in aqueous NH₄OH for 2 hours where it turned orange. The orange powder remained insoluble in common organic solvents and was doped

with iodine vapour over 72h to yield a black powder which is presumably the polymer in its doped state. Magnetic characterisation of this material will, of course, be affected by the presence of iron salts.

Another interesting route to similar polymers could be the Suzuki polymerisation of dibromo-dialkylbithiophene with 1,3-phenylene bis(1,3,2-benzodioxaborole) as shown in **Scheme 10**.



Scheme 10

Due to a lack of 5,5'-dibromo-4,4'-dimethyl-2,2'-bithiophene, which is light sensitive, we were unable to perform this reaction.

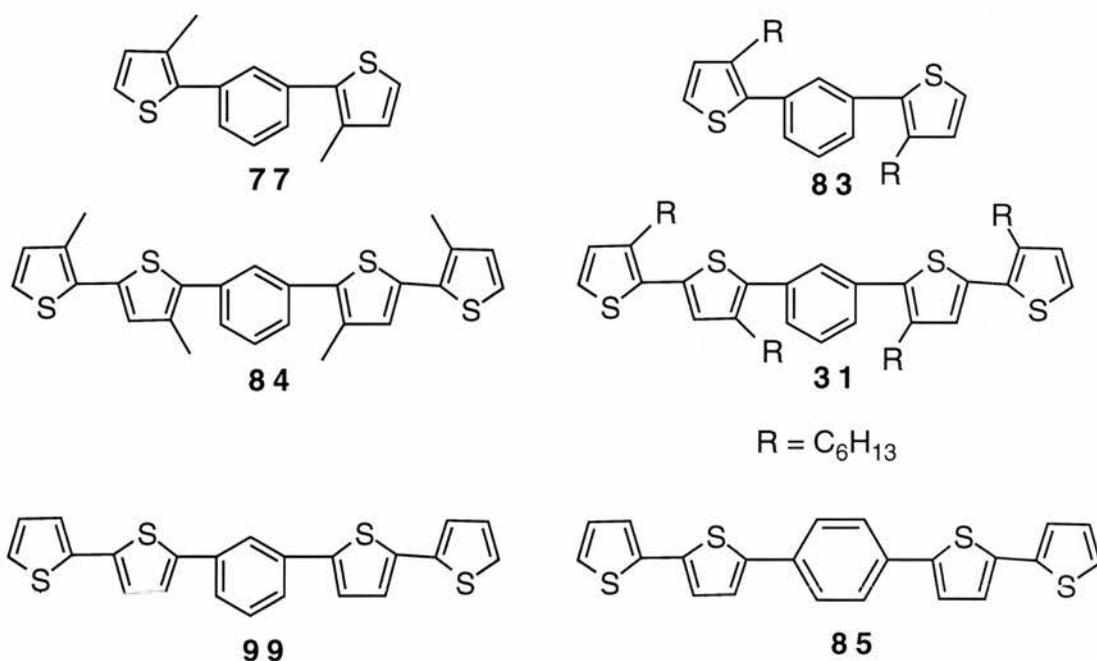
Conclusions of Chemical Polymerisation

The most common method of thiophene polymerisation, utilising iron trichloride, was eliminated due to the contamination of polymers by paramagnetic iron species. The McCullough polymerisation route was also dismissed due to poor yields of product and a difficulty in forming the reaction precursors. We chose oxidative polymerisation using NOPF₆ to produce polymers of compounds **77**, **85** and **99**. This method seemed to be the most

promising but involved exhaustive purification and afforded poor yields of polymers in their doped state. A consequence of this was that the recovered polymers could not be fully characterised nor could their structure be deduced. The polymers will be examined by variable temperature ESR spectroscopy and submitted for magnetic characterisation. An electrochemical study of monomers **31**, **77**, **83**, **84**, **85**, and **99** will now be described.

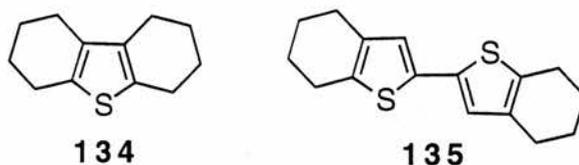
4.2 Electrochemical Characterisation and Polymerisation of 1,3-Phenylene bis(thienyl) Derivatives

Our investigation into the chemical polymerisation of 1,3-phenylene bis(thienyl) highlighted the deficiencies of such methods. This prompted a study of the electrochemical properties of our monomers **31**, **77**, **83**, **84**, **85**, and **99** and the resultant polymers **P31**, **P77**, **P83**, **P84**, **P85**, and **P99**.



Cyclic voltammetry has been utilised in the study of various poly(thiophenes) and oligomers. For example, Bäuerle's study of end-capped oligothiophenes allowed the characterisation of oligomers in various oxidation states.³² He determined that cations of **134** and **135** were not

stable and undergo follow up reactions resulting in completely irreversible cyclic voltammograms.



Bäuerle found that with compound 136 known as EC4T, stable cations and dications could be created.

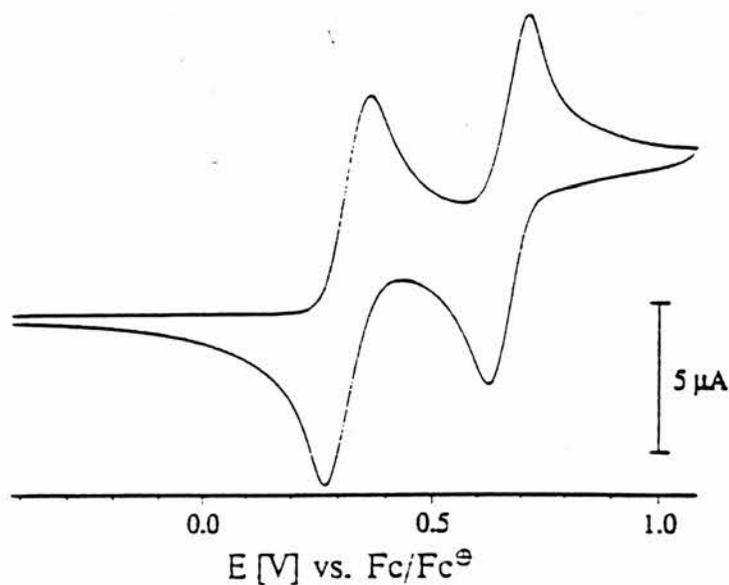
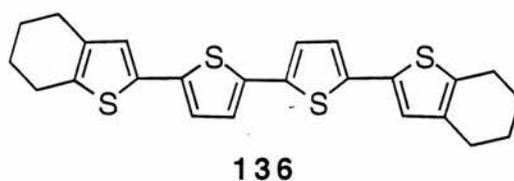


Figure 3 Cyclic voltammogram of EC4T in CH₂Cl₂ / TBAP 0.1 M at a platinum disk electrode ; Reference electrode Ag / AgCl internally calibrated vs. Fc / Fc⁺; Sweep rate 100 mVs⁻¹

Indeed, as they increased the π -system of the oligomers the oxidation potentials of both the mono and dication were shifted to lower values. The energy difference between the first and second oxidation potential gradually decreased as the chain length of the π -system increased until the gap vanished completely as the ideal infinite chain length was approached. A study of the oxidation potentials and UV-vis absorption spectra of further oligomers allowed the extrapolation of oligomer data to predict the properties of an ideal poly(thiophene) devoid of defects and interruptions of the conjugated backbone in the bulk material.

The extrapolation of both data sets to the intercept ($1/n=0$) reveals that exactly at this limiting point the regression lines for both mono and dicationic species intersect, **Figure 4**. This result clearly implies that in the case of very long chains a second electron can simultaneously be removed at the same energetic level as long as the defect can reside sufficiently separated on the conjugated π system without any interaction.

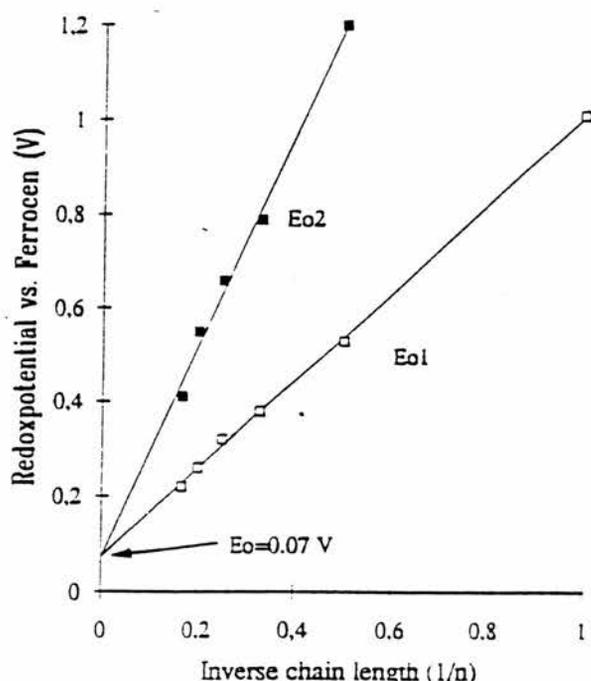
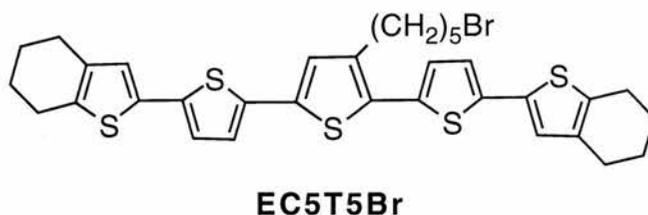


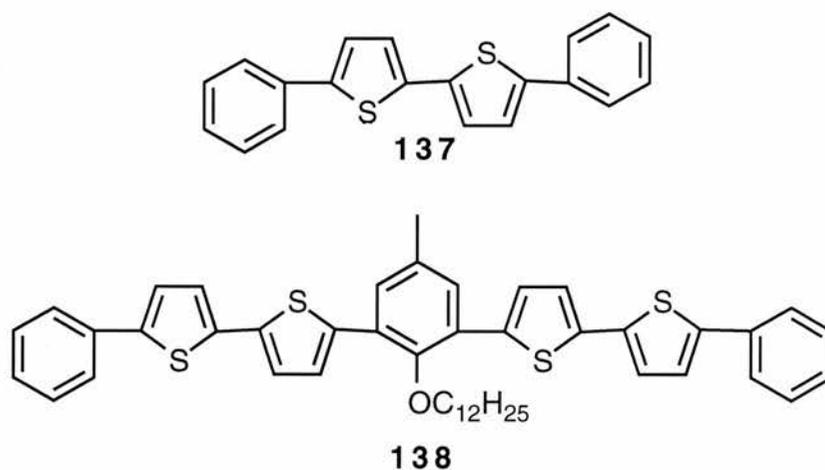
Figure 4 Correlation of the first and second oxidation potential of the end-capped oligothiophenes **EC1T-EC6T** versus the inverse chain length.

Bäuerle also investigated the effect of introducing alkyl substituents by synthesising EC5T5Br.³³



Bäuerle observed that the steric interaction of the alkyl chain with the thiophene rings caused a distortion of the conjugated π system. This effect dominated over the electron donating properties of the substituent and the ensuing reduction in the overlap of the corresponding π orbitals resulted in a lower electron density in EC5T5Br, and hence, in an increased first oxidation potential. Upon oxidation, the twisted neutral π system was planarised to a cationic quinoidal structure, analogous to the well known polarons in the corresponding polymers.³⁴ Consequently, the inductive effect of the alkyl chain lowers the corresponding redox potential in the second oxidation step.

In a similar study Janssen³⁵ showed that **137** undergoes two chemically reversible, one-electron oxidation waves with peak-to-peak separations between oxidation potential E_p^a and reduction potential E_p^c of 70-100 mv. These relate to the formation of the cation radical **137^{•+}** and the dication **137²⁺**, **Figure 5 (top)**, and contrast with Bäuerle's conclusion that cations of bithiophene units were unstable.



The CV of compound **138**, **Figure 5 (bottom)**, reveals two partially resolved one electron oxidation waves centred at around 1.08V. When compared to the first redox wave of **137** (1.10V) it suggests that the wave represents the process $\mathbf{138} \rightarrow \mathbf{138}^{\bullet+} \rightarrow \mathbf{138}^{2\bullet2+}$. In contrast to **137**, compound **138** cannot be oxidised reversibly beyond the di(radical cation) state. The only possible explanation of why $\mathbf{138}^{4+}$ cannot be formed could be due to the coulombic overload involved in producing a tetracation on a relatively small molecule.

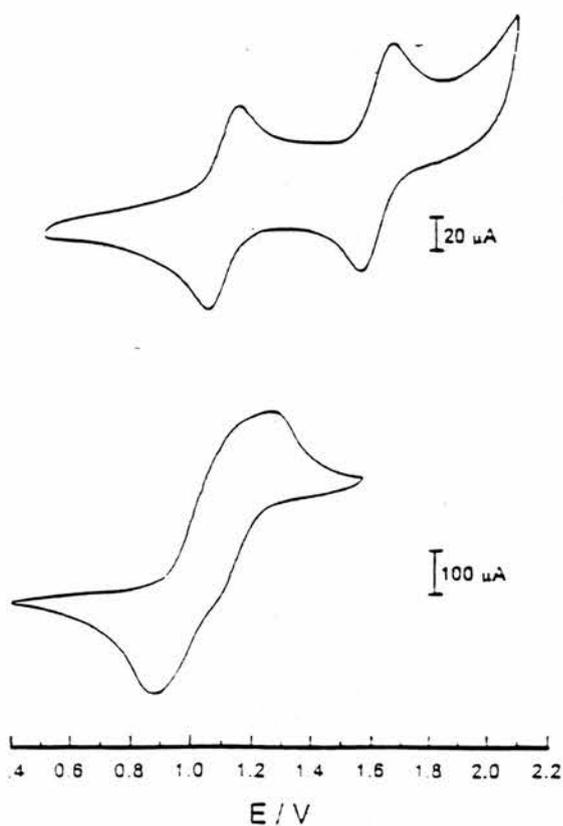


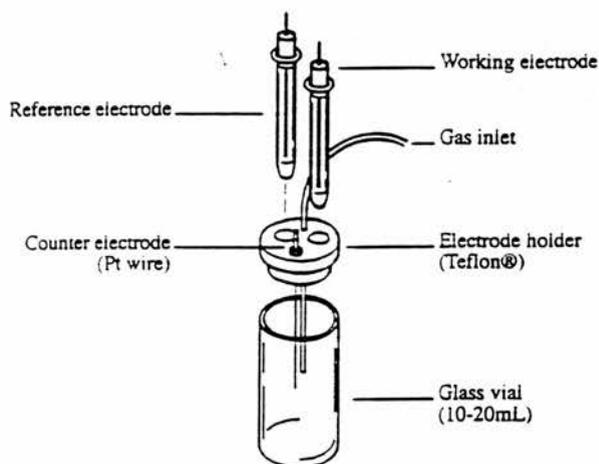
Figure 5 Cyclic voltammogram of **137 (top)** and **138 (bottom)** at 295K in dichloromethane / TBAP 0.1 M; scan rate 100 mVs⁻¹; Potential vs. SCE calibrated against Fc / Fc⁺.

Results

Typically, with the majority of electrochemical work, our system employed three electrodes:

(a) the working electrode, in our case a polished platinum electrode, which defines the interface under study (b) a reference electrode, which maintains a constant reference potential. We chose a commercial saturated calomel electrode (c) A counter electrode which supplies the current. A simple platinum wire (99.99% Aldrich) was used as the counter electrode.

Our electrochemical analysis was carried out in a simple glass voltammetry cell containing a Teflon[®] top which holds the three electrodes and the argon inlet tube, **Figure 6**.



Basic electrochemical cell set-up.

Figure 6

After scrupulously cleaning the cell and electrodes, the monomer or polymer was dissolved in solvent, typically freshly distilled acetonitrile and added to the cell. The supporting electrolyte, tetrabutylammonium hexafluorophosphate (TBAP) was added and the solution degassed by bubbling argon through the solution for a few minutes. Degassing serves to eliminate any

dissolved oxygen from the solution which is reduced to either the hydroxide or peroxide ion. The cyclic voltammograms were then recorded and interfaced with a personal computer.

We shall now describe the observed electrochemical behaviour of **P77-P99** and attempt to rationalise the data in the summary which follows.

1,3-Phenylene bis(5-methyl-2-thiophene) 77 and 1,3-Phenylene-bis(5-hexyl-2-thiophene) 83

Figure 7 shows the CV for 1,3-phenylene bis(5-methyl-2-thiophene) **77** which is oxidised at ≈ 1.50 V. Repetitive scanning to 1.5 V results in the deposition of a yellow film which becomes darker as polymer growth continues. The polymer has a lower oxidation potential than the monomer and we observe the evolution of a peak at 1.3 V corresponding to oxidation of the polymer.

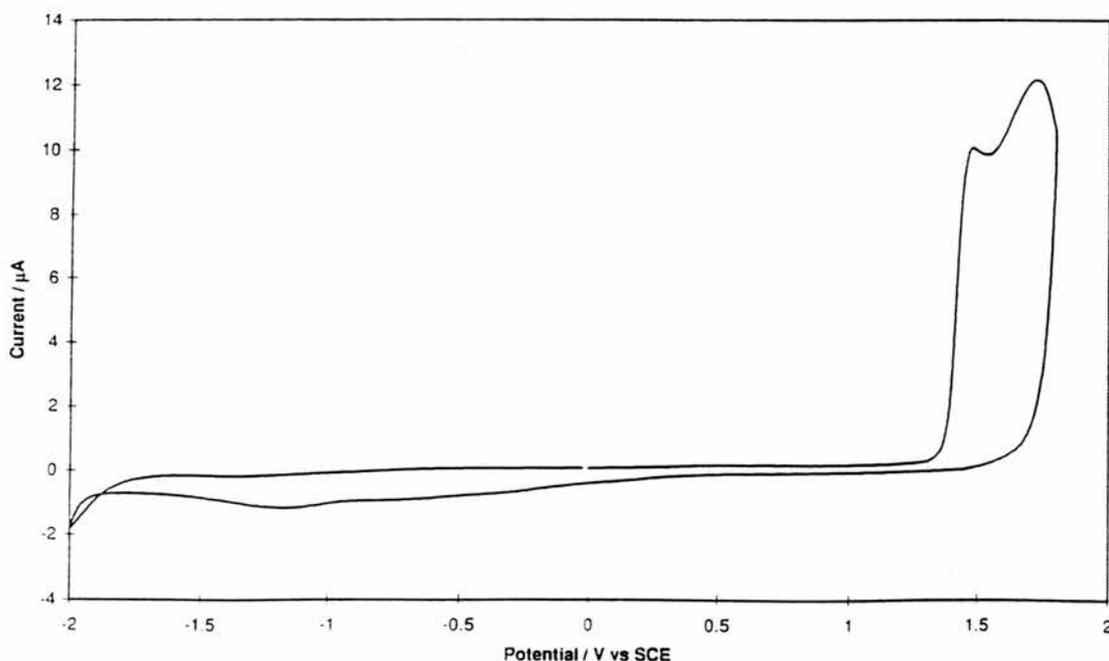


Figure 7 Cyclic voltammogram (100 mVs^{-1}) of **77** in MeCN / 0.1 M TBAP at a platinum electrode vs. SCE.

P77 was also produced by galvanostatic growth, **Figure 8**. This involves electrolysis of the monomer at constant current, while the dependence of the electrode potential with time is

recorded. As can be seen, the potential moves to a value characteristic of oxidation of the monomer (≈ 1.50 V). Eventually, as the concentration of the monomer at the electrode surface decreases, the flux of monomer to the surface is insufficient to accept all of the electrons being forced across the electrode/solution interface and we see a sharp rise to a potential where other electrode processes can take place. It should be noted that we do not observe a minimum in potential as we would for polythiophene. This minimum is due to the difficulty of growing a single layer of polymer at the electrode surface. Growth becomes easier as more layers are deposited.

