Oligomeric tetrathiafulvalenes in supramolecular chemistry

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A Thesis submitted for the degree of Doctor of Philosophy
at the University of Durham

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ABSTRACT

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A range of highly ordered dendritic and oligomeric macromolecules, functionalised with tetrathiafulvalene (TTF) derivatives as a redox-active sub-unit were assembled. In particular, the first dendritic macromolecules incorporating TTF were constructed by the reaction of poly-acid chlorides and alcohol functionalities. Electrochemical techniques showed the novel redox-superstructures to be efficient π-electron donors that are able to undergo two reversible, multi-electron oxidations. The TTF-units were established to be acting independently, and the extent to which the redox groups could be oxidised was evaluated. UV studies demonstrated the redox-assemblies to be capable of forming charge-transfer complexes in solution and showed potential for the formation of conducting charge-transfer complexes. Preliminary studies showed the precursors to these compounds to be suitable for use as electrochemical detectors for dopamine.

Structural variation of the core units increased the air and thermal stability of the dendritic materials, whilst retaining the characteristics of the multi-redox system. These systems formed stable aggregates of the radical cation and afforded conducting charge-transfer complexes with TCNQ.

The new precursors to multi-TTF systems were then used in attempts to impart redox characteristics on [2]pseudorotaxanes and rotaxanes.

Preliminary attempts were made to assemble multi-TTF systems using a TTF derivative as a core and at the periphery.

CONTENTS

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I would now like to thank the one person who served as my primary motivation and has always been my inspiration, my fiancée Christy, this work is for her.

Wayne Devonport, July 1995.

Declaration

The work described in this thesis was carried out by the author, in the Department of Chemistry, University of Durham and at the Université d'Angers, France, between October 1992 and July 1995. It has not been submitted previously for a degree at this, or any other university.

Statement of Copyright

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List of Abbreviations

BEDT-TTF	Bis(ethylenedithio)TTF
c	Coupling Site
CA	Chronoamperometry
CI	Chemical Ionisation
CV	Cyclic Voltammetry
D	Dendrimer
DMAP	4-Dimethylaminopyridine
DMF	*N,N*-Dimethylformamide
DMSO	Dimethyl Sulfoxide
EI	Electron Ionisation
ESR	Electron Spin Resonance
FAB	Fast Atom Bombardment
f_p	Protected Functionality
f_r	Reactive Functionality
LDA	Lithium Diisopropylamide
NMR	Nuclear Magnetic Resonance
PAMAM	Poly(amidoamine)
PDMS	Plasma Desorption Mass Spectroscopy
s	Surface Functionality
TCNQ	7,7,8,8-Tetracyano-*p*-quinodimethane
tlc	Thin Layer Chromatography
TMTSF	Tetramethyltetraselenafulvalene
TBAF	Tetrabutylammonium Fluoride
TTF	Tetrathiafulvalene
THF	Tetrahydrofuran
UME	Ultra Micro Electrode
UV	Ultraviolet
W	Dendron Wedge

"We shall not cease from exploration

And the end of all our exploring

Will be to arrive where we started

And know the place well for the first time"

T.S. Eliot.

... For Christy.

CHAPTER ONE

INTRODUCTION

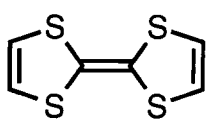
1.1 General Introduction

'Supramolecular chemistry may be defined as the chemistry beyond the molecule, bearing on the organised entities of higher complexity that results from the association of two or more chemical species...'

A citation from Jean-Marie Lehn's definition of supramolecular chemistry[1]

We are part of a world that exists due to the ability of biological systems to self-assemble complex materials in an ordered and precise manner with high structural definition and accuracy. This fascinating occurrence of order, structure and symmetry is apparent in the environment that surrounds us. Chemists are now attempting to mimic nature with the assembly of large molecular structures by utilisation of conventional and novel synthetic strategies. Chemistry has started to take the steps out from the molecule, to chemistry beyond the molecule, into the realms of supramolecular chemistry. In this context, the work in this Thesis describes the construction of highly ordered, oligomeric and polymeric macromolecules containing accurately placed redox-active moieties at their periphery.

The macromolecular structures assembled in the course of this work share two common features; in that they are all i) oligoesters ii) decorated with the redox-active subunit, tetrathiafulvalene (TTF) **1**.



Tetrathiafulvalene (TTF) **1**

The tetrathiafulvalene system has remarkable properties that have led to varied exploitation and derivatisation by many workers since the first publication in 1970 by Wudl *et al.*[2] Recently, the tremendous value that TTF can have when incorporated into other materials has been recognised. There is a hope that molecular designs

incorporating TTF units will impart redox-activity to the host structure, to create a range of materials with novel and exciting properties, which have the potential to be applied to many different uses.