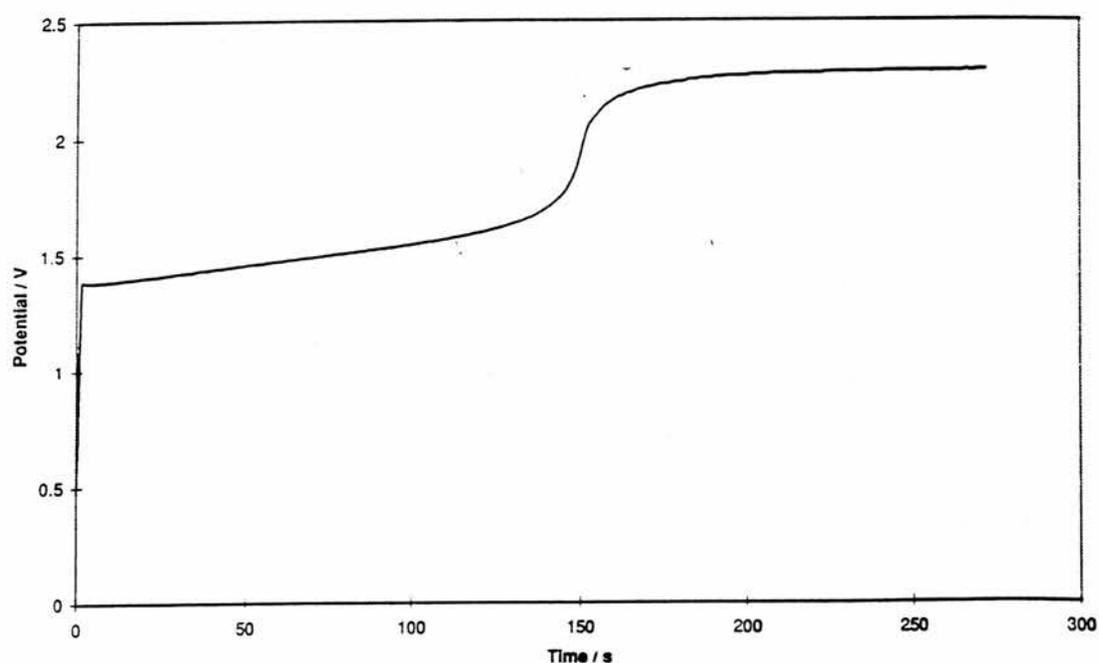


Figure 8 Galvanostatic growth of **77** at a Pt electrode in MeCN / 0.1 M TBAP solution; $I = 1.6 \mu\text{A}$, $t = 150$ s.

In all polymerisation experiments the working electrode was removed to reveal a black film of polymer. **P77**, for example, was transferred to monomer free solution and oxidised at 1.275 V, **Figure 9**, compared to 0.77 V vs. SCE for poly(3-methylthiophene). A literature search revealed that Reynolds and co-workers had reported the synthesis and electrochemical

characterisation of poly(1,4-dimethoxy-2,5-bis(thienyl)phenylene).³⁶ Not surprisingly, the E_p^a of this polymer is much lower than **P77** or **P83**.

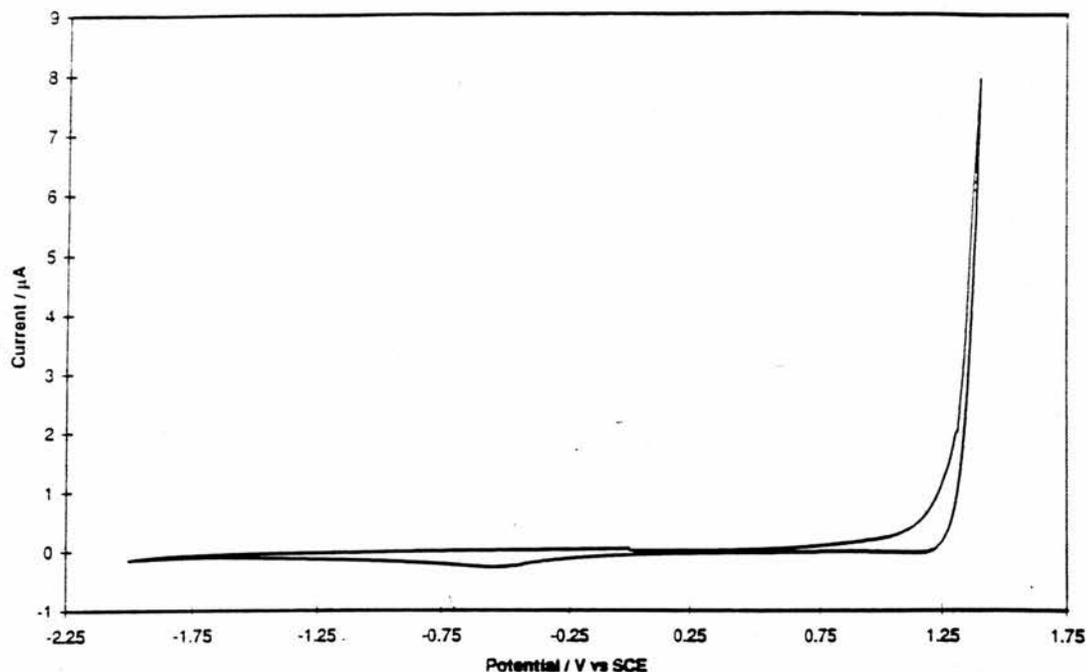


Figure 9 Cyclic voltammogram (100 mVs^{-1}) of **P77** in MeCN / 0.1 M TBAP at a platinum electrode vs. SCE.

Polymer films of **77** were also grown on an indium-tin oxide coated glass electrode, producing a blue/black film of doped polymer which could be reduced to its neutral state by reversing the potential. UV-vis spectroscopy of the orange neutral polymer and the black doped polymer revealed the formation of polarons in going from the neutral to the oxidised state. This will be explained in greater detail later in this chapter.

The CV of 1,3-phenylene bis(5-hexyl-2-thiophene) **83**, **Figure 10**, was similar to that of **P77**, with oxidation of the monomer **83** occurring at 1.5 V. The polymer **P83** was grown at a Pt electrode by recurrent potential sweeps and the electrode transferred to monomer-free MeCN/TBAP solution. The polymer CV showed what could possibly be two polymer waves with $E_p^{a1} = 1.2 \text{ V}$ and $E_p^{a2} = 1.5 \text{ V}$.

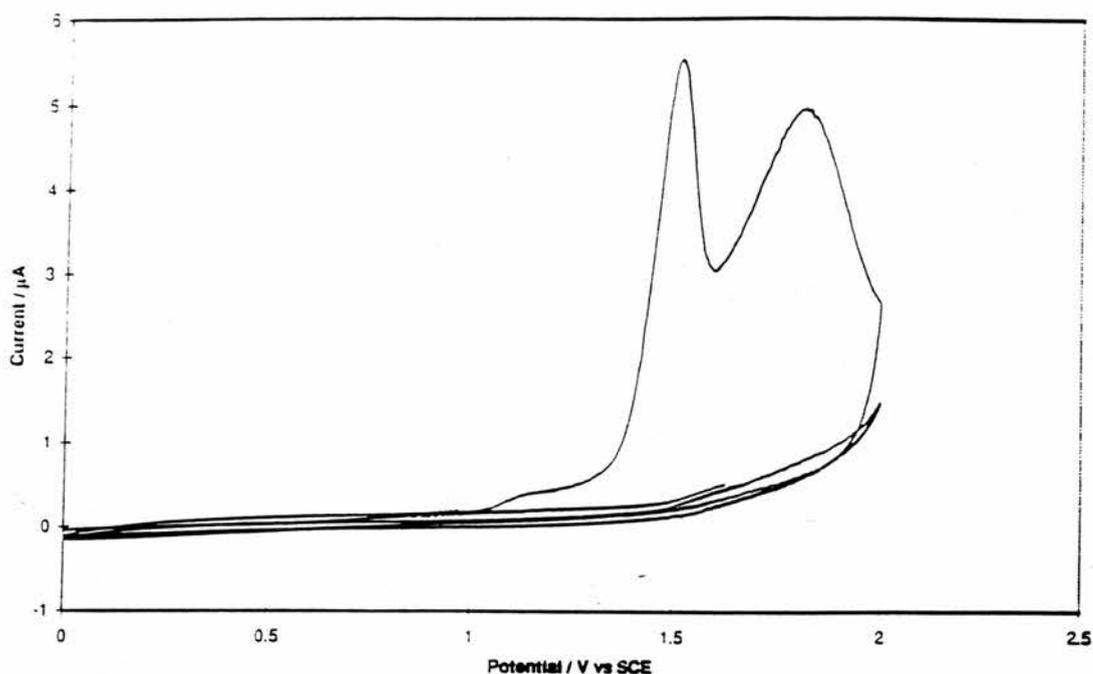


Figure 10 Cyclic voltammogram (100 mVs^{-1}) of **P83** in MeCN / 0.1 M TBAP at a platinum electrode vs. SCE.

Although **P83** was also formed by potentiostatic growth at a Pt electrode at 1.2 V, where a constant current of 200 nA was observed, the poor solubility of monomer **83** in the electrolyte prevented the growth of polymer films on ITO coated electrodes.

1,3-Phenylene bis(5,3-dimethyl-3,2'-bithiophene) 84 and 1,3-Phenylene bis(5,3-dihexyl-3,2'-bithiophene) 31.

The CV of monomer **84** is shown in **Figure 11**. On scanning to 2.0 V we observed two reversible oxidation waves at 1.0 V and 1.37 V and a prominent spike at 1.90 V, probably due to over oxidation of the adsorbed monomer. As shown previously, Janssen observed dication formation in compound **137** at a much higher potential of 1.66 V. We therefore explain the monomer CV in terms of a $\mathbf{84} \rightarrow \mathbf{84}^{\bullet+} \rightarrow \mathbf{84}^{2+}$ process rather than bipolaron formation to

produce 84^{2+} . However, it is harder to explain why the two waves are far from the ideal lineshape, unless the compound is adsorbing onto the electrode.

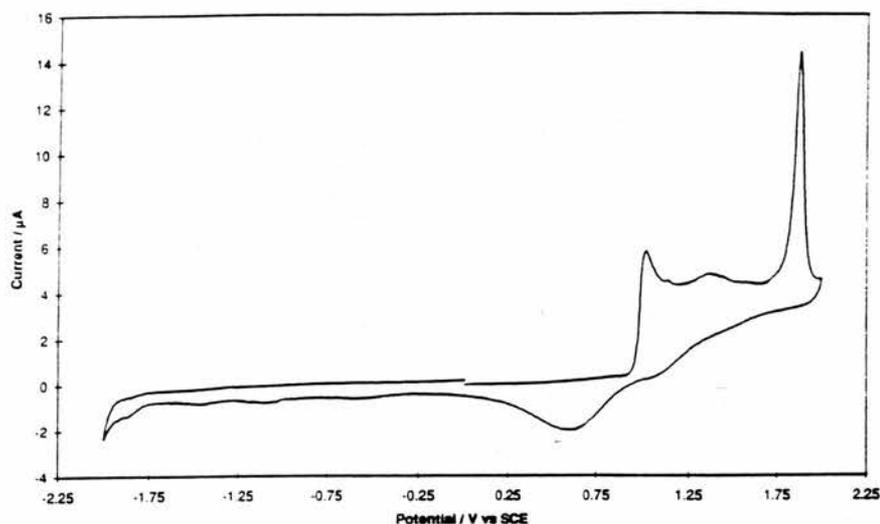
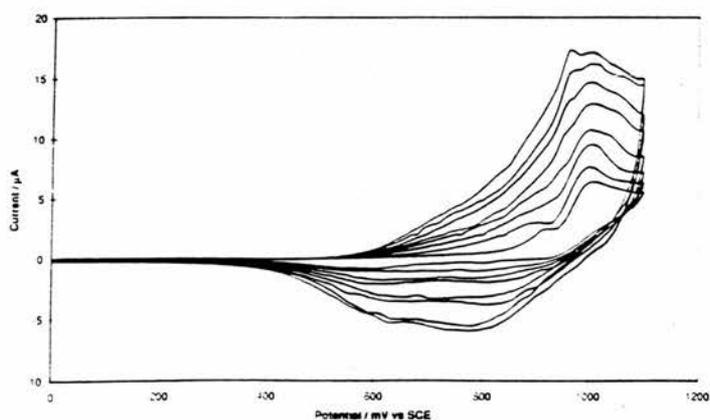


Figure 11 Cyclic voltammogram (100 mVs^{-1}) of **84** in MeCN / 0.1 M TBAP at a platinum electrode vs. SCE.

The polymerisation of **84** was achieved by recurrent potential sweeps to 1.1 V, **Figure 12**, and also by galvanostatic growth and potentiostatic methods.



Each cycle to 1.1V results in an increase in the observed current

Figure 12 Recurrent potential sweeps (100 mVs^{-1}) of **84** to 1.1V in MeCN / 0.1 M TBAP at a platinum electrode vs. SCE;

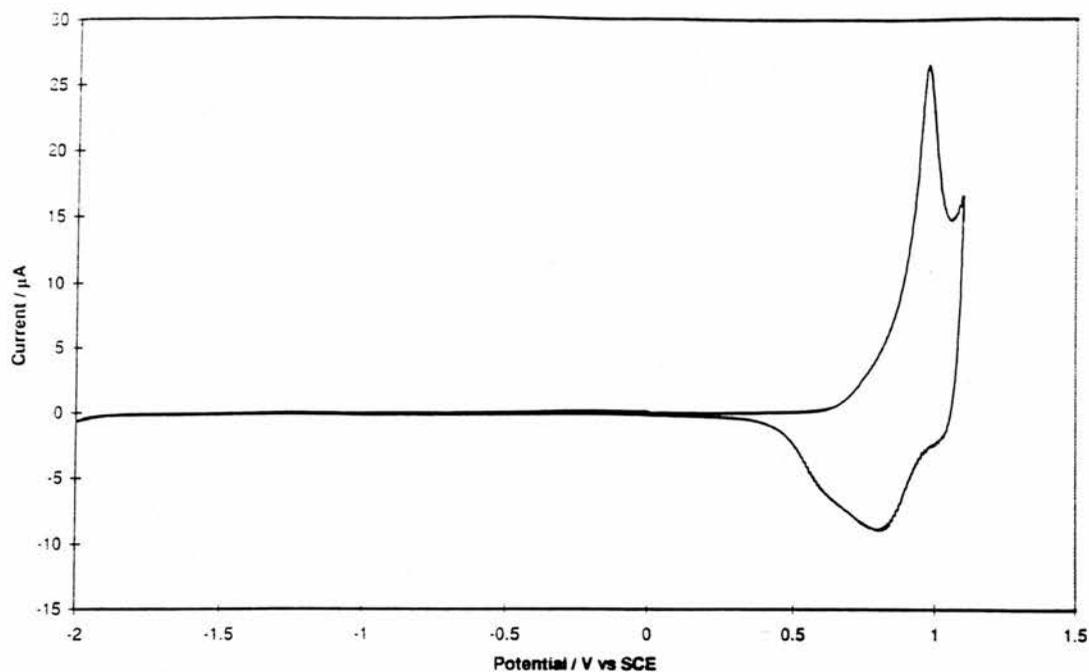


Figure 13 Cyclic voltammogram (100 mVs^{-1}) of **P84** in MeCN / 0.1 M TBAP at a platinum electrode vs. SCE.

The polymer coated working electrode was transferred to monomer-free MeCN/TBAP solution. The CV of **P84**, **Figure 13**, revealed a single reversible wave with $E_p^a = 0.95 \text{ V}$. This contrasts with Bäuerle's EC4T compound which shows two reversible waves corresponding to radical cation ($E_p^{a1} = 0.32 \text{ V vs Fc}$, 0.82 V vs SCE) and dication formation ($E_p^{a2} = 0.66 \text{ V vs Fc}$, 1.16 V vs SCE). In our polymer we would expect the energy difference between the first and second potentials to vanish as the chain length of the π system increases (see **Figure 4**). Therefore the absence of a second oxidation peak in **P84** and **P31**, even upon scanning to 1.8V, does not necessarily mean that bipolaron formation does not occur, since the alkyl substituents in **P84** and **P31** could stabilise the bipolaron to such an extent that the second oxidation potential occurs at a similar potential to that of E_p^{a1} .

The E_p^a value observed for **P84** is significantly higher (130mV) than the E_p^{a1} value viewed by Bäuerle. This is unusual considering the extended conjugation which should be present in **P84** and **P31**, but can be explained by considering the planarity of the backbone in EC4T and **P84**. In **P84** the alkyl substituents cause the polymer backbone to twist out of

conjugation. This reduction in electron density along the polymer chain results in a higher first oxidation potential when compared to unsubstituted **EC4T**.

Polymer growth of **P84** on ITO coated glass electrodes was extremely efficient and allowed the formation of thick layers of doped polymer. UV-vis absorption spectra of **P84** in both the doped and undoped states were obtained, **Figure 14**.

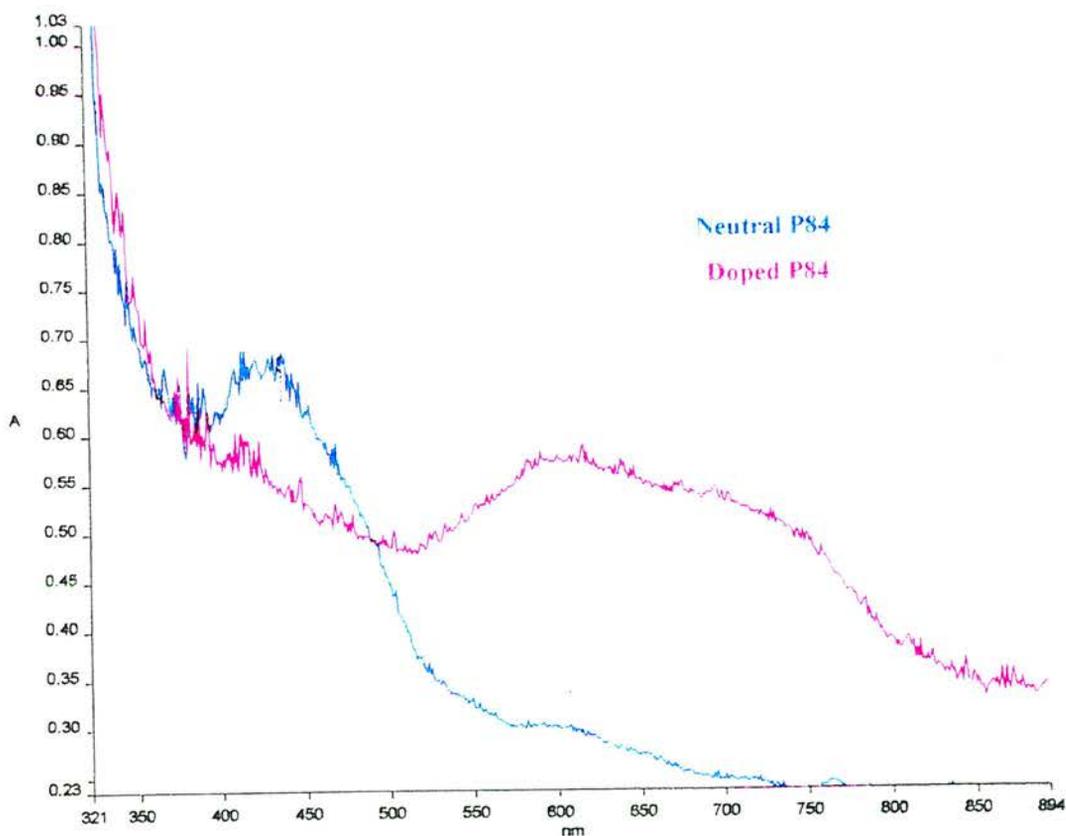


Figure 14 UV-vis spectroscopy of (a) neutral **P84** and (b) doped **P84** on ITO coated glass electrodes, produced by galvanostatic methods.

Curve **a** shows the absorption spectra of **P84** in its undoped state and curve **b** the polymer in its doped state. The λ_{max} 440 nm band ($\pi \rightarrow \pi^*$ transition) shows somewhat less conjugation than electrochemically polymerised poly(3-methylthiophene) ($\lambda_{\text{max}} = 480$ nm), but greater than quaterthiophene ($\lambda_{\text{max}} = 337$ nm).

As mentioned previously, doping of conjugated organic polymers leads to an important modification of the UV-vis absorption spectrum. The 400-500 nm band should disappear to yield broad bands between 600-2000 nm. For **P84** we observed a decrease in the intensity of the absorption at 440 nm and the emergence of two partially resolved transitions, a strong absorption at 610 nm and a shoulder at 720 nm. These new bands are a result of electronic transitions between intra-gap states which arise upon polaron and bipolaron formation. We can compare our results with the absorption spectra of EC4T which changed from a single $\pi \rightarrow \pi^*$ transition at 408 nm to three strong transitions in the visible and near IR ($\lambda_1 = 1180$ nm, $\lambda_2 = 910$ nm and $\lambda_3 = 690$ nm) associated with polaron formation. On applying more positive potentials, dication EC4T²⁺ was formed, resulting in the successive formation of two strong bands $\lambda_4 = 775$ nm and $\lambda_5 = 600$ nm. The measurements were made at 0.0 V, 1.0 V and 1.7 V, vs. ferrocene respectively, which contradicts their own earlier claims that the dication was formed at 0.66 V vs Fc. To conclude, the spectrum of oxidised **P84** may indicate the presence of both polarons (broad band centred at 610 nm) and bipolarons (shoulder at 720 nm).