1.2 Introduction to Dendritic Macromolecules

Dendritic Macromolecules (dendrimers) have their basis in polymer chemistry; they are assembled by the iterative reaction of a monomer unit with a reactive, growing, polymer chain. The materials obtained by this process have a molecular weight distribution, due to the polymer chains in the sample having a variety of lengths and weights. This area of chemistry is relatively well understood in terms of the physical and chemical characteristics of the molecules formed.[3]

The principles behind the assembly of dendrimers are apparent in the world of nature. All around us we see complex constructions with a strictly controlled symmetry and topology, which have been based upon smaller sub-units being brought together to form larger superstructures. Examples of this type of assembly in nature include trees and coral. It was when the power of nature's ability to produce such supramolecular entities was recognised, that the idea of the chemical assembly of branched polymeric systems was born.

1.2.1 The History of Dendritic Macromolecules

The theory behind the production of branched polymeric systems was first discussed in 1952 in the pioneering work of Flory.[4] His theoretical paper introduced the preparation of polymers from the "branch-on-branch" approach. Monomer units had a single type A functional group and two or more type B functional groups, so-called AB_X type monomers, where X is the number of branched functionalities (Figure 1.2.1). Reactions were restricted to those between a type A and a type B functional group and each polymer assembly would contain one unreacted type A functionality, provided that no intermolecular reaction took place. With no intermolecular reaction

occurring, the systems produced would be extensively branched, but would not form cross-linked networks, hence producing a hitherto unknown polymeric system.

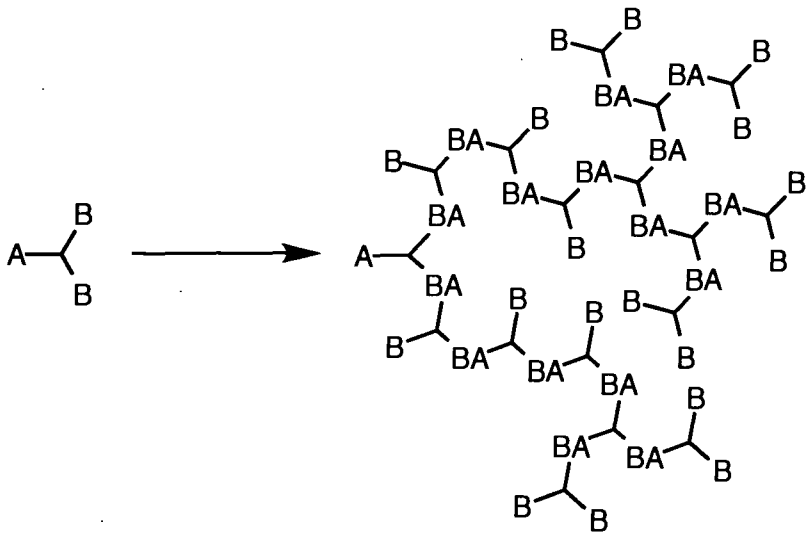
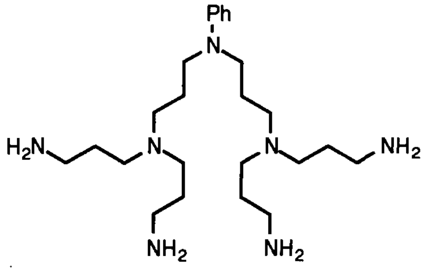


Figure 1.2.1 *A Schematic View of AB_2-type Polymerisation*

The theories of Flory were first realised in 1978 when Vögtle *et al.* reported an isolated example of the preparation of a series of "cascade" molecules.[5] The work utilised a protection/deprotection scheme involving assembling branches upon branches. A Michael addition of an amine to acrylonitrile was employed, followed by the reduction of the nitrile group to an amino functionality. The resulting amine could then be treated further with acrylonitrile and reduced to produce branched structure **2.**

Whilst Vögtle's work was pioneering, it was carried out with difficulty and resulted in poor yields. It is perhaps due to this fact that there were no subsequent reports of "cascade" synthesis until the mid-1980's. By this time, the research groups of Newkome and Tomalia had published their initial work. Newkome *et al.* studied poly(amidoalcohol) structures,[6] such as **3**, which they named "Arborols" (derived from the Latin word for "tree-like") and Tomalia *et al.* studied poly(amidoamine) structures (PAMAM)[7] which they termed "Starburst", or "Dendritic" (Greek word *dendritic*, meaning branched) polymers.



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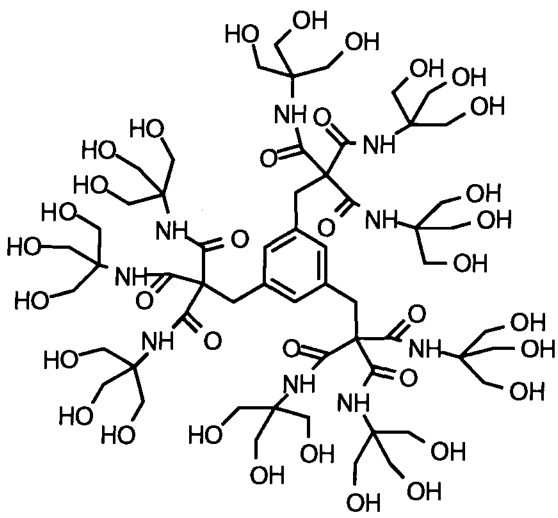
Tomalia's PAMAM dendrimers were synthesised from a nucleophilic core, by exhaustive Michael addition of an amine, *e.g.* ammonia to methyl acrylate, to yield a triester. Subsequent addition of a large excess of ethylenediamine produced a terminal triamine. Repetition of these steps leads to the construction of a larger dendritic macromolecule (Scheme 1.2.1).