The electrochemical behaviour of monomer **31** proved to be very similar to that observed for **84** exhibiting an oxidation peak at 1.1 V and a second faint oxidation peak at 1.45 V. The second oxidation peak is more pronounced when the CV is run in dichloromethane rather than acetonitrile.

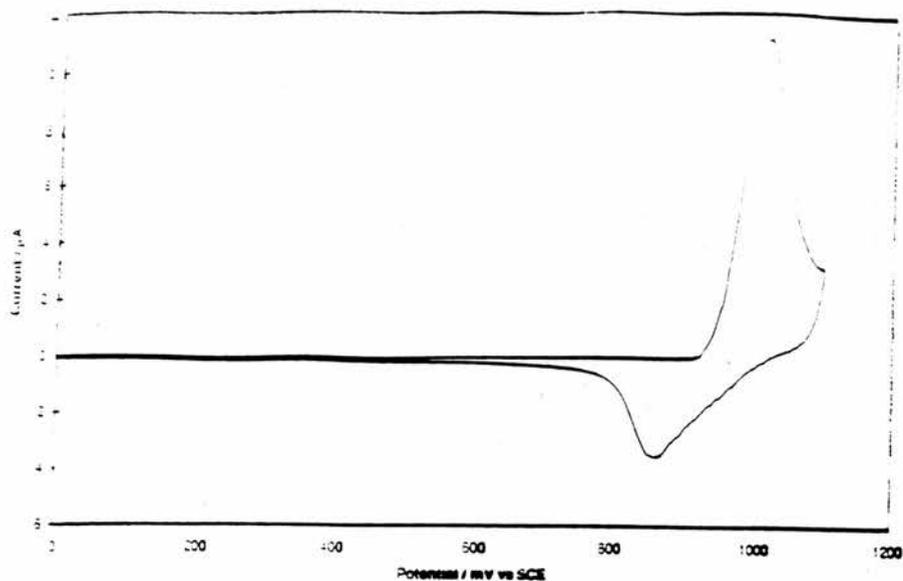


Figure 15 Cyclic voltammogram (100 mVs^{-1}) of **P31** in MeCN / 0.1 M TBAP at a platinum electrode vs. SCE.

Oxidation of **P31**, **Figure 15**, which was grown by recurrent potential sweeps at a Pt electrode, occurred at 1.013 V. This was a slightly higher potential than witnessed for the methyl derivative **P84**, suggesting a slightly more twisted polymer backbone in **P31**. As with **P83**, we failed to prepare ITO coated glass films of **P31** due to the poor solubility of the compound in acetonitrile. We then dissolved the monomer in dichloromethane and attempted to form **P31** by galvanostatic growth, however due to the high potentials observed during polymerisation we switched to potentiostatic growth at 1.8 V. This produced a steady current of $\approx 1.5 \mu\text{A}$ and a thick black coating on the electrode, though when the electrode was removed from the solvent the polymer dropped back into solution. The polymer could not be collected by filtration since the polymer proved soluble in dichloromethane. Attempts to overcome this problem by carrying out the polymerisation in acetonitrile/dichloromethane solution, by dipping the ITO working electrode in 2,2-bithiophene solution and by scratching the surface of the electrode to aid adhesion were not successful.

1,3-Phenylene bis(3,2'-bithiophene) **99** and 1,4-phenylene bis(3,2'-bithiophene) **85**

The electrochemical polymerisation of 1,3-phenylene bis(3,2'-bithiophene) **99** was carried out in MeCN solution containing TBAP and the starting monomer. The CV of **99** is shown in **Figure 16**. It reveals two oxidation peaks similar to those observed for monomers **84** and **31**; however, the redox processes produce very broad waves and occur at much lower potentials than previously obtained, $E_p^{a1} = 0.75$ V and $E_p^{a2} = 1.1$ V, due to the extended conjugation along the polymer backbone in **P99**, in the absence of alkyl substituents.

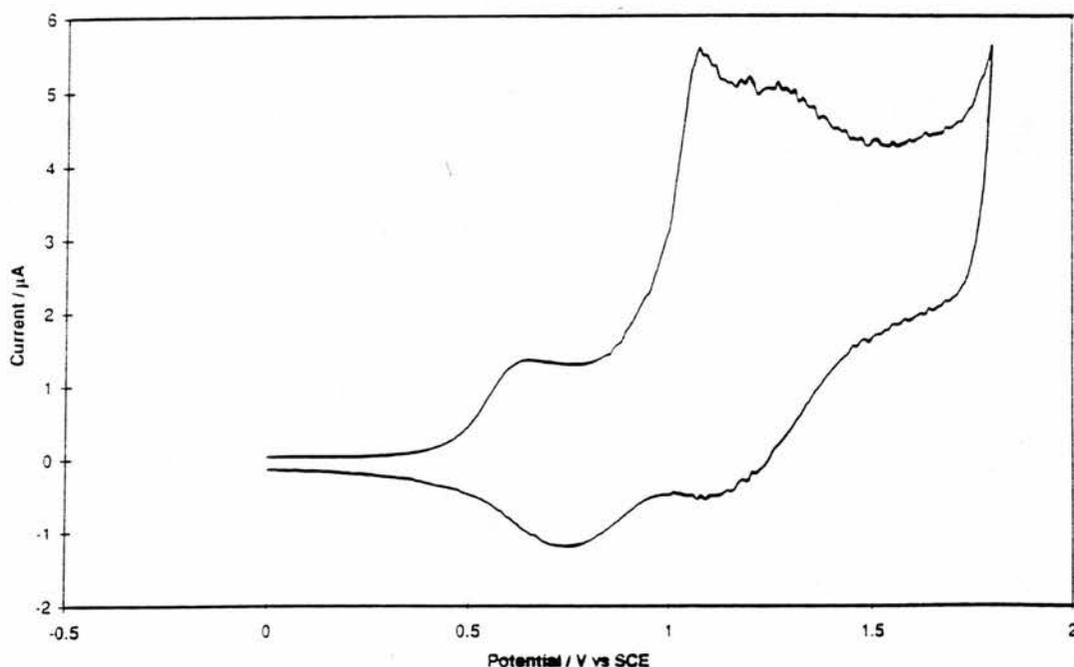


Figure 16 Cyclic voltammogram (100 mVs^{-1}) of **99** in MeCN / 0.1 M TBAP at a platinum electrode vs. SCE.

Polymerisation of **99** proceeded *via* recurrent potential sweeps, galvanostatic and potentiostatic growth to yield the desired polymer. A second oxidation peak in the CV of **P84** and **P31** could not be observed, yet the CV of **P99** showed two oxidation peaks, $E_p^{a1} = 0.75$ and $E_p^{a2} = 1.15$ V, **Figure 17**.

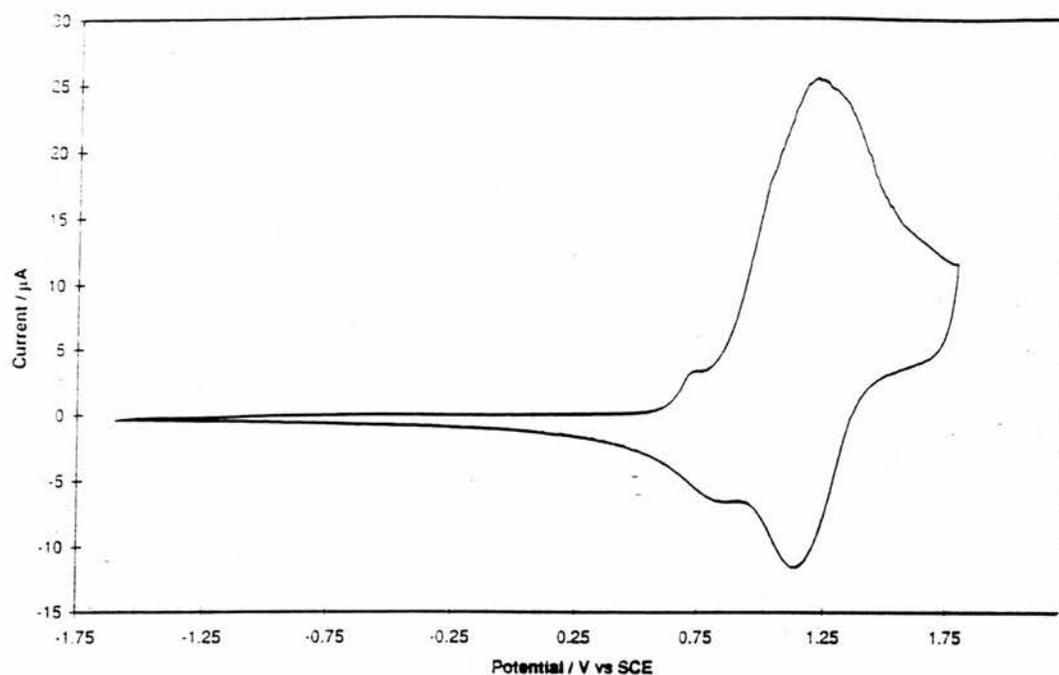
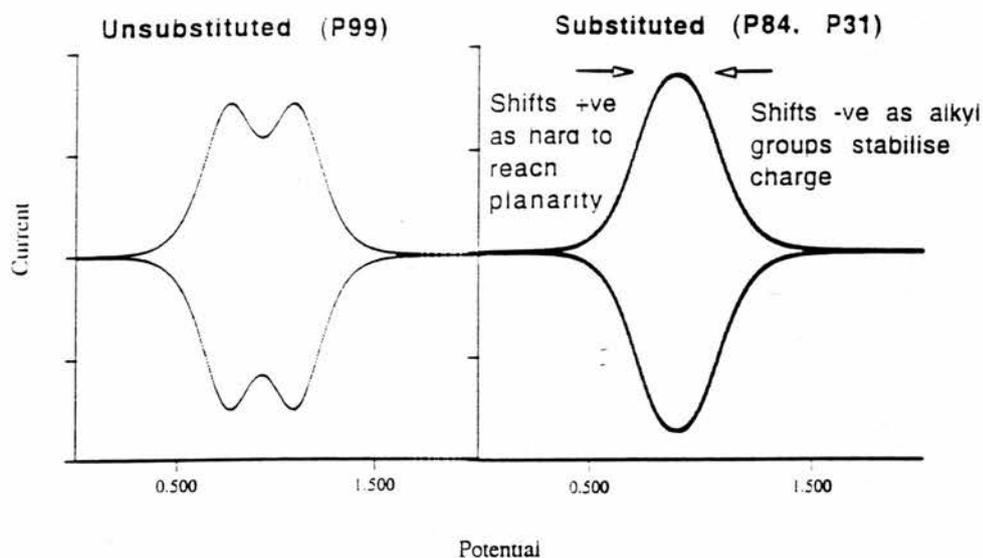


Figure 17 Cyclic voltammogram (100mVs⁻¹) of **P99** in fresh MeCN / 0.1M TBAP at a platinum electrode vs. SCE.

This can again be explained by applying Bauerle's idea that the planarity of the polymer backbone determines the value of the first oxidation potential (i.e. the more planar the backbone, the lower the potential), whereas the second oxidation potential is governed by the ability to stabilise the resultant polarons. **P84** and **P31** have higher first oxidation potentials when compared to **P99** because the alkyl substituents twist the polymer backbone out of conjugation. A second oxidation potential may not be observed for **P84** and **P31** due to the stabilisation of radical cations by the alkyl substituents, resulting in first and second oxidation potentials becoming very close, whereas electron deficient **P99^{•+}** requires a much higher applied potential to form the dication (See diagram on p189).



Explanation of trends in oxidation potential for **P99** compared with **P84 / P31**

In late 1998 Sato *et. al.* reported similar electrochemistry of **P99**, but with slightly higher oxidation potentials to ourselves.³⁷ The slightly higher oxidation potentials reported may indicate a smaller degree of conjugation than present in our polymers. Sato *et. al.* assigned the second redox process to the formation of the dication in quaterthiophene units, contradicting the view expressed by Bredas *et. al.*³⁸ that only a stable cation could be observed in quaterthiophene and that a bipolaron would be unstable.

1,4-Phenylene bis(3,2'-bithiophene) **85** has been synthesised by Pelter³⁹ and found to exhibit very poor solubility in common organic solvents. Nevertheless a CV of **85** could be obtained in acetonitrile/TBAP solution, **Figure 18**.

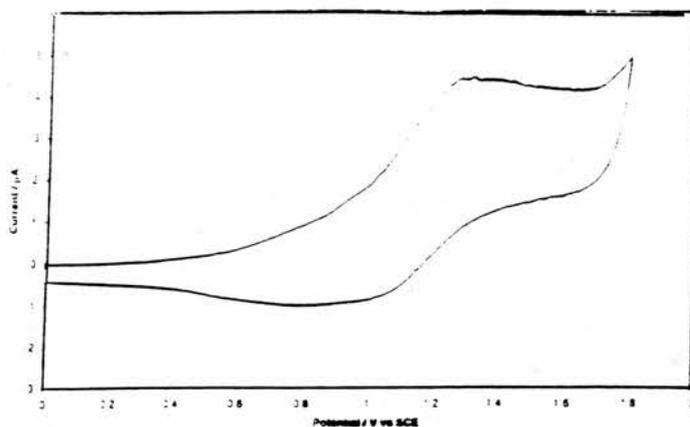


Figure 18 Cyclic voltammogram (100 mVs⁻¹) of **85** in MeCN / 0.1 M TBAP at a platinum electrode vs. SCE;

The CV of **85** shows a single oxidation peak at 1.35 V and possibly a second partially resolved peak at 0.95 V. The polymer was then grown using galvanostatic methods and the CV of the resultant polymer carried out again in MeCN/TBAP solution.

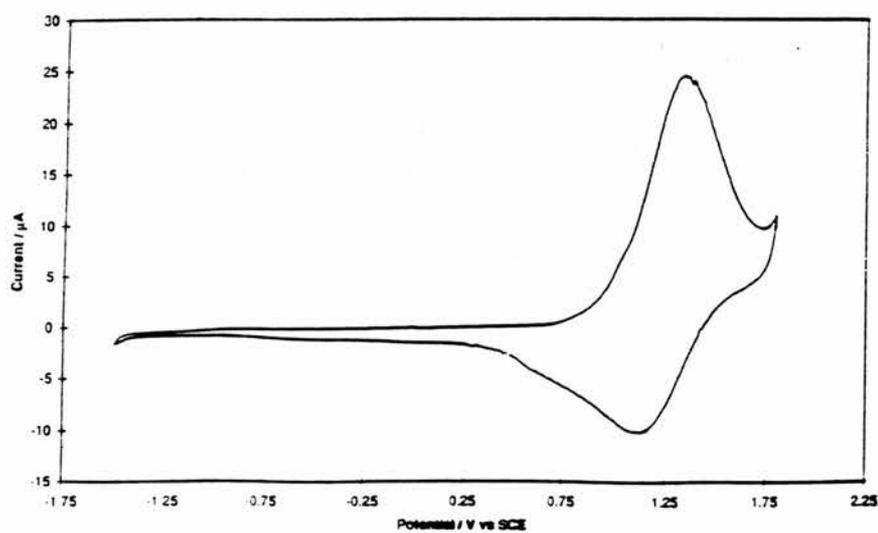


Figure 19 Cyclic voltammogram (100 mVs⁻¹) of **P85** in MeCN / 0.1 M TBAP at a platinum electrode vs. SCE.

A very similar CV to the monomer was acquired for **P85** with two partially resolved peaks at ≈ 1.0 V and 1.35 V. These potentials are considerably higher than those obtained for **P99** and are more in line with those observed for poly(quarterthiophene), $E_p^{a1} = 1.04$ and $E_p^{a2} = 1.36$ V.

Bushby has shown that coulombic repulsion (as measured by ΔE) is substantially greater in co-extensive diradical cations, like **P99**²⁺, than in disjoint radical dications, like **P85**²⁺.⁴⁰ This should result in larger ΔE values for coextensive doped polymers such as **P99** ($\Delta E = 350$ mV) and smaller ΔE values for dis-joint doped polymers such as **P85** ($\Delta E = 0$ mV). However, perhaps our ΔE 's are dominated by coulombic repulsion within the quarterthiophene segments, rather than between segments as mediated by the FCU.

Unfortunately, due to the extremely limited solubility of **85** in various organic solvents we could not obtain films of **P85** on ITO coated glass however we did manage to obtain films of **P99** in both the doped and undoped states. UV-vis absorption spectra of both these films are shown in **Figure 20**.

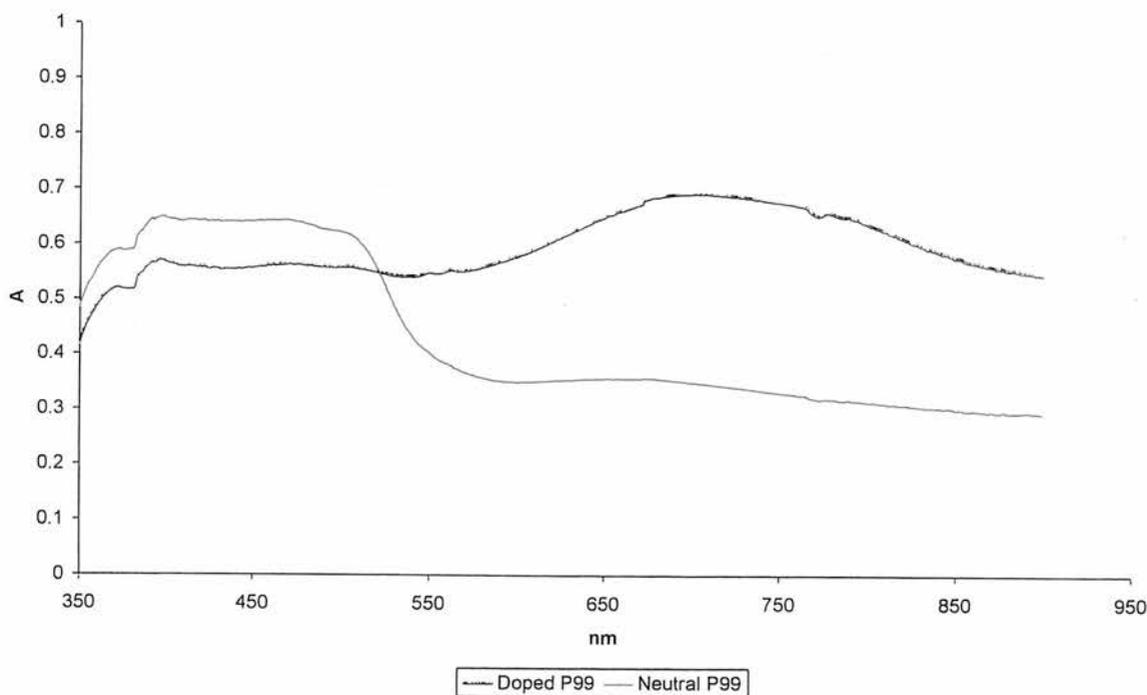


Figure 20 UV-vis spectroscopy of (a) neutral **P99** and (b) doped **P99** coated ITO glass electrodes, produced by galvanostatic methods.

As witnessed previously for **P84**, on oxidising the polymer the intensity of the peak between 400-500 nm decreases and a broad band between 600 nm and 850 nm is established. Neutral **P99** exhibits a $\lambda_{\text{max}} = 450$ nm, close to that of **P84**. The doped polymer **P99** shows a single broad peak with $\lambda_{\text{max}} = 710$ nm compared with a $\lambda_{\text{max}} = 610$ nm for the methyl substituted polymer **P84**. The lower wavelength observed for **P84** can be explained by the stabilisation of polarons by alkyl substituents. Although there are significant differences in the CVs and UV-vis spectra of doped **P84** compared with doped **P99** we cannot yet conclude with certainty that bipolaron formation occurs in **P99** whereas only polaron formation is observed for **P84**.

Electrochemistry: Summary and Conclusions

A table of monomer and polymer oxidation potentials and polymerisation data is contained in appendix I of this chapter.

Monomers **77** and **83** proved difficult to polymerise compared to monomers **84** and **31**. This is most probably due to the fact that radical cations of **77** and **83** are unstable and undergo follow-up reactions resulting in completely irreversible cyclic voltammograms. The oxidation potentials of **P77** and **P83** were similar. The λ_{max} value of **P77** in its neutral state (360 nm) suggests a limited π -system or thiophene rings which are twisted out of conjugation.

The CV of monomer **84** shows two redox processes at 1.0 V and 1.37 V vs SCE, while monomer **31** shows similar behaviour at slightly higher potentials. These waves have been assigned to the formation of di(cation radicals) $\mathbf{84} \rightarrow \mathbf{84}^{\bullet+} \rightarrow \mathbf{84}^{2+2\bullet}$ and $\mathbf{31} \rightarrow \mathbf{31}^{\bullet+} \rightarrow \mathbf{31}^{2+2\bullet}$ respectively.

Monomer **84** was readily polymerised but polymerisation of monomer **31** was complicated by solubility and adhesion difficulties associated with the hexyl substituents. Both polymers

show a single oxidation peak at approximately 1.0 V vs. SCE. The lower oxidation potentials reflect the higher degree of conjugation present in these polymers compared to **P77** and **P83**, as does the higher λ_{max} value of 440 nm. The unsubstituted derivative of **P84** and **P31**, **P99**, exhibits two oxidation peaks at 0.75 V and 1.1 V as a result of the lack of stabilisation of the polarons by alkyl substituents. The single oxidation peaks at higher potentials observed for **P84** and **P31** are evidence for the non-planarity of these systems. The fact that only a single oxidation peak is witnessed for **P84** and **P31** despite scanning to higher potentials suggests that polarons are formed exclusively upon doping **P84** and **P31**. This may be explained by the stabilising effect of the alkyl substituents.

The formation of polarons upon doping **P84** and **P99** has been confirmed by UV-vis absorption spectroscopy. **P84** has a maximum absorption at 610 nm in the doped state, compared to 710 nm for **P99**. This is explained by the inductive effect of the methyl substituents in **P84**.

The CV of the para substituted polymer **P85** shows a single oxidation peak at 1.35 V. This is a higher value than observed for **P99**, which, as mentioned previously, shows two peaks at 0.75 V and 1.10 V vs SCE. We have suggested that the absence of a second oxidation peak in the CV of **P85** is a result of the disjoint coulombic interaction resulting from the AFC employed, whereas **P99** employs a FCU resulting in co-extensive coupling and hence a large value for ΔE .

4.3 ESR Spectroscopic Studies

Electron spin resonance spectroscopy has been used to confirm the metallic properties of doped poly(3-methylthiophene)⁺¹, **Figure 21**, and, as mentioned previously has been used to establish that conduction in polyheterocycles does not involve the molecular orbitals of the heteroatom.

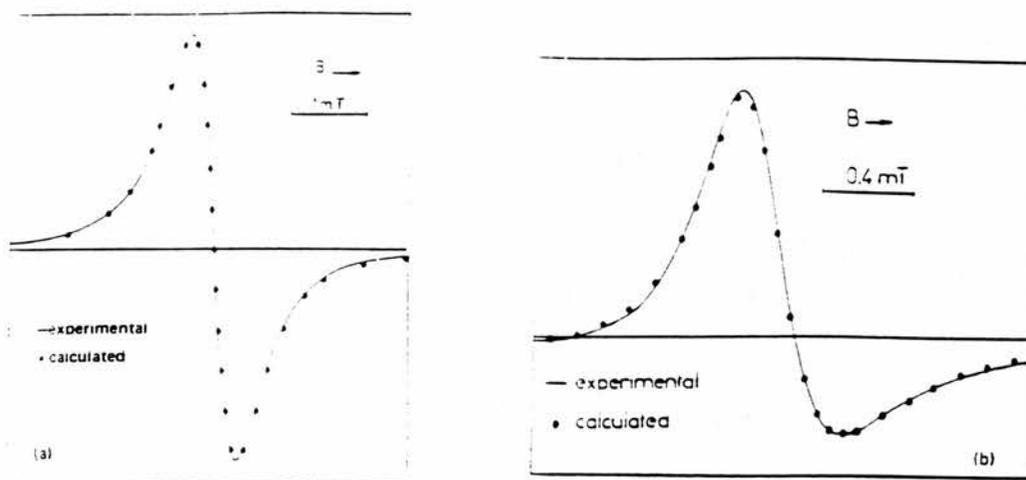


Figure 21 ESR spectrum of polymethylthiophene doped with the SO_3CF_3^- ion at two levels. (a) 30% dopant with a symmetrical Lorentzian line shape and (b) 50% dopant with an asymmetrical Dysonian line shape, due to the increased number of spins.

ESR spectroscopic studies of electrochemically doped poly(1,3-phenylene bis[3,2'-bithiophene]) at various doping levels were carried out by Sato, Hori and Tanaka.³⁷ They found that the ESR signal intensities of the doped poly(1,3-phenylene bis[3,2'-bithiophene]) gradually increased with dopant concentration. The spin concentrations were of the order 10^{19} spins per gram with the maximum value at a dopant concentration of 50%. At this concentration, the doped polymer has one spin per 17 quaterthienyl units. The spin concentration was found to be one order of magnitude smaller than estimated by dopant concentration. That is, at 50 % dopant concentration, there should be one spin for every two quaterthienyl units. Moreover, the intensity of the ESR signal considerably decreased with increasing dopant concentration (60-73 %). This was interpreted as the generated spins being

partially cancelled out by effects such as interchain antiferromagnetic interactions which become dominant at dopant concentrations $> 50 \%$.

ESR spectroscopy was carried out at room temperature on a number of our doped polymers. The ESR spectra of all the doped samples gave very strong signals even at low gains. The signal was a single line with no structure. The polymers which could not be grown sufficiently on ITO (**P83** and **P31**) were generated *in situ* by the addition of NOPF_6 to a solution of the monomer in hexafluoropropanol which is known to enhance the lifetime of radical cations for spectroscopic observation. As the polymerisation occurred, a strong signal was observed.

In general, the ESR lineshapes were narrow with peak-to-peak linewidths (ΔH_{pp}), for example **P84** $\Delta H_{pp} = 1.89\text{G}$ and $g = 2.0019$, **Figure 22**. The g value was reminiscent of values for π -radicals delocalised on a carbon skeleton, and close to that of polythiophene (2.0022 - 2.0026).

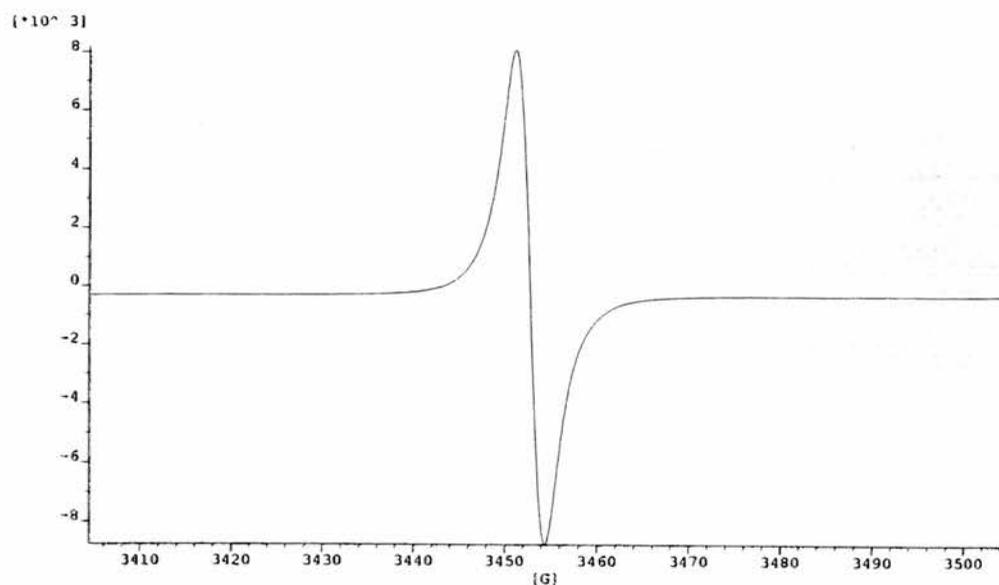


Figure 22 ESR spectrum of solid **P84** at 80K.

In addition to low frequency room temperature ESR, we also investigated the high frequency low temperature ESR spectrum of **P84** at the University of St. Andrews Department of Physics . The ESR spectra of doped **P84** at 178 GHz at a variety of temperatures is shown in **Figure 23**

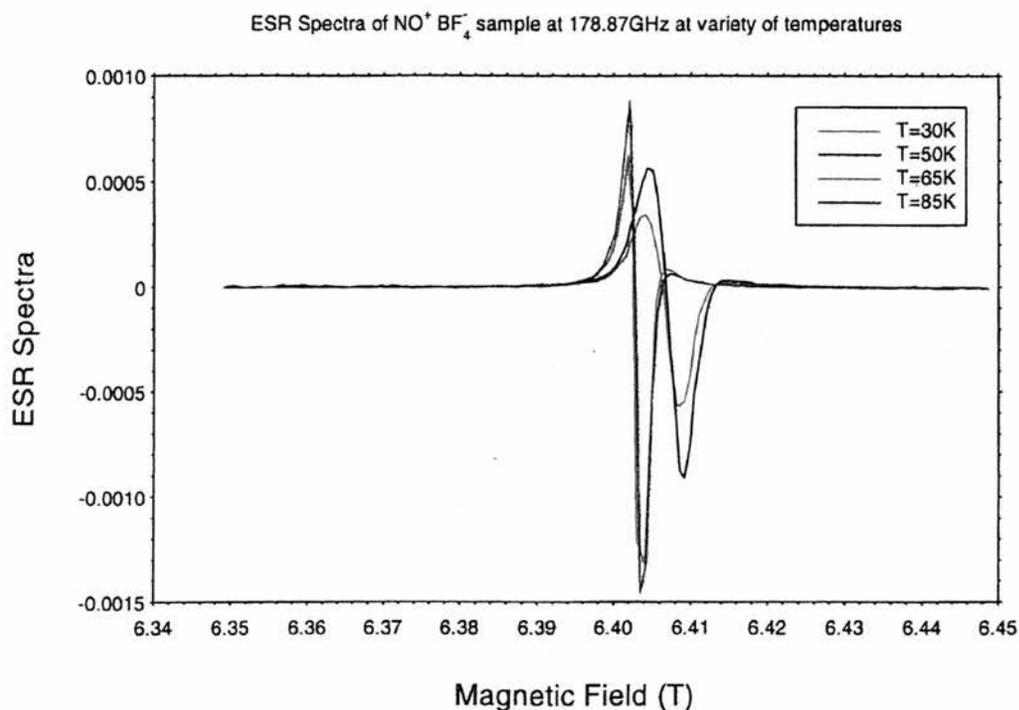


Figure 23 High frequency (178 GHz) ESR spectrum of **P84** at a range of temperatures.

The signal was again a narrow single line ($\Delta H_{pp} = 10.5$ G) with no structure. However, a change in the field centre of 300 G was observed on cooling from 65 K to 50 K. This was accompanied by a broadening of the signal which continued at lower temperatures. For example, the field centre at 30 K was 64060 G and at 2.8 K increased to 64140 G, i.e.increasing g . The only literature description known to us of such behaviour is found in the study of a compound containing alternate manganese (II) ions and nitronyl nitroxide radicals in a chain. The coupling between the atoms is antiferromagnetic, but since the two spins are different, the moments are not compensated and a one dimensional ferrimagnet results. At

lower temperatures the g value parallel to the chain decreased, coupled with a large increase in the line width.⁴² This may suggest conformational changes within the polymer resulting in localised ferromagnetic states at low temperatures. However, as yet, we do not fully understand the change in resonance or the line broadening observed in **P84** upon cooling from 65 K to 50 K.

We then carried out spin concentration studies of various doped polymers at a variety of temperatures against a DPPH standard. The results of these experiments are summarised in appendix II of this chapter.

Observations From ESR Data

The highest number of spins per mole of polymer (4.73×10^{23}) was evident in **P84**, which was produced by electrochemical methods. It is interesting that the highest value occurs in an alkyl-substituted polymer where the substituent may be responsible for stabilisation of the polaron. In contrast to the high frequency, low temperature ESR data mentioned previously we did not observe a significant shift in the field centre of the signal. The field centre changed from 3452.8 G at 80K to 3454.9 G at 4.8K and was accompanied by a corresponding increase in the peak-to-peak linewidths from 1.90 G to 4.81 G. This is significant since ΔH_{pp} of polythiophene decreases as temperature decreases, due to the Elliot mechanism, which is simply a broadening of the signal due to the collisions of mobile electrons. This suggests that we simply observe the effect on the linewidth by suppressing exchange-narrowing on cooling.

In general the intensity of the ESR signals decreased with a reduction in temperature, although in some instances the signal intensity increased significantly e.g. polymer **P84** at 10 K and chemically synthesised **P99** at 4.3 K. The general decline of the signal intensity may support the π -dimerisation theory proposed by Janssen.³² The sudden rise in the observed number of spins per mole at low temperatures (10 K and 4.3 K) cannot be explained and is possibly an

instrumental artifact. This could be investigated by monitoring the signal intensity over a larger range of temperatures.

When comparing chemical and electrochemical polymerisation and doping of **P99** the values obtained show that electrochemical methods lead to a greater number of unpaired electrons and are therefore more efficient at introducing a large number of spins into these systems. We have not carried out elemental analysis of the doped polymers and therefore cannot estimate the doping levels obtained for chemical and electrochemical doping of these polymers.

The intensity of the signal for chemically synthesised and chemically doped **P99** was greater than that of chemically synthesised and chemically doped **P85**. The integrated signal intensity is proportional to the imaginary part of the magnetic susceptibility, χ .⁴³ This may suggest that ferromagnetic interactions are present within **P99**, whilst anti-ferromagnetic interactions are dominant within **P85**, as a result of the AFC.

The ESR spectrum of **P77A** which was synthesised using iron trichloride showed a slight shoulder, which may correspond to the presence of iron(III) species. The ESR spectrum of **P77A**, dedoped in ammonium hydroxide solution, showed the reduction to be incomplete.

Linewidth dependence on Temperature

The linewidth of the polymers with the largest number of spins (**P84** and **P99** (electrochemically polymerised) were closest to the value of ≈ 2 G reported for polythiophene itself, **Figure 24**. These are presumably exchange narrowed lines, resulting from efficient doping of **P84** and electrochemically synthesised **P99**, since they are much narrower than those observed for trapped spins in polythiophene (6-9 G).

Chemically synthesised **P99** and **P85** exhibit much broader lines, presumably because the exchange interactions are reduced due to the lower number of spins. This is commonly

observed for non-interacting or dilute spins within a solid. Clearly, none of the polymers have the metallic like behaviour of decreasing linewidth with temperature as observed for polythiophene.

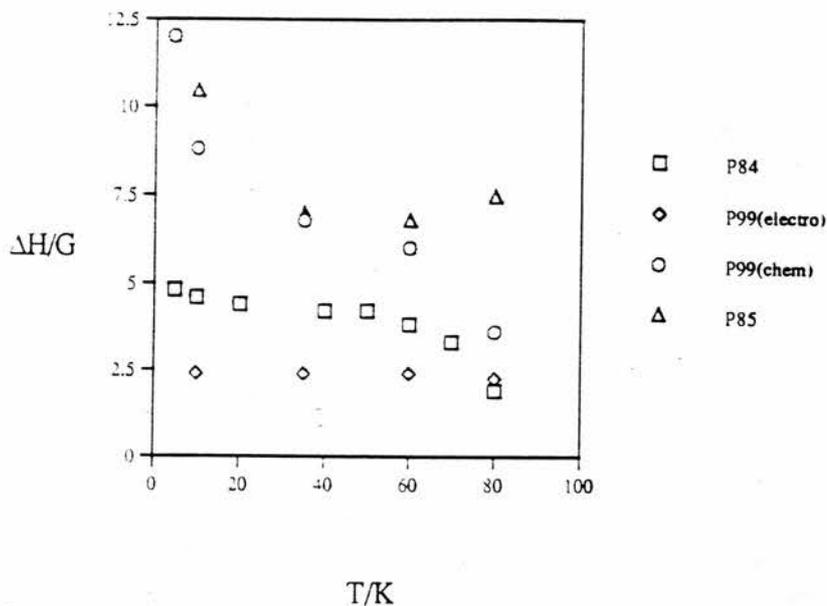


Figure 24 Linewidth dependence on temperature for **P99** (chemically polymerised), **P99** (electrochemically polymerised), **P84** (electrochemically polymerised) and **P85** (chemically polymerised).

Conclusion

Hexyl- substituted polymers such as **P83** and **P31** could not be polymerised as efficiently as methyl substituted polymers such as **P84**, due to poor solubility in the electrolyte and poor adhesion at the electrode.

The first oxidation potential of **P84**, when compared to **P99**, suggests that its polymer backbone is slightly twisted due to the methyl substituents. However, these methyl substituents stabilise the resultant polaronic states, resulting in the highest number of spins per mole being recorded for **P84**. ESR spectroscopy showed the linewidth of **P84** to be ≈ 2 G. This exchange-narrowed linewidth is also indicative of a large number of spins being present in

P84. However, as stated previously we cannot yet conclude with certainty that only polaron formation is observed for **P84**.

Some interesting changes in linewidth, field centre and intensity of signal were recorded for **P84**. Unfortunately, time did not allow a more comprehensive investigation of these observations.

4.4 Experimental

Cyclic voltammograms were generated using an EG&G PARC Potentiostat / Galvanostat Model 273A and controlled using version 4.11 of the Electrochemistry Research Software running on a PC. ESR spectra were obtained using a Bruker variable temperature unit and an Oxford Instruments ITC⁵⁰³ temperature controller. A Perkin Elmer Lambda 14P spectrophotometer, running UV Winlab software, was used to obtain UV-vis spectra. Acetonitrile and dichloromethane used as solvents for CV were dried over CaH₂. Hexafluoropropanol was purchased from Aldrich chemical company, and used as received. For all other methods of data collection etc. refer to the experimental section in chapter 2.

Attempted McCullough Polymerisation of 3-Hexylthiophene 33

A three necked round bottomed flask, equipped with a magnetic stirrer bar, nitrogen and septum inlet was charged with freshly dried THF (40cm³), diisopropylamine (2.11cm³, 15mmol) and 1.6M n-butyl lithium (9.37cm³, 15mmol) at room temperature. The mixture was allowed to stir at room temperature for 40 min. to allow formation of LDA. An acetone/dry ice bath was then used to cool the solution to -70°C whereupon (3.7g, 15mmol) of 2-bromo-3-hexylthiophene was added at -70°C and stirred for 15 min., before being warmed to -40°C for 40 min. The solution was again cooled to -60°C and magnesium bromide etherate (3.78g, 15mmol) added. The solution was stirred at -60°C for 40 min. and the temperature then allowed to rise to -5°C, before being cooled to -70°C and NiCl₂(dppp) added (0.3g,

0.55mmol). The temperature was then allowed to rise overnight. The reaction mixture was poured over ice and the organic layer extracted with CH_2Cl_2 , the combined extracts were dried over MgSO_4 and the solvent removed by rotary evaporation to yield the crude product as a dark oil. ^1H NMR spectroscopy revealed that the cross-coupling reaction had not taken place and that we had recovered unreacted and reduced starting materials.

The reaction was repeated excluding the addition of diisopropylamine and worked up as described above. ^1H NMR spectroscopy differed from the previous example in that a triplet at 2.72ppm was observed. As mentioned previously this is characteristic of the α -protons of the hexyl chain resulting from a head-to-tail coupling. 3-Hexylthiophene, 2-bromo-3-hexylthiophene, 2-butyl-4-hexylthiophene, 2,5-dibutyl-3-hexylthiophene and dihexyl-2,2'-bithiophene were observed by GCMS.

Attempted Bromination of 1,3-phenylene bis(5-hexyl-2-thiophene)

83

To a solution of 1,3-phenylene bis(5-hexyl-2-thiophene) (0.3g, 0.73mmol) in a mixture of chloroform and acetic acid (50/50 v/v, 20cm³), portions of NBS (0.26g, 1.46mmol) were added at 0°C over 30 minutes. After stirring for 30 minutes, the mixture was diluted with water, extracted with chloroform (2 x 25cm³) and the combined extracts neutralised with KOH and dried over MgSO_4 . The solvent was then removed to yield a dark brown oil. ^1H NMR spectroscopy suggested a complex mixture of products and due to the disappearance of the signal at 7.5ppm it would appear that bromination has occurred at position 2 of the phenylene ring.

General Procedure for Oxidative Polymerisation using NOBF_4 and NOPF_6

Into a dry three necked round bottomed flask equipped with a pressure equalising dropping funnel, nitrogen inlet and magnetic stirring bar were added 2.5 equivalents of the oxidant

the conjugation of the polymer increased. The solution was stirred overnight and the solution filtered. The filtrate was then washed with methanol (600cm³) and subjected to soxhlet extractions with methanol followed by chloroform to yield the doped polymer as a black powder in typical yields of 25-30%.

Polymer	% Yield
1,3-phenylene bis(5-methyl-2-thiophene)	25%
1,3-phenylene bis(3,2'-bithiophene)	36%
1,4-phenylene bis(3,2'-bithiophene)	29%

FeCl₃ Catalysed Polymerisation of 1,3-phenylene bis(5-methyl-2-thiophene) 77.

A solution of monomer **77** (0.170g, 0.630mmol) in CCl₄ (30cm³) was added dropwise, under nitrogen to a solution of FeCl₃ (0.41g, 2.50mmol) in CCl₄ (25cm³). Upon stirring the solution rapidly became darker in colour suggesting an increase in conjugation of the species being formed. The solution was stirred for 48h and precipitated into MeOH and a brown green powder collected by filtration. The powder was washed with methanol, chloroform, diethyl ether and water and stirred in aqueous ammonium hydroxide (100cm³) for 2h which invoked a colour change from green to orange which is typical for neutral polythiophenes. The powder was then filtered and dried under vacuum to yield 0.05g (32 %) of crude polymer. A fraction of the sample was doped with I₂ vapour for 72h causing the powder to turn black and was then stored for ESR spectroscopic analysis.

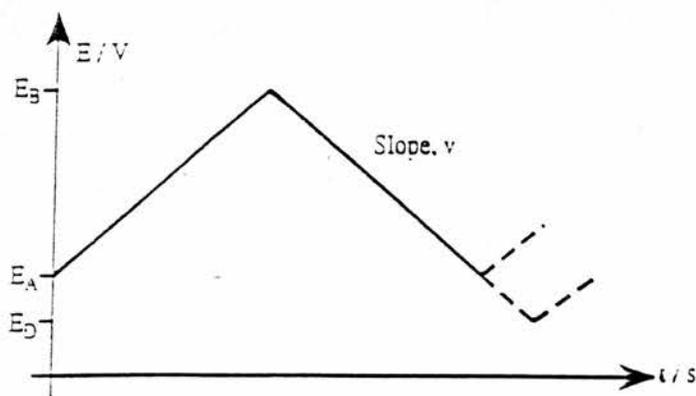
4.5 Basic Aspects of Cyclic Voltammetry

In cyclic voltammetry the polymer under investigation can either be preformed and deposited onto the electrode surface, using techniques such as spin coating, or formed on the electrode during the potential cycling process.

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In cyclic voltammetry the polymer under investigation can either be preformed and deposited onto the electrode surface, using techniques such as spin coating, or formed on the electrode during the potential cycling process.

The potential time waveform used in sweep experiments is depicted in **Figure 25**.



Potential-time profiles for sweep voltammetry.

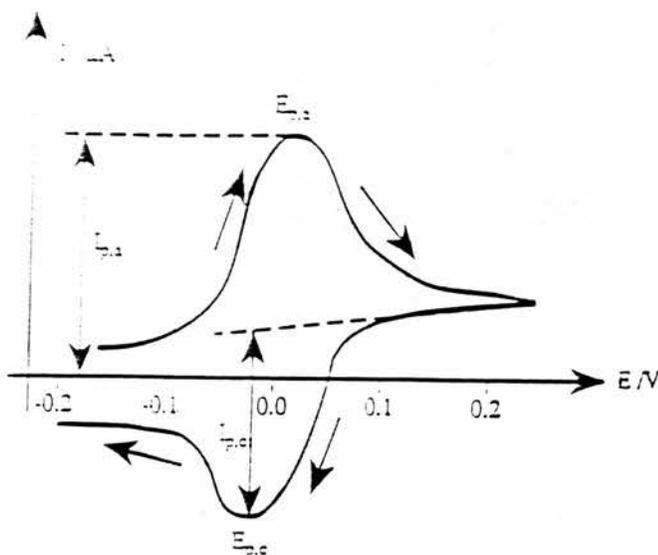
Figure 25

Before the advent of modern electronics, the simplest experiment, linear sweep voltammetry, involved the electrode potential being swept between E_A and E_B at a known sweep rate, V , before stopping the potential sweep.

Cyclic voltammetry again involves sweeping the potential of an electrode (the working electrode) within the fixed limits and at a constant scan rate. The waveform is essentially the same but when the potential reaches E_B the sweep is reversed. When the potential again

reaches E_A the sweep can be terminated, reversed again or continued to another potential value E_D .

In all these cases measurements of current relative to the working electrode and a reference electrode are made. A graph of current as a function of potential can then be plotted and these graphs known as voltammograms have some basic components which are detailed in **Figure 26**



Basic cyclic voltammogram for a reversible process.

Figure 26

The theory behind cyclic voltammetry is very complex and is based on a solution of differential equations, these will not be detailed here but have been covered in detail elsewhere.^{44, 45}

Assuming that in an electrochemical system the kinetics of the various components are sufficiently fast, then the system will follow the Nernst equation (below).

$$E = E^0 + \frac{RT}{nF} \ln \left(\frac{C_O^\sigma}{C_R^\sigma} \right)$$

E = Potential difference at zero current E^0 = Electromotive force,

R = Gas constant, n = charge no. for an electrochemical reaction,

F = Faradays constant, T = Absolute Temp

C_O^σ / C_R^σ = capacitance of oxidation / reduction.

and the system is called a reversible one. For any reversible system the cyclic voltammogram will have various components that are similar to those shown previously. **Figure 26** outlines the basic cyclic voltammogram of a reversible process where E_p^a and E_p^c are the potential values for the peak anodic and cathodic currents and I_p^a and I_p^c represent the respective current densities.

Certain diagnostic tests exist for the cyclic voltammograms of the reversible process.

1. $E_p = E_p^a - E_p^c = 59/n$ (mv)
2. $E_p - E_{p/2} = 59/n$ (mv)
3. $I_p \propto v^{1/2}$
4. $I_p^a / I_p^c = 1$
5. At potentials beyond E_p , $I^{-2} \propto t$

In an irreversible system, where the rate of electron transfer is insufficient to maintain the Nernstian equilibrium at the electrode surface, these conditions do not apply. The most noticeable difference in the cyclic voltammogram of an irreversible process is that there is no reverse peak. Similar to the reversible system there are certain criteria which can be studied to check that the system is in fact irreversible:

1. No reverse peak.
2. $E_p - E_{p/2} = 48/\alpha_a n_a$ (mV).
3. E_p^a shifts $30/\alpha_a n_a$ (mV), for each decade increase in V
4. $I_p^a \propto V^{1/2}$.

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Appendix I

Electrochemical Data for Monomers and Polymers

Electrochemical data for monomers and polymers

Monomer	E _{pa1} ¹ monomer	E _{pa2} ² monomer	E _{pa1} ¹ polymer	E _{pa2} ² polymer	E ^o steady	t(polymer) sec.	λ _{max} nm undoped	λ _{max} nm doped
77	1.50	/	1.30	/	1.4	150	360	650
83	1.50	/	1.20	1.50	1.5	130	/	/
84	1.00	1.37	0.95	/	1.4	>350	440	610
31	1.10	1.45	1.0	/	3.9 [†]	>850	/	/
99	0.75	1.10	0.75	1.10	1.25	>450	450	720
85	0.95 [‡]	1.35	1.35	/	0.95	>450	/	/

All potentials related to V vs. SCE.

[†] Actual polymer growth was carried out using potentiostatic growth at 1.8V generating a constant current of 1.5 μA at t > 450 s.

[‡] This wave was very poorly resolved and has been attributed to di(radical cation) formation

Appendix II
ESR Spectroscopy Data for P77-P99

ESR Data Tables

Polymer 85: Chemically polymerised and doped with NOPF₆, 0.77mg.

Temperature	ΔH_{pp} (G)	Field Centre	Double Integral	no. of spins / gram	no. spins / mole
80K	7.46	3451.9	38.2×10^6	9.63×10^{18}	3.91×10^{21}
60K	6.8	3451.8	9.42×10^6	1.78×10^{18}	7.23×10^{20}
35K	7.0	3452.0	6.30×10^6	6.95×10^{17}	2.82×10^{20}
10K	10.46	3453.2	27.9×10^6	4.41×10^{17}	1.79×10^{20}

Polymer 99: Chemically polymerised and doped with NOPF₆, 0.44mg.

Temperature	ΔH_{pp} (G)	Field Centre	Double Integral	no. of spins / gram	no. spins / mole
80K	3.6	3451.6	0.05×10^6	1.11×10^{18}	4.50×10^{21}
60K	6.0	3451.5	0.14×10^6	2.38×10^{18}	9.44×10^{20}
35K	6.8	3452.0	1.17×10^6	1.13×10^{17}	4.60×10^{20}
10K	8.8	3454.0	2.98×10^6	8.50×10^{17}	3.45×10^{20}
4.3K	12.0	3453.2	1.60×10^8	1.91×10^{20}	7.76×10^{22}

Polymer 99: Electrochemically polymerised and doped, 1.26mg

Temperature	ΔH_{pp} (G)	Field Centre	Double Integral	no. of spins / gram	no. spins / mole
80K	2.26	3451.6	1.16×10^7	8.97×10^{20}	3.64×10^{23}
60K	2.40	3452.8	1.35×10^7	7.81×10^{20}	3.17×10^{23}
35K	2.40	3452.8	1.47×10^7	4.98×10^{20}	2.02×10^{23}
10K	2.40	3454.0	1.54×10^7	1.49×10^{20}	6.06×10^{22}

Polymer 84: Electrochemically polymerised and doped, 1.04mg

Temperature	ΔH_{pp} (G)	Field Centre	Double Integral	no. of spins / gram	no. spins / mole
80K	1.90	3452.8	2.20×10^7	1.03×10^{21}	4.73×10^{23}
70K	3.31	3453.2	2.26×10^7	9.26×10^{20}	4.26×10^{23}
60K	3.81	3453.5	2.28×10^7	8.00×10^{20}	3.68×10^{23}
50K	4.20	3453.9	2.37×10^7	6.93×10^{20}	3.18×10^{23}
40K	4.20	3454.3	2.53×10^7	5.92×10^{20}	2.72×10^{22}
20K	4.40	3455.0	4.03×10^7	4.71×10^{20}	2.17×10^{22}
10K	4.60	3454.4	2.79×10^8	8.18×10^{20}	3.76×10^{22}
4.8K	4.80	3454.9	1.08×10^8	3.04×10^{20}	1.40×10^{22}

Polymer 77A: Chemically polymerised using FeCl_3 , doped with I_2 and dedoped with hydrazine.

Temperature	ΔH_{pp} (G)	Field Centre	Double Integral	no. of spins / gram	no. spins / mole
Doped - 80K	14.06	3445.1	14.9×10^6	1.23×10^{20}	3.32×10^{22}
Dedoped - 80K	1.6	3457.4	0.49×10^6	4.05×10^{17}	1.09×10^{20}

Chapter Five

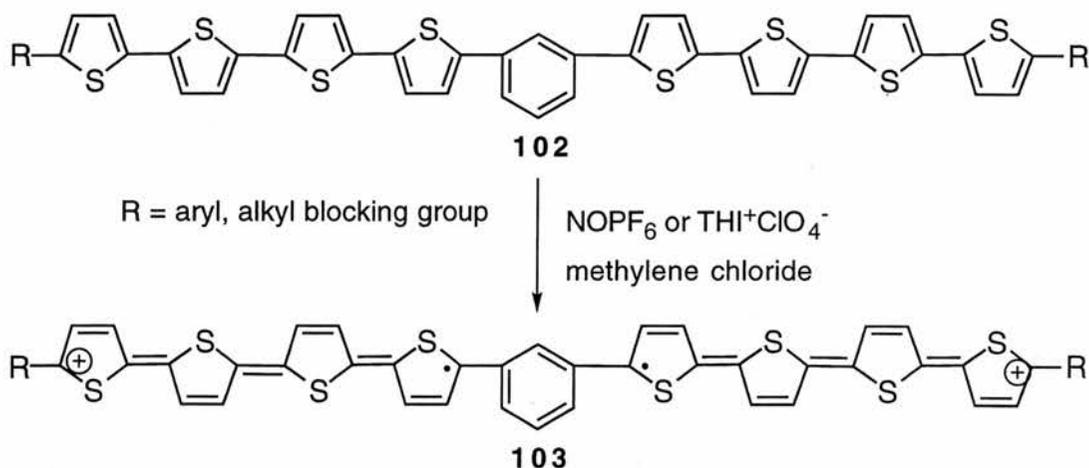
End-Capped Oligomers

5.0 End Capped Oligomers

5.1 Introduction

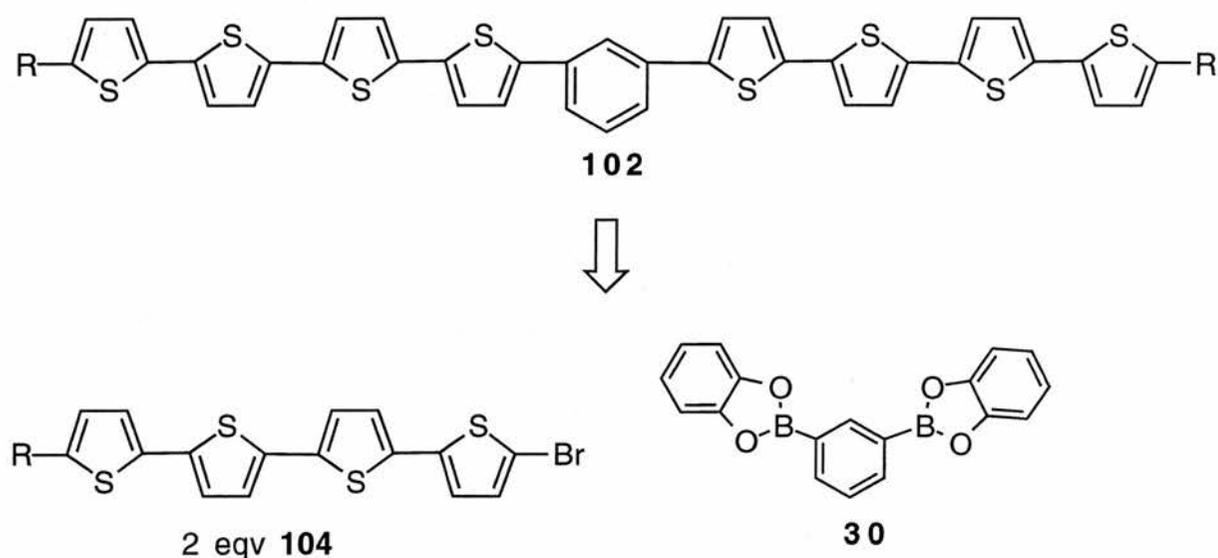
Although polythiophenes and functionalised polythiophenes have received considerable attention due to their fascinating electronic and optical properties, there are difficulties involved in measuring certain physical properties of these polymers such as magnetism. Inhomogeneous doping, structural defects and antiferromagnetic interactions between polymer chains produce inaccurate values for the magnetic moment and hinder the determination of structure-property relationships. Bäuerle and others have shown that thiophene oligomers when protected at the α -position can be quantitatively oxidised to the corresponding cation radicals which are stable at ambient temperature.¹ Given a high enough degree of conjugation the thiophene oligomers inherently possess the basic and even improved electronic and optical properties of polythiophenes.²

Their defect free chemical structures make oligothiophenes ideal as model compounds for the intractable polythiophenes and enable a more accurate study of structure property relationships to be undertaken. With this in mind, we attempted to synthesise 1,3-phenylene-bis (quaterthiophene) **102** which would allow us to study the interaction between spins in the oxidised species **103** by treating **102** with thianthrenium perchlorate or nitrosonium hexafluorophosphate in dichloromethane.



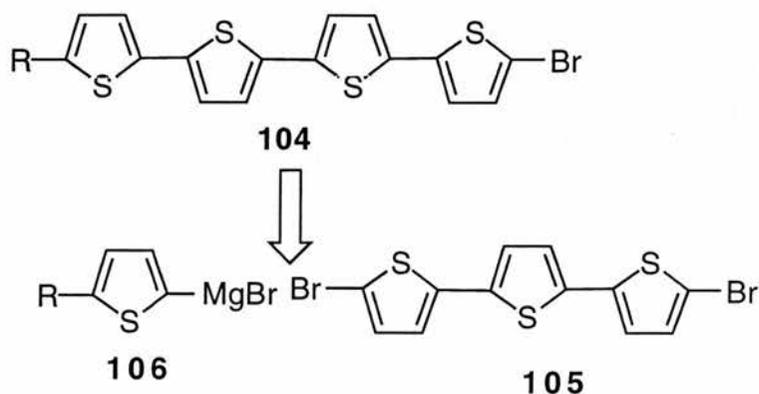
The R groups which prevent oxidative polymerisation should be chosen such that they enhance the solubility of the compound since the extended conjugation present in **102** could render it fairly insoluble.

Using our previous experience of Suzuki coupling reactions, we intended to form **102** via the Suzuki coupling of two equivalents of 5-bromo-5'''-alkyl-2,2':5',2'':5'',2'''-quaterthiophene with 1,3-phenylene bis(1,3,2-benzodioxoborole), **Scheme 1**.



Scheme 1

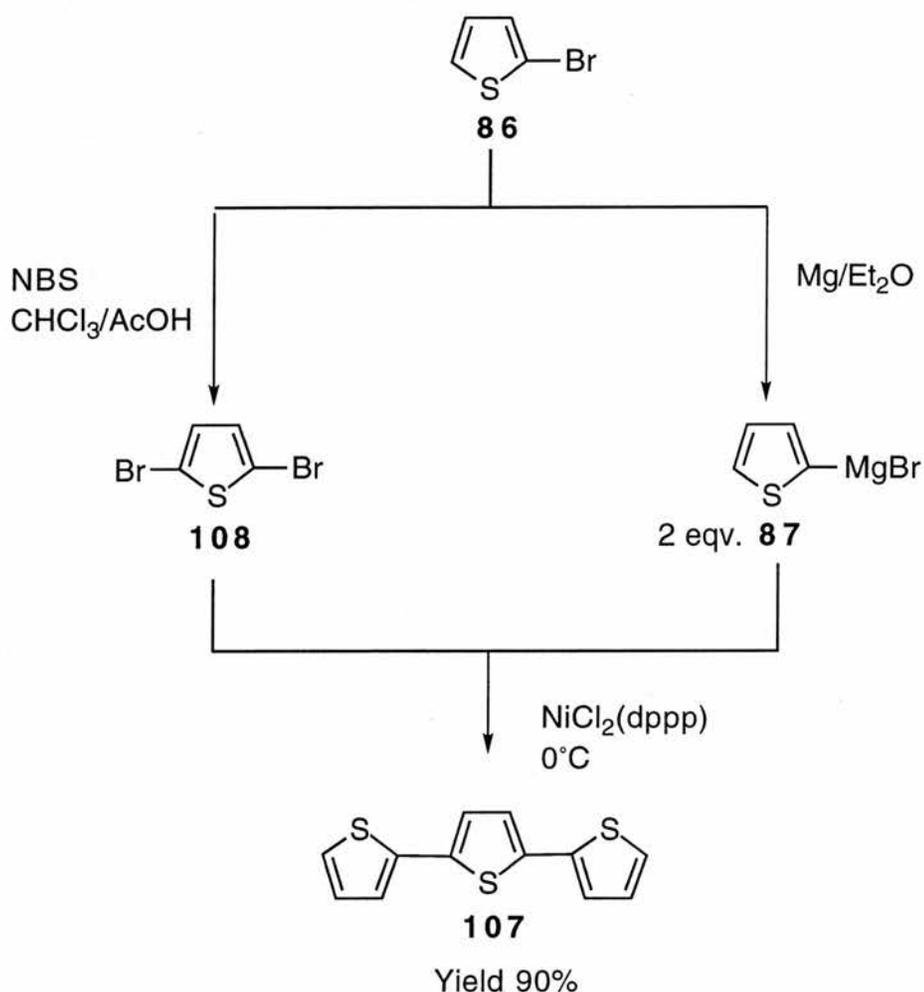
The boronic ester could be synthesised by the route described in chapter 2. Further disconnection of 5-bromo-5'''-alkyl-2,2':5',2'':5'',2'''-quaterthiophene **104** leads us to a mono or dibrominated terthiophene **105** which was expected to undergo a nickel catalysed coupling with a 2-alkyl-5-bromomagnesium species **106**, **Scheme 2**.



Scheme 2

5.2 Attempted Synthesis of End-Capped Oligomer 102

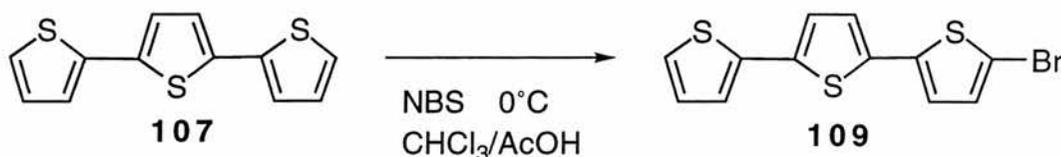
Our first step involved the preparation of 2,2':5',2''-terthiophene **107**. This was achieved by the bromination of 2-bromothiophene **86** using N-bromosuccinimide in acetic acid/chloroform, followed by the subsequent reaction of the resultant 2,5-dibromothiophene **108** with 2 equivalents of 2-bromomagnesiothiophene **87**, **Scheme 3**.



Scheme 3

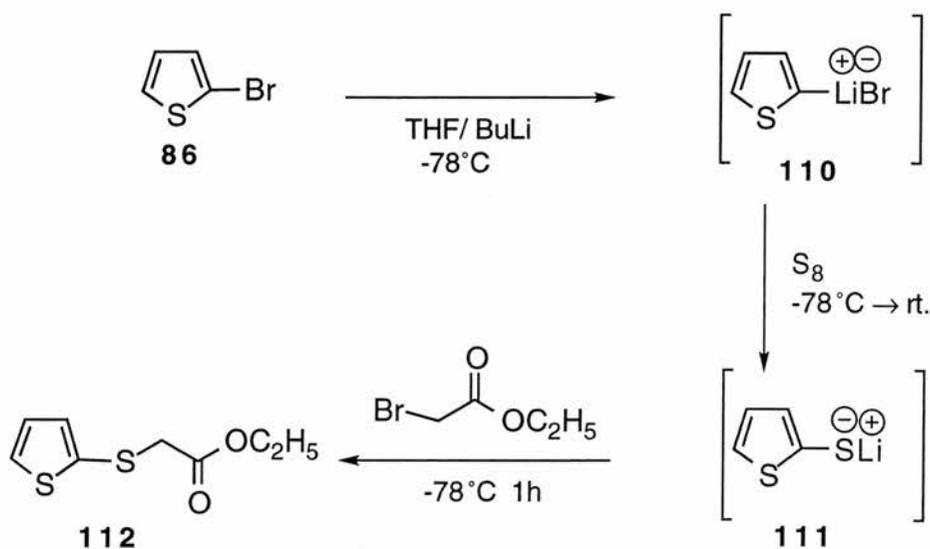
This cross coupling reaction was very similar to those described in appendix I of chapter 2, which afforded only limited amounts of the cross-coupled product. The notable difference in the reaction shown in **Scheme 3** is the absence of long β -alkyl chains which we felt sterically hindered the cross-coupling reaction. This idea was reinforced by the fact that terthiophene

was formed in yields of 85-90% presumably because the reaction is not sterically hindered by the presence of alkyl groups. Despite contrary claims by H. Zimmer *et al.*³ we found that 2,2':5',2''-terthiophene could be brominated using 1 equivalent of N-bromosuccinimide to afford 5-bromo-2,2':5',2''-terthiophene in good yield, **Scheme 4**.



Scheme 4

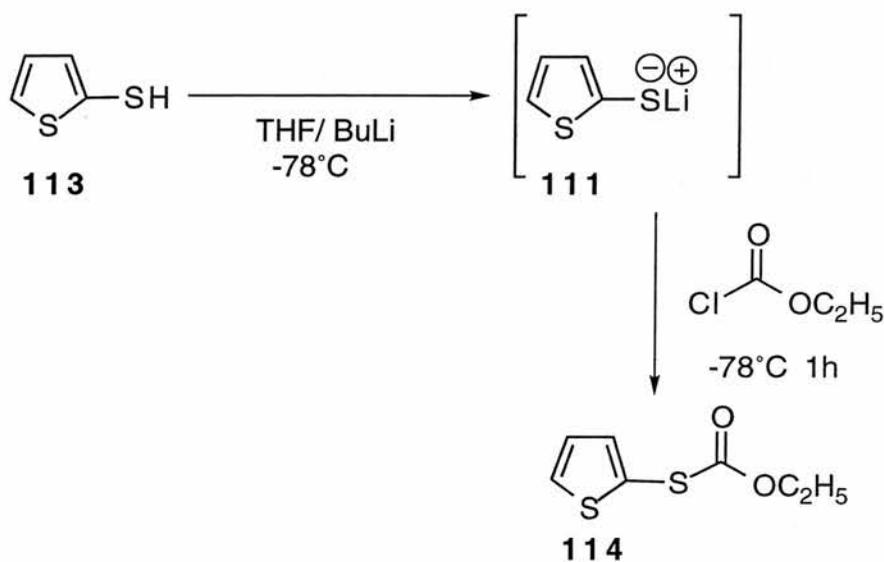
5-bromo-2,2':5',2''-terthiophene **109** could then be coupled to a 5-bromo-2-alkylthiophene using Grignard chemistry producing an end capped quaterthiophene. A communication by Miller *et al.*⁴ showed that terminal alkylthio- groups substantially increased radical cation stability compared to terminal alkyl groups, allowing the observation of 'monothiophene' cation radicals in addition to bi- and terthiophene radical cations. When the alkylthio end capped thiophene monomers were doped using NOPF₆ in 1,1,1,3,3,3-hexafluoropropan-2-ol rather than methylene chloride a further stabilisation of the radical cation was observed. We decided to attempt the synthesis of a 2-alkylthio(thiophene) which would hopefully provide solubility and stabilise the radical cations formed. Miller *et al.* failed to provide a method for attaching thioacetate groups to thiophene and we therefore used the route shown in **Scheme 5**.



Scheme 5

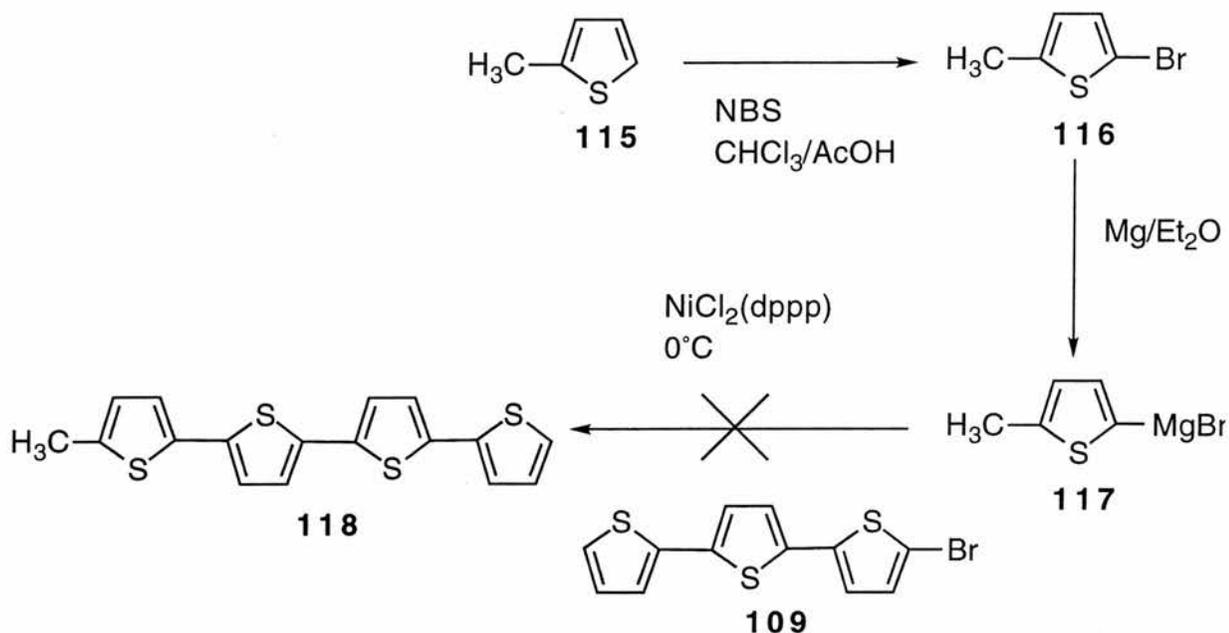
The reaction was carried out as shown in **Scheme 5**. Analysis of the reaction mixture by GCMS suggested that the conversion of thienyl lithiate to the thiol anion took place. However, nucleophilic attack at the bromine of ethyl bromoacetate occurred only to a small degree forming the desired ethyl 5-2-thienyl(thioacetate) in meagre yield. The major product from the reaction was 2-butylthio(thiophene) together with unreacted bromoethyl acetate.

A simpler alternative route could have been to start from thiol(thiophene) which could be deprotonated using base, followed by the addition of an alkylchloroformate to yield the thioacetate as shown in **Scheme 6**. This might occur more readily because the chloroformate should be more susceptible to nucleophilic attack.



Scheme 6

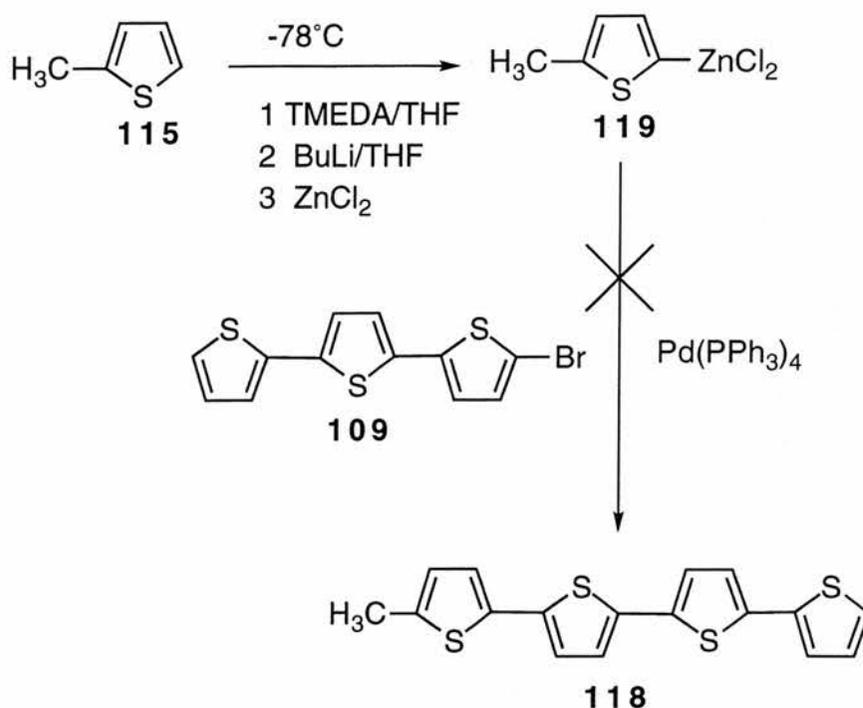
Before carrying out the reaction shown in **Scheme 6**, we synthesised 5-bromo-2-methylthiophene **116** and attempted a nickel catalysed cross-coupling reaction with 5-bromo-2,2':5,2''-terthiophene **109**, **Scheme 7**.



Scheme 7

The reaction produced an orange solid which was purified by column chromatography on silica gel using hexane/ethyl acetate. Trace amounts of 5-bromo-2-methylthiophene were observed in addition to large amounts of 2-methylthiophene and 5-bromo-2,2':5,2''-terthiophene however the desired 5-methyl-2,2':5,2''-quaterthiophene was not present in the recovered fractions. Before repeating this reaction we attempted to form the Grignard of 5-bromo-2-methylthiophene and assumed that it was present in an almost quantitative amount, simply by carrying out the Grignard formation reaction with an excess of magnesium, removing the liquid when the reaction was complete, and weighing the unreacted magnesium. Repetition of the cross-coupling reaction shown in **Scheme 7** was then carried out using an extended reaction time. Again an orange powder was produced which was purified by column chromatography to reveal the presence of unreacted bromoterthiophene and 2-methylthiophene despite the Grignard of 5-bromo-2-methylthiophene clearly being formed.

Another variation we attempted was the zinc mediated coupling of 2-methylthiophene with 5-bromo-2,2':5,2''-terthiophene as suggested by Garnier *et. al*⁵., **Scheme 8**.

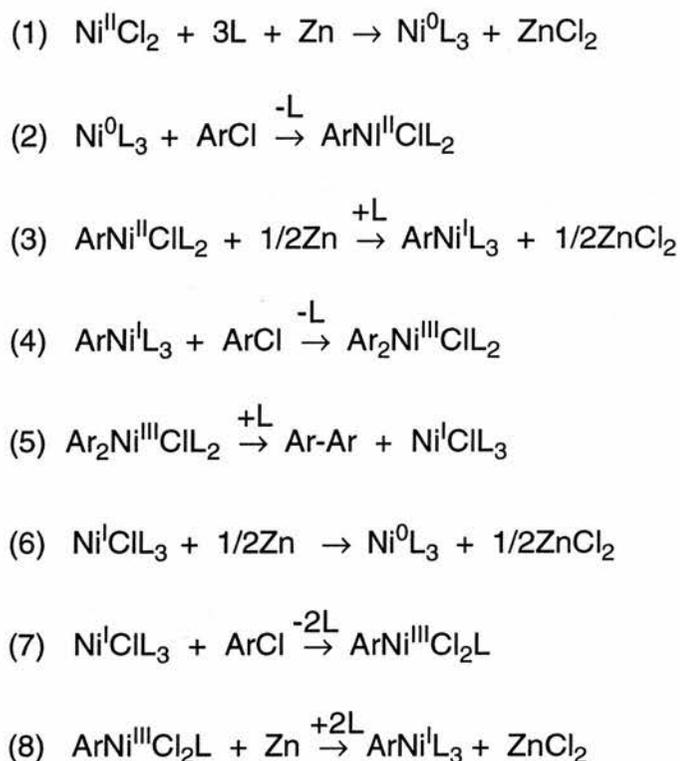


Scheme 8

Spectroscopic analysis of the crude product (again an orange powder) was encouraging, having methyl signals at 2.64 and 2.73ppm which did not correspond with those of the starting material. Column chromatography highlighted fractions containing 2-methylthiophene, terthiophene and bromotriphenylene however the signals at 2.64 and 2.73ppm were not observed in any of the recovered fractions. A possible explanation for this was the inherent insolubility of the target compound which may have resulted in the compound being deposited on the column media.

The crucial step would appear to be the coupling of monothiophene to a terthiophene to form a quaterthiophene. Although the Grignard of the monothiophene was readily formed, the displacement of the halide of the terthiophene does not take place. We therefore decided to investigate alternative coupling reactions to form a quaterthiophene unit. Colon and Kelsey developed a method for synthesising biaryls from aryl chlorides.⁶ The coupling reagent was a catalytic mixture of anhydrous nickel salt and triphenylphosphine in the presence of a reducing metal such as zinc. The reaction occurs rapidly under mild conditions, tolerates a variety of

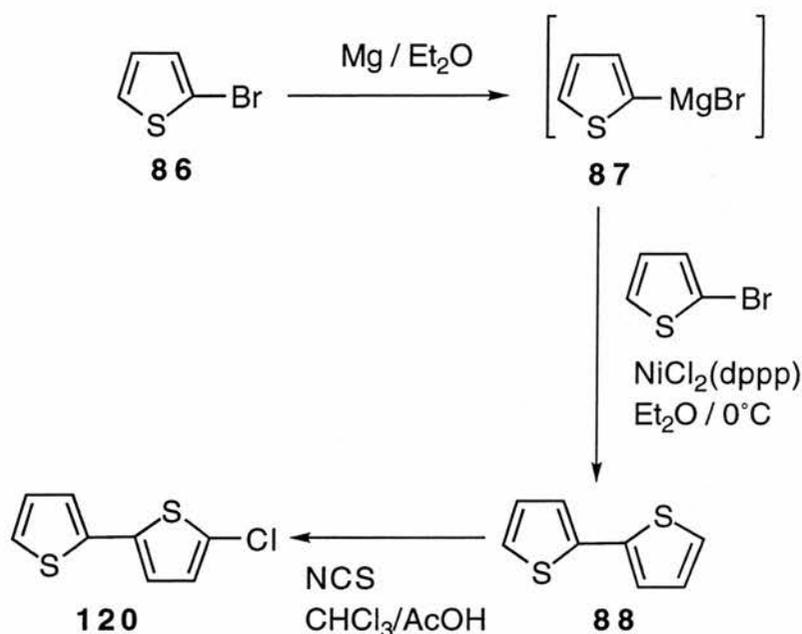
functional groups and employs air stable starting materials. The reaction mechanism is complex but is thought to follow the route shown in **Scheme 9**.



Scheme 9

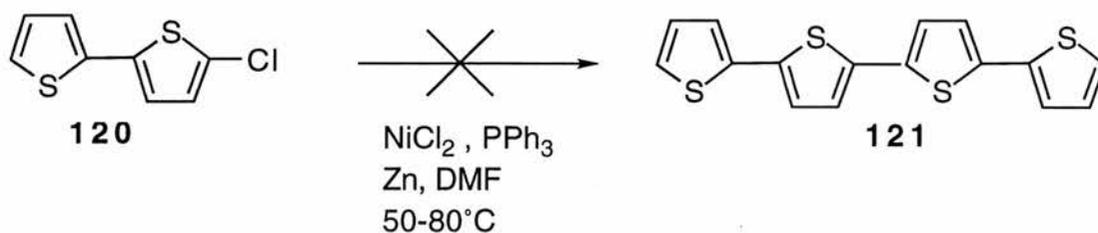
The first step involves reduction of the nickel(II) salt to zero valent nickel by zinc. The second step is oxidative addition, which occurs rapidly to form an aryl nickel(II) intermediate.⁷ Under the reducing conditions of excess zinc, the aryl nickel(II) complex is reduced to an aryl nickel(I) complex (3). This complex oxidatively adds aryl chloride to form a diaryl nickel(III) complex (4), which is known to undergo rapid reductive elimination (5).⁸ The nickel(I) produced in step 5 may be reduced to nickel(0) (6) which re-enters the reaction cycle at step 2. Alternatively it may react with aryl chloride by oxidative addition (7) to yield an aryl nickel(III) intermediate which under highly reducing conditions is reduced to aryl nickel(I) and continues the cycle in step 4.

2,2'-Bithiophene was again formed by the nickel catalysed coupling of 2-bromomagnesiothiophene with 2-bromothiophene. Chlorination of 2,2'-bithiophene was attempted using N-chlorosuccinimide in chloroform/acetic acid, **Scheme 10**.



Scheme 10

This afforded a mixture of 2,2'-bithiophene, 5-chloro-2,2'-bithiophene and 5,5'-dichloro-2,2'-bithiophene. The desired 5-chloro-2,2'-bithiophene was isolated by column chromatography on silica gel using hexane as the eluent. The 5-chloro-2,2'-bithiophene was then used in a nickel catalysed coupling reaction as described by Colon and Kelsey, **Scheme 11**.

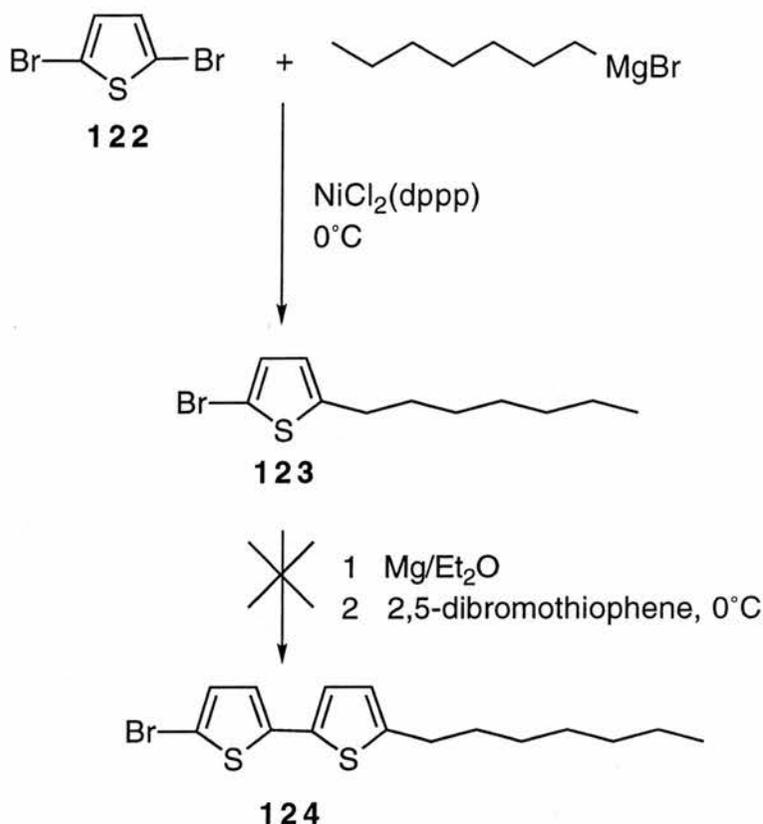


Scheme 11

Upon mixing the anhydrous nickel chloride with triphenylphosphine and zinc dust in dry dimethylformamide under a nitrogen atmosphere a colour change from green to brown/red

occurred. This was indicative of the formation of nickel triphenylphosphine. A nitrogen purged solution of 5-chloro-2,2'-bithiophene was then added which caused the reaction mixture to turn green. According to the paper by Colon and Kelsey when the reaction is complete the characteristic red/brown colour should return; however this was not observed in our reactions. The reaction product was analysed by GCMS and was found to contain mostly triphenylphosphine. The reaction was repeated using 2-chlorothiophene rather than 5-chloro-2,2'-bithiophene on the basis that the intended reaction product 2,2'-bithiophene would be easily detected by GCMS. However the expected colour change in the reaction mixture, indicating the completion of the reaction, was not observed. GCMS of the reaction mixture showed a large excess of triphenylphosphine. This was successfully removed by filtering the excess zinc and removing the solvent by rotary evaporation. The crude product was stirred in xylene with excess methyl iodide to form the insoluble Wittig salt which was removed by filtration. The product was recovered by removal of the solvent and excess methyl iodide to yield a pale yellow powder. Spectroscopic analysis of the product showed the presence of triphenylphosphine oxide but no trace of the coupled product.

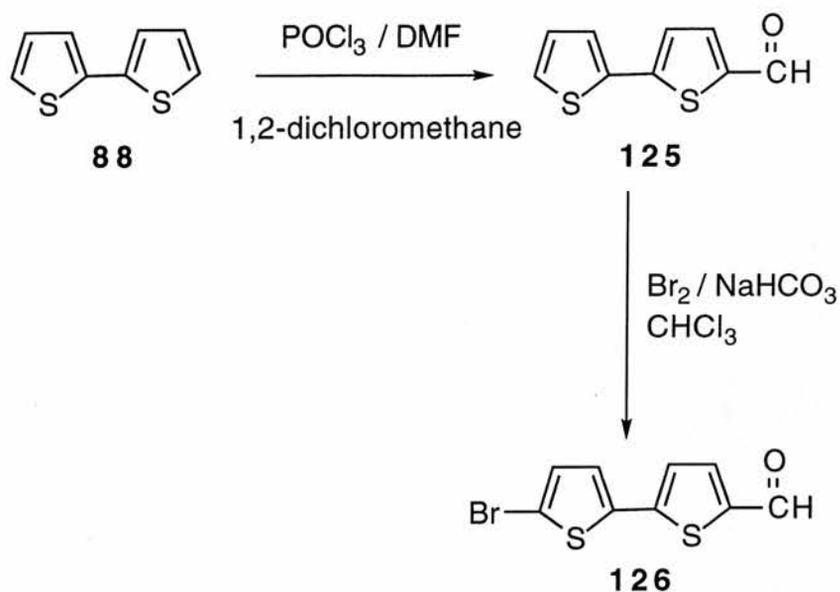
Having failed to produce the quaterthiophene unit by the method of Colon and Kelsey we envisaged forming an alkylated quaterthiophene unit *via* the Stille coupling reaction of 5-alkyl-5'-bromo-2,2'-bithiophene **124** with 5-trimethyltin-2,2'-bithiophene. This would involve the alkylation of 2-bromothiophene with a suitable alkyl group *via* a Grignard reaction. **123** could then be used in a further Grignard coupling reaction with 2,5-dibromothiophene, **Scheme 12**.



Scheme 12

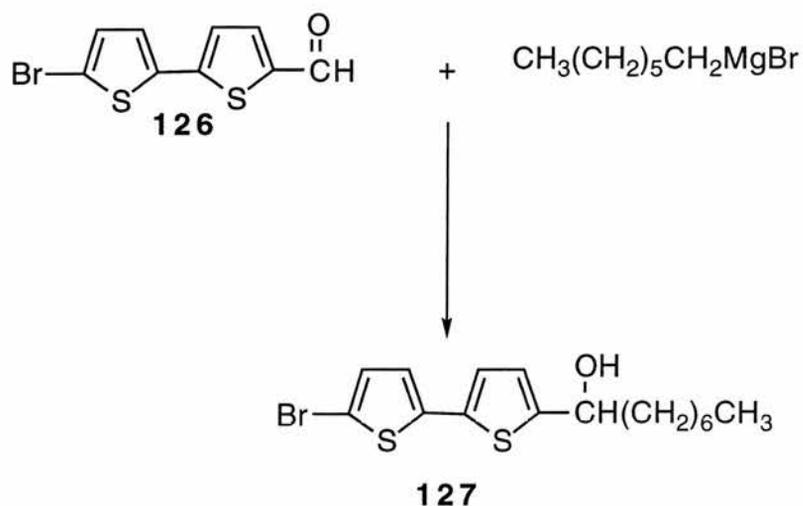
Repeated attempts to couple bromomagnesioalkyls with 2,5-dibromothiophene or 2-bromothiophene yielded only small amounts of the desired product in addition to significant amounts of aryl halide, reduced alkyl halide and long chain alkanes which are formed as a result of homo-coupling of the Grignard reagent. Despite increasing the time for Grignard formation, using fresh catalyst and using an excess of magnesium turnings these side products could not be eliminated. This was surprising given the ease with which 3-hexylthiophene was formed under similar conditions.

We persevered with the idea of forming the quaterthiophene unit via Stille coupling but sought an alternative method for the introduction of the alkyl chain. 2,2'-Bithiophene was formylated using phosphorous oxychloride in dimethylformamide to afford 5-formyl-2,2'-bithiophene **125** in excellent yield. **125** was brominated using a combination of bromine and sodium hydrogen carbonate in chloroform forming 5-bromo-5'-formyl-2,2'-bithiophene, **126** **Scheme 13**.



Scheme 13

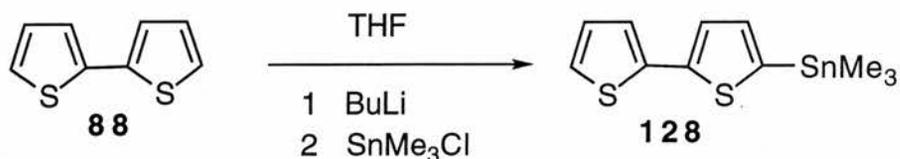
We now felt that treatment of **126** with a bromomagnesioalkyl would result in attack at the carbonyl of **126** affording a brominated bithiophene incorporating a solubilising long chain alcohol as shown in **Scheme 14**.



Scheme 14

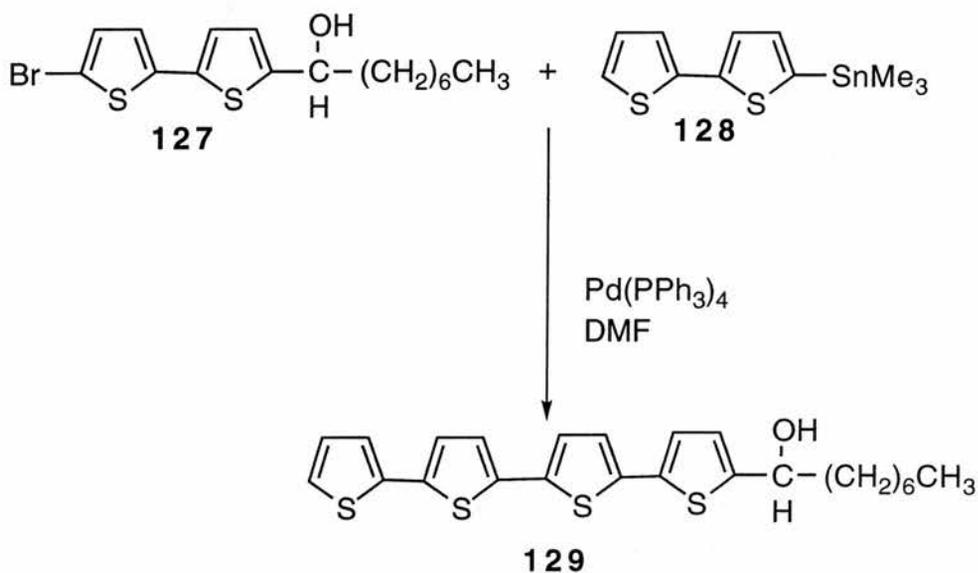
The Grignard of bromoheptane was formed in the usual manner and added dropwise to 5-bromo-5'-formyl-2,2'-bithiophene **126**. Analysis of the ^1H NMR spectrum of the crude

product showed the disappearance of the carbonyl hydrogen and the appearance of signals corresponding to the alkyl chain and the proton adjacent to the resultant alcohol. We then lithiated bithiophene as shown in **Scheme 15** and added one equivalent of trimethyltin chloride to form 5-trimethyltin-2,2'-bithiophene **128**.



Scheme 15

We then attempted to couple the crude products from both reactions, 5-bromo-5'-octan-1-ol-2,2'-bithiophene **127** and 5-trimethyltin-2,2'-bithiophene **128** via a Stille coupling reaction, **Scheme 16**.

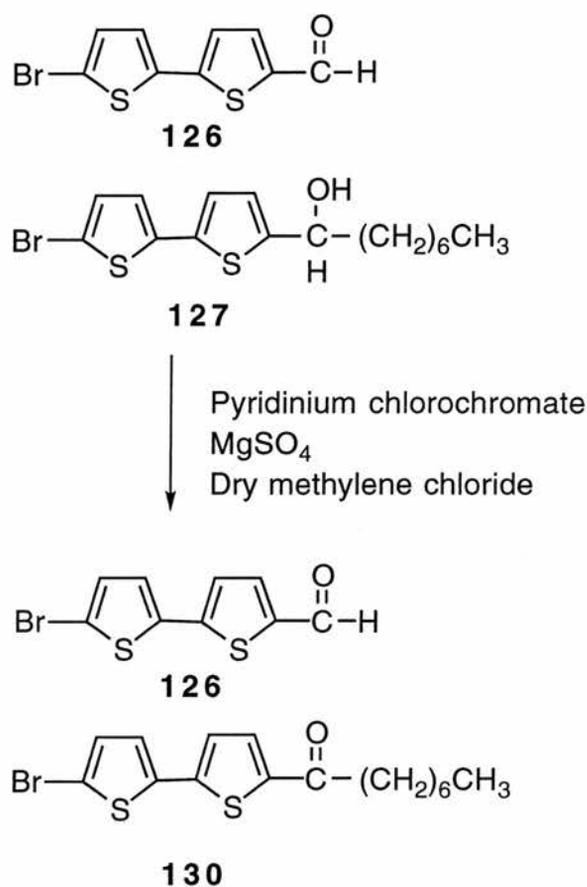


Scheme 16

The resultant red/orange residue was washed with hexane, dichloromethane and ethanol and dried under vacuum. TLC of the crude reaction product indicated a mixture of compounds. Preparative TLC on silica gel using hexane was performed and the fractions analysed by ¹H NMR spectroscopy. The desired product could not be identified but other side products such

as 2,2'-bithiophene were observed. These were present as a result of a failure to purify the starting materials prior to performing the Stille coupling reaction.

We were forced to repeat the reaction between 5-bromo-5'-formyl-2,2'-bithiophene and 1-bromomagnesioheptane whereupon it was found that some of the Grignard reagent was involved in a homo-coupling reaction and as a result we recovered unreacted 5-bromo-5'-formyl-2,2'-bithiophene. Removing the 5-bromo-5'-formyl-2,2'-bithiophene **126** from the 1-(5'-bromobithienyl)heptan-1-ol **127** by column chromatography proved difficult. We therefore performed an oxidation reaction on the mixture using pyridinium chlorochromate which converted the alcohol to the ketone **130**, **Scheme 17**.



Scheme 17

This allowed the isolation of the desired 1-(5'-bromobithienyl)heptan-1-one by column chromatography on silica gel using hexane/ethyl acetate as eluent. Several attempts at forming 5-trimethyltin-2,2'-bithiophene using 1 equivalent of butyl-lithium followed by the addition of

1 equivalent of trimethyltin chloride resulted in an incomplete reaction leaving residual 2,2'-bithiophene which could not be easily removed by distillation or column chromatography. This was rectified however by repeating the reaction using fresh 1.6M butyl lithium solution. Due to time restrictions we were unable to perform the Stille coupling reaction shown in **Scheme 16** using the purified reagents. We would expect to form 5-(1-oxooctan)-2,2':5',2'':5'',2'''-quaterthiophene which could then be brominated to form the necessary component for the Suzuki coupling reaction with 1,3-phenylene bis(1,3,2-benzodioxoborole) as shown in **Scheme 1**.

5.3 Conclusion

We have shown that nickel catalysed coupling of brominated thiophenes with thienyl Grignards can afford high yields of terthiophene, only when sterically demanding alkyl groups are absent. We have also determined that both magnesium and zinc mediated coupling reactions, catalysed by nickel and palladium respectively, cannot be used to form quaterthiophene units. This would appear to be the result of the poor solubility of the starting materials in the reaction solvent. We have also been unsuccessful in our attempts to form quaterthiophene by nickel tris(triphenylphosphine) catalysed coupling of 5-chloro-2,2'-bithiophene.

A potentially successful route would appear to involve introducing the solubilising group by the Grignard reaction of bromomagnesiumheptane with 5-bromo-5'-formyl-2,2'-bithiophene **126**, to yield 5-bromo-5'-(1-oxooctan)-2,2'-bithiophene **127**. This provides a compound which is soluble in organic solvents and incorporates bromine, facilitating a Stille coupling reaction with 5-trimethylstannyl-2,2'-bithiophene **128**. The resultant alkylsubstituted quaterthiophene **129** could be purified as described in this chapter and brominated in order to take part in the Suzuki coupling reaction with a bisboronic acid **30** to afford the desired end-capped oligothiophene **102** as shown in **Scheme 1**.

5.4 Experimental

Refer to the experimental section from chapter 2 for information regarding the collection of experimental data etc.

2,5-Dibromothiophene 108

2-Bromothiophene (20g, 123mmol) was dissolved in 60cm³ of a 50/50 v/v solution of chloroform and acetic acid and the solution cooled to 0°C. N-Bromosuccinimide (21.9g, 123mmol) was added portionwise over 1h at 0°C and the solution was stirred for a further 1h. The solution was diluted with water and the organic layer separated. The aqueous layer was extracted with chloroform (4 x 30cm³) and the combined organic extracts were washed with 2M potassium hydroxide and dried over MgSO₄ to yield a mixture of thiophene, 2-bromothiophene and 2,5-dibromothiophene as a result of a failure to purify the starting material. The title compound was isolated by distillation (88°C/10mmHg) to yield an orange/brown liquid (22.3g, 75%) (lit.⁹ 200-210°C); δ_{H} 6.8(2H, s); δ_{C} 111.5, 130.27.

2,2':5',2''-Terthiophene 107

To a 250cm³ round bottomed flask equipped with a condenser, magnetic stirring bar and septum inlet were added magnesium turnings (2.67g, 111mmol) followed by freshly dried diethyl ether (50cm³) under a nitrogen atmosphere. Freshly distilled 2-bromothiophene was added dropwise over 15min and the solution stirred at reflux for 4h to allow Grignard formation. The solution was then allowed to cool and transferred *via* catheter to a dropping funnel and added slowly to a flask containing 2,5-dibromothiophene (10.0g, 41.36mmol) and nickel chloride diphenyl(phosphino)propane (0.30g, 0.55mmol) over 2h before being stirred at reflux for 24h. The solution was then poured over ice and the organic layer separated. The aqueous layer was extracted with ether and the combined organic fractions dried over MgSO₄

before removal of the solvent to yield the crude product which was recrystallised from hexane to yield 2,2':5',2''-terthiophene as yellow/green crystals (9.2g, 89%); m.p. 94-95°C (lit. 94-95°C¹⁰); δ_{H} 7.22 (2H, dd J 5.1 and 1.0), 7.16 (2H, dd J 3.7 and 1.2), 7.05 (1H, dd J 3.9), 7.01 (2H, dd J 5.1 and 3.7), 6.99 (1H, d J 3.9); δ_{C} 124.2, 124.8, 125.0, 128.3;

5-Bromo-2-methylthiophene¹¹ 116

To a solution of 2-methylthiophene (10.0g, 102mmol) in 50/50 v/v chloroform/acetic acid (80cm³), portions of N-bromosuccinimide (18.1g, 102mmol) were added at 0°C over a 1h period. The solution was then allowed to stir for a further 1h before being diluted with water. The mixture was poured into a separating funnel and the organic layer separated. The aqueous layer was extracted with chloroform (3 x 30cm³) and the combined organic extracts washed with 2M potassium hydroxide. The solution was then dried over MgSO₄ and the solvent removed by rotary evaporation to yield 14.3g (79%) of the title compound; δ_{H} 2.44 (3H, s, CH₃), 6.53 (1H, d J 2), 6.85 (1H, d J 2); m/z 178 (M⁺, 18%), 176 (M⁺, 18%), 97 (100), 81(5), 69(22), 57 (19), 53 (52), 45 (49), 39 (19), 27 (14);

5-Bromo-2,2':5',2''-terthiophene 109

2,2':5',2''-Terthiophene (5.0g, 20mmol) was dissolved in a 50/50 v/v chloroform/acetic acid solution and the solution cooled to 0°C. N-Bromosuccinimide (3.6g, 20mmol) was added portion wise over a 1h period and the solution allowed to stir for a further 1h. The solution was diluted with water and transferred to a separating funnel where the organic layer was removed and the aqueous layer extracted with chloroform. The combined organic extracts were washed with 2M potassium hydroxide and dried over MgSO₄ and the solvent removed by rotary evaporation. The residue was dissolved in hot CHCl₃ containing charcoal, filtered through Celite and concentrated in vacuo. The final residue was purified by crystallisation from a mixture of THF and hexane to yield the title compound (3.6g, 54%); m.p. 132-134°C (lit. 135-136°C¹²); δ_{H} 7.22 (1H, dd J 5.1 and 1.0), 7.16 (1H, dd J 3.7 and 1.2), 7.05 (1H,

dd J 3.9), 7.01 (1H, dd J 5.1 and 3.7), 6.99 (1H, d J 3.9), 6.96 (1H, d J 3.9), 6.89 (1H, d, J 3.9); δ_C 124.2, 124.4, 124.8, 125.0, 125.2, 128.4, 131.18, 131.2;

Attempted preparation of 2-(thiomethylethanoate)thiophene 112

A solution of freshly distilled 2-bromothiophene (5.0g, 31.2mmol) in dry THF (30cm³) was cooled to -78°C whereupon 1.6M n-butyl lithium in hexanes (19.6cm³, 31.2mmol) was added and the solution allowed to warm to 0°C and stirred at 0°C for 10min. The solution was cooled to -78°C and powdered sulphur (1.0g, 31.2mmol) added with further stirring until the solution warmed to room temperature. The solution was again cooled to -78°C and a solution of bromoethylacetate (3.5cm³, 31.2mmol) added. The solution was allowed to stir overnight and was then poured over ice. The organic layer was separated and the aqueous layer extracted with dichloromethane. The combined organic extracts were dried over MgSO₄ and the solvent removed by rotary evaporation. Analysis of the reaction mixture by GCMS showed a mixture of products; **bromoethylacetate** m/z 168 (M⁺, 2%), 166 (M⁺, 2%), 138 (5), 121 (10), 93 (9), 42 (19), 29 (100); **2-butylthio(thiophene)** m/z 172 (M⁺, 20%), 116 (100), 71 (52), 57 (26), 45 (33), 41 (53), 29 (100); **2-(ethoxythioacetate)thiophene** m/z 202 (M⁺, 24%), 174 (4), 129 (48), 115(22), 85(29), 71 (51), 45 (100), 39 (22), 29 (49), 18 (57);

Attempted preparation of 5-methyl-2,2':5',2'':5'',2'''-quaterthiophene 118 via Grignard coupling.

To a flask containing dry Mg turnings (0.44, 18.5mmol) was added 2-bromo-5-methylthiophene (2.5g, 14.2mmol) in dry diethyl ether under a nitrogen atmosphere. The solution was refluxed for 5h before being transferred to a pressure equalising dropping funnel *via* catheter and added dropwise to a flask containing 5-bromo-2,2':5',2''-terthiophene and nickel chloride(diphenylphosphino)propane (0.25g, 0.48mmol) in dry THF, at 0°C. The solution was then refluxed for 24h before being poured over ice and the organic layer separated and the aqueous layer extracted with dichloromethane. The combined organic extracts were

then dried over MgSO_4 and then concentrated to yield an orange solid. The material was then absorbed onto silica gel and subjected to dry column flash chromatography using hexane/ethyl acetate as eluent. The recovered fractions were analysed by ^1H NMR spectroscopy and GCMS but were found to contain 2-methylthiophene, 5-bromo-2,2':5',2''-terthiophene and trace amounts of 5-bromo-2-methylthiophene. The reaction was repeated but similar results were obtained.

Attempted preparation of 5-methyl-2,2':5',2'':5'',2'''-quaterthiophene 118 via zinc mediated coupling.

Into a dry three necked round bottom flask was placed 5-bromo-2-methylthiophene (1.2g, 6.6mmol) in dry THF (40 cm^3). To this solution was added freshly distilled TMEDA (1.2 cm^3 , 7.8mmol) followed by 1.6M butyl lithium in hexanes (4.91 cm^3 , 7.8mmol) at -60°C . The solution was left to stir at -60°C for 1h before a solution of ZnCl_2 (1.0M in ether, 7.8 cm^3) was added at -60°C and the temperature allowed to rise to rt. To this was added a solution of 5-bromo-2,2':5',2''-terthiophene (2.0g, 6.6mmol) in 40 cm^3 of dry THF, dropwise, in the presence of $\text{Pd}(\text{PPh}_3)_4$ (0.30g, 0.25mmol). The mixture was stirred for 24h and the THF removed by rotary evaporation to yield an orange solid. The orange solid was dissolved in dichloromethane then washed with water. The organic phase was then separated and dried over MgSO_4 . ^1H NMR spectroscopy of the crude product showed 3 methyl signals at 2.42, 2.64 and 2.73ppm. The integral of the peak at 2.42ppm suggested that the majority of the starting materials had been consumed in the reaction. The crude product was purified by column chromatography however only 2-methylthiophene and 5-bromo-2,2':5',2''-terthiophene were identified in the recovered fractions. The signals at 2.64 and 2.73ppm were not observed.

2,2'-Bithiophene 88

To Mg turnings (0.88g, 36.8mmol) in dry THF (25cm³) was added 2-bromothiophene (4.5g, 27.6mmol) and the solution stirred at reflux for 4h to allow formation of the Grignard. The Grignard was then transferred via catheter to a dropping funnel and added dropwise to 2-bromothiophene (4.5g, 27.6mmol) in THF (20cm³) in the presence of a NiCl₂(dppp) catalyst (0.25g, 0.46mmol) at 0°C. The solution was stirred at this temperature for 45 min. before being refluxed overnight whereupon it had turned dark orange in colour. The solution was then poured over ice and extracted with dichloromethane. The combined extracts were then dried over MgSO₄ and the solvent removed by rotary evaporation, to yield a green/brown solid 3.96g (87%).m.p. 32-33°C (lit. 32-33°C¹³; δ_{H} 7.00-7.05 (2H, m), 7.20-7.25 (4H, m); δ_{C} 123.69, 124.25, 127.66, 137.33; GCMS, **peak no.**, *m/z* (relative intensity): **447**, 166(M⁺, 100), 134(27), 127(12), 121(70), 108(18), 102(6), 90(13), 77(25), 69(50), 63(25), 58(30), 51(19), 45(75), 39(2).

5-Chloro-2,2'-bithiophene¹⁴ 120

2,2'-Bithiophene (1.0g, 6.0mmol) was dissolved in a 50/50 v/v solution of chloroform/acetic acid (60cm³) and the solution cooled to 0°C. N-Chlorosuccinimide (0.8g, 6mmol) was then added over 1h and the solution left to stir for 1h. The solution was then diluted with distilled water and the organic layer separated. The aqueous layer was further extracted with chloroform and the organic layers combined. The combined layers were washed with 2 x 100cm³ portions of 2M potassium hydroxide and dried over MgSO₄ and the solvent removed by rotary evaporation to yield 1.1g of crude product. GCMS showed the product to consist of 2,2'-bithiophene, 5-chloro-2,2'-bithiophene and 5,5'-dichloro-2,2'-bithiophene. **5-Chloro-2,2'-bithiophene** (0.52g, 43%) was isolated by column chromatography on silica gel using hexane as eluent; δ_{H} 7.22 (1H, d *J* 3), 7.10 (1H, d *J* 3), 7.00 (1H, t, *J* 4), 6.92 (1H, d *J* 3), 6.80 (1H, d *J* 3); δ_{C} 123.2, 124.5, 125.3, 127.9, 128.5; *m/z* 200 (M⁺, 84%), 165 (68), 155 (15), 121(100), 69 (87), 63 (33), 45 (95), 39 (25);

Attempted preparation of 2,2':5',2'':5'',2'''-quaterthiophene 121

The catalyst was prepared by stirring anhydrous nickel chloride (0.017g, 0.13mmol) with triphenylphosphine (0.26g, 0.98mmol) and zinc dust (0.26g, 4.0mmol) in dry dimethylformamide (15cm³) under a nitrogen atmosphere between 40-50°C. The reaction mixture changed colour from green to brown/red which indicated the formation of nickel tris(triphenylphosphine). A nitrogen purged solution of 5-chloro-2,2'-bithiophene (0.52g, 2.6mmol) in dimethylformamide (10cm³) was then added which turned the reaction green and the mixture was heated between 50-80°C. On completion of the reaction, the colour should return to a red/brown, however, after 24h the reaction mixture remained a grey/green colour. The zinc dust was removed by filtration and the filtrate diluted with chloroform (500cm³) and washed with distilled water (4 x 500cm³) followed by brine (250cm³). The organic phase was dried over MgSO₄ and the chloroform removed by rotary evaporation. The product was isolated from dimethylformamide by dilution with distilled water and continuous extraction into diethyl ether. The ether was removed by rotary evaporation to yield a yellow crystalline solid which was discovered to be triphenylphosphine by both ¹H NMR spectroscopy and GCMS.

Attempted preparation of 2,2-bithiophene 88 via Ni(PPh₃)₃ catalysed coupling of 2-chlorothiophene.

The catalyst was prepared by stirring anhydrous nickel chloride (0.13g, 1.0mmol) with triphenylphosphine (2.0g, 7.6mmol) and zinc dust (2.0g, 30.6mmol) in dry dimethylformamide (15cm³) under a nitrogen atmosphere between 40-50°C. The reaction mixture changed colour from green to brown/red which indicated the formation of nickel tris(triphenylphosphine). A nitrogen purged solution of 2-chlorothiophene (2.37g, 20.0mmol) in dimethylformamide (10cm³) was then added which turned the reaction green and the mixture was heated to between 50-80°C. On completion of the reaction, the colour should return to red/brown, however, after 24h the reaction mixture remained a grey/green colour. The zinc

dust was removed by filtration and the filtrate diluted with chloroform (500cm³) and washed with distilled water (4 x 500cm³) followed by brine (250cm³). The organic phase was dried over MgSO₄ and the chloroform removed by rotary evaporation. The product was isolated from dimethylformamide by dilution with distilled water and continuous extraction into diethyl ether which was removed by rotary evaporation. The crude product was stirred in xylene with excess methyl iodide to form the insoluble Wittig salt which was then removed by filtration. The product was recovered by removal of the solvent and methyl iodide to yield a pale yellow powder which was found to contain triphenylphosphine oxide. Signals corresponding to the desired 2,2-bithiophene were not observed by either ¹H NMR spectroscopy or GCMS.

General procedure for coupling of alkyl bromides to 2,5-dibromothiophene

Magnesium turnings (1.3 eqv.), diethyl ether and 1-bromoalkane (1 eqv.) were stirred, under nitrogen, in a 500cm³ three necked flask, fitted with a reflux condenser. After refluxing for 5h, the mixture was transferred via catheter and added dropwise at 0°C to a 1000cm³ three neck flask containing 2,5-dibromothiophene or 2-bromothiophene (1 eqv.), NiCl₂(dppp) (250mg, 0.46mmol) and diethyl ether. The mixture was then refluxed overnight and poured over a mixture of ice and HCl. After extraction with Et₂O (3 x 100cm³), the mixture was dried over MgSO₄ and the product obtained by fractional distillation.

We attempted this reaction with 1-bromotetradecane, 1-bromoheptane and 1-bromohexane however on each occasion the Grignard reagent preferred to take part in a homo-coupling reaction rather than take part in cross-coupling reaction with the aryl halide. As a result of this competitive side reaction only moderate amounts of 2-alkylthiophene were formed.

5-Formyl-2,2'-bithiophene 125

Phosphorous oxychloride (3.25cm³, 35mmol) was added to a solution of 2,2'-bithiophene (5.0g, 30mmol) and dimethylformamide (2.75cm³, 35mmol) in 1,2-dichloroethane (100cm³) cooled in an ice bath. The solution was then warmed to room temperature and heated to reflux. After refluxing overnight the yellow suspension was cooled to room temperature and poured into a saturated aqueous sodium acetate solution (500cm³) and stirred for 2h to complete the hydrolysis. The suspension was then extracted with dichloromethane (3 x 300cm³). The organic layers were combined and washed with water (1 x 100cm³), dried over MgSO₄ and concentrated in vacuo to yield the title compound as yellow crystals (5.48g, 94%); m.p. 56-58°C (lit.¹⁵ 58-59°C); δ_{H} 7.08 (1H, t *J* 4.3), 7.25 (1H, d, *J* 3.8), 7.36 (2H, d *J* 4.3), 7.67 (1H, d *J* 3.8), 9.86 (1H, s); δ_{C} 124.7, 126.7, 127.6, 128.9, 137.9, 183.1.

5-Bromo-5'-formyl-2,2'-bithiophene 126

To a solution of 5-formyl-2,2'-bithiophene (5.0g, 25mmol) in chloroform (100cm³) was added sodium bicarbonate (4.28g, 30mmol), followed by the dropwise addition of a solution of bromine (4.8g, 30mmol) in chloroform (100cm³) over a period of 1h. The reaction mixture was refluxed for 4h and then cooled and filtered. The filtrate was washed with water (2 x 100cm³) and dried over MgSO₄. Upon evaporation of solvents, the solid residue was chromatographed on silica gel using hexane/ethyl acetate as eluent to yield the title compound as a yellow solid (5.95g, 85%); m.p. 141-144°C (lit.¹⁶ 141-145°C); δ_{H} 7.04(1H, d *J* 4.0, 7.11(1H, d *J* 4.0), 7.18(1H, d *J* 4), 7.66(1H, d *J* 4), 9.87(1H, s).

Cross-coupling reaction of 1-bromomagnesioheptane with 5-bromo-5'-formyl-2,2'-bithiophene

Freshly distilled diethyl ether (30cm³) was added to Mg turnings (0.18g, 7.6mmol) under a nitrogen atmosphere. 1-Bromoheptane (1.0g, 5.7mmol) was introduced and the solution

stirred at reflux for 5h. The solution was allowed to cool and transferred to a dropping funnel and added dropwise to a suspension of 5-bromo-5'-formyl-2,2'-bithiophene (1.55g, 1.6mmol) in THF (30cm³) at -78°C over a period of 30min. The reaction was slowly warmed to room temperature and stirred for 4h under nitrogen. A saturated aqueous NH₄Cl solution (20cm³) was added and the mixture extracted with ether (3 x 50cm³). The combined organic fractions were washed with water and dried over MgSO₄ and evaporated to give the crude alcohol as a yellow solid (1.8g, 85%). ¹H NMR spectroscopy showed a triplet at 0.9ppm and two broad singlets at 1.3 and 1.8ppm, suggesting the incorporation of the alkyl chain. The signal corresponding to the aldehyde proton had disappeared and been replaced by a triplet at 2.85ppm and broad singlets at 3.7ppm and 4.8ppm relating to the hydrogens adjacent to the alcohol on the alkyl chain, the hydrogen directly attached to the hydroxylated carbon and the hydroxyl proton respectively. The crude product was then utilised in a Stille coupling reaction with 5-trimethylstannyl-2,2'-bithiophene.

5-Trimethylstannyl-2,2'-bithiophene **128**

1.6M Butyllithium (12.3cm³, 19.8mmol) was added to 2,2'-bithiophene (3.0g, 18mmol) in THF (40cm³) at -70°C and the mixture stirred for 30 minutes. After addition of trimethyltin chloride (3.58g, 18.0mmol) in THF (15cm³) the solution was stirred at -70°C for 45min. and allowed to stir, with the temperature rising, overnight. The yellow solution was poured into water and extracted with diethyl ether. The combined organic layers were washed with water and dried over MgSO₄. Evaporation of the solvent afforded the title compound as a green oil (4.33g, 73%); ¹H NMR (CD₃CN) δ_H 7.15 (1H, d, *J* 3.3), 7.10 (1H, dd *J* 1.0 and 5.1), 7.05 (1H, dd *J* 1.0 and 3.7), 6.98 (1H, d *J* 3.3), 6.87 (1H, dd *J* 3.7 and 5.1), 0.27 (9H, s); δ_C -8.2, 123.5, 124.1, 125.0, 127.7, 135.8, 138.2, 138.8, 143.5; *m/z* 330 (M⁺, 6%), 315 (18), 285 (10), 207 (1), 166 (9), 133 (100), 121 (22), 89 (40), 77 (14), 69 (19), 63 (22), 45(24), 39 (13), 18(11);

Attempted Stille coupling of 5-bromo-5'-octan-1-ol-2,2'-bithiophene with 5-trimethylstannyl-2,2'-bithiophene

5-Trimethylstannyl-2,2'-bithiophene (0.9g, 2.73mmol) was dissolved in dimethylformamide (25cm³) and 5-bromo-5'-octan-1-ol-2,2'-bithiophene (1.0g, 2.73mmol) added followed by Pd(PPh₃)₄ (0.2g, 0.17mmol). The solution was degassed twice and was then heated at 70-80°C overnight. The resultant red orange solution was cooled and filtered and washed with hexane (400cm³), dichloromethane (400cm³) and ethanol (200cm³) before being dried under vacuum. The crude product was subjected to prep. TLC on silica gel using hexane as the eluent. The fractions were analysed by ¹H NMR spectroscopy, however, the coupled product could not be identified. It was found that compounds such as 2,2-bithiophene and 5-bromo-5'-formyl-2,2'-bithiophene had been carried through from previous reactions.

Isolation of 5-bromo-5'-(oxooctan)-2,2'-bithiophene **130 via oxidation and column chromatography**

A mixture of 5-bromo-5'-octan-1-ol-2,2'-bithiophene and 5-bromo-5'-formyl-2,2'-bithiophene (1.0g) were dissolved in dry methylene chloride (50cm³). To this solution pyridinium chlorochromate (3.23g, 15mmol) was added under nitrogen followed by oven dried MgSO₄ (5.0g). The mixture was stirred at room temperature for 5h. Diethyl ether (200cm³) was added and the resultant mixture filtered through Celite. The filtrate was dried over MgSO₄ and concentrated in vacuo. Chromatography of the residue on silica gel using hexane/ethyl acetate afforded 5-bromo-5'-(oxooctan)-2,2'-bithiophene (0.6g, 87%)[†]; 0.90(3H, t *J* 4), 1.30(8H, bs), 1.72(2H, bt, *J* 4), 2.85(2H, t, *J* 9), 7.01(1H, d *J* 4), 7.05(1H, d *J* 4.0), 7.10(1H, d *J* 4), 7.58(1H, d *J* 4); δ_C 14.6, 23.1, 25.4, 29.6, 29.8, 32.18, 39.58, 113.8, 124.7, 126.0, 131.53, 132.9, 143.3, 193.7;

[†] Yield based on the mass of isolated aldehyde **128**, formed by the oxidation of alcohol **127**.

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Chapter Six

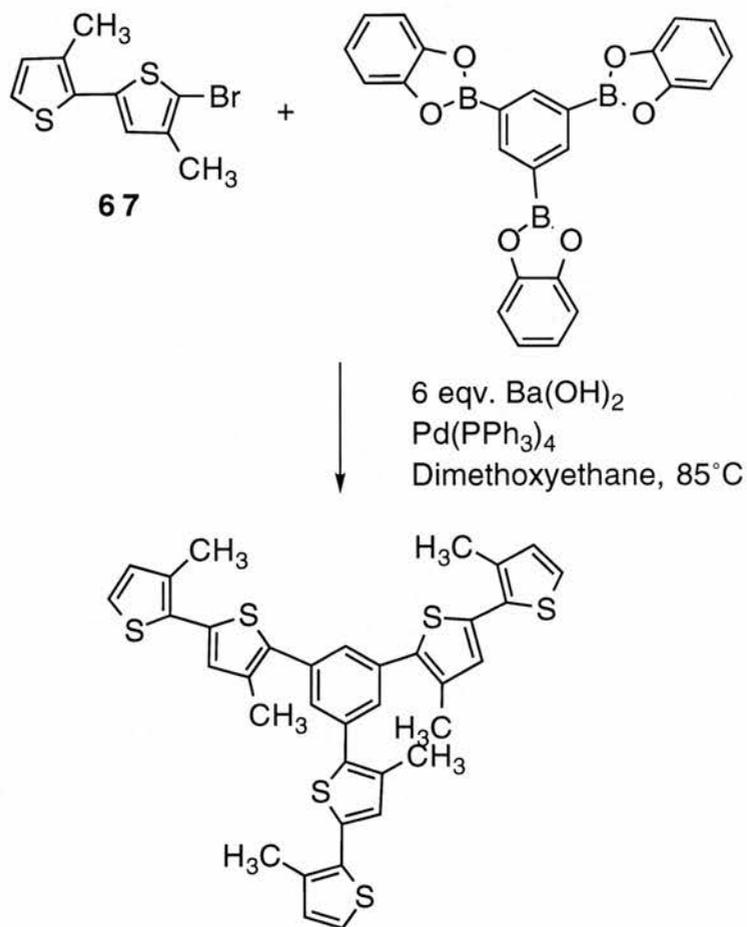
Conclusions and Future Work

6.0 Conclusions and Future Work

A series of polymers (**P31**, **P77**, **P83**, **P84**, **P85** and **P99**) have been synthesised and characterised by cyclic voltammetry and ESR spectroscopy. Polymers such as **P99** were easily synthesised and polymerised. However, although **P99** exhibited a high number of spins it may suffer from bipolaron formation as suggested by the two oxidations peaks observed in the CV of **P99**. We have suggested that bipolaron formation could be avoided by the incorporation of alkyl substituents on the SCU. **P31** and **P84** both contained alkyl substituents to prevent π -dimerisation and also stabilise the resultant polarons. However the methyl substituted polymer, **P84**, proved easier to synthesise and polymerise than the hexyl substituted polymer **P31** which was not soluble in the solvents required for electropolymerisation. Cyclic voltammetry and ESR studies of **P84** suggested that the alkyl substituents prevented bipolaron formation and also that local intramolecular and weak intermolecular ferromagnetic interactions may occur in **P84**. The next logical step would therefore be to study the magnetic properties of **P84** by SQUID magnetometry, if sufficient quantities of **P84** are available.

Characterising polymeric materials such as **P84** can be hindered by spin defects, intermolecular ferromagnetic interactions between chains and the effect of extended conjugation on oxidation potentials. To avoid these problems a study of the spin interactions in an end-capped oligomeric model should be undertaken. This would allow doping of the SCU to be carried out without polymerisation. A route towards an end capped oligomer similar to **P84** and **P99** has been initiated and outlined in Chapter 5.

A more ambitious, but rewarding, project would involve the synthesis of a 3-dimensional variant of **P84**. This would involve a Suzuki coupling reaction involving three equivalents of 3,4'-dimethylbithiophene and 1,3,5-ter boronic ester, **Scheme 1**. 1,3,5-ter(trimethylsilyl)benzene could be converted to the boronic ester using the conditions detailed in chapter 2.



Scheme 1

The experimental conditions for these reactions have been established in chapter 2.

The product of the Suzuki coupling reaction could then be electrochemically polymerised to yield a polymer which would have 3-dimensional ferromagnetic interactions and hopefully a higher T_c value