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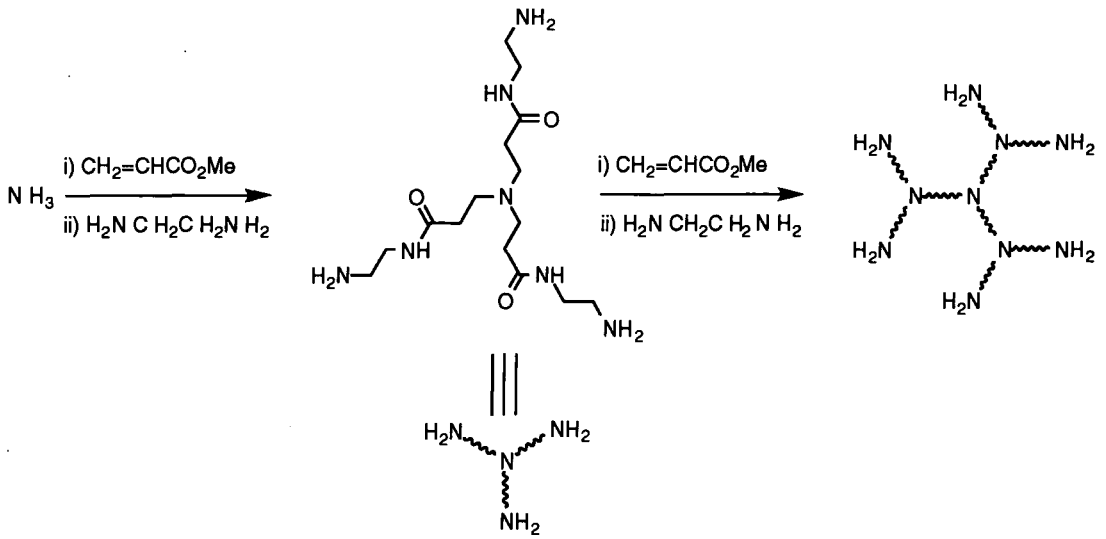
The term *dendritic* is now established as the adjective for branched, polymeric systems of various size, shape, topology and molecular distribution. In this Thesis, the word *dendritic* will define a branched, oligomeric, or polymeric, monodisperse structure with a well-defined topology, which has been coupled to a central core in a controlled manner.



Scheme 1.2.1 *A Schematic Representation of the Assembly of PAMAM Dendrimers*[7a]

1.2.2 Dendrimer Architecture

It was in the course of his PAMAM work that Tomalia defined many of the principles and terminologies used in dendrimer synthesis. He established that dendrimers contain three distinct architectural regions: the **Core**, the **Interior** region, and the **Exterior** region (Figure 1.2.2), which are all inter-related in terms of the physical and chemical characteristics of the final dendrimer. Attention has been paid to varying the structure of each region, with regard to studying systematically the resulting changes in dendrimer properties.

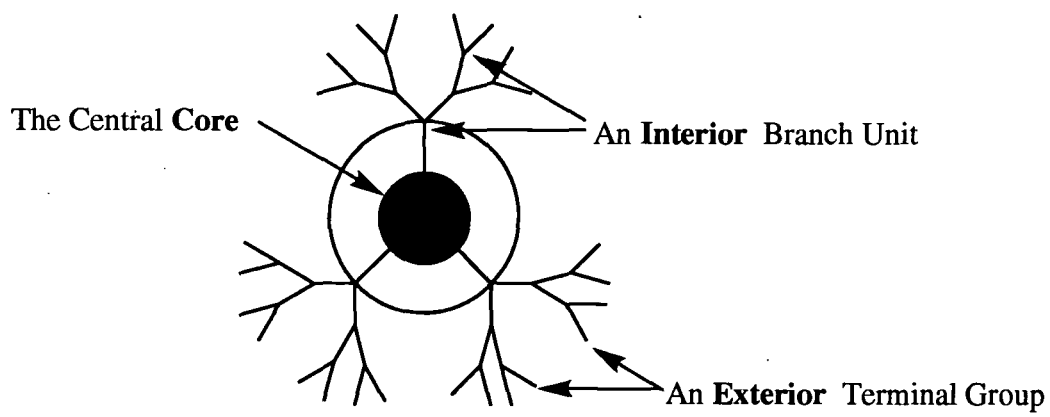


Figure 1.2.2 *The Architectural Regions of a Dendrimer*

i) The ***core*** region is the focal point of the dendrimer. It can be a single atom, *e.g.* nitrogen, or a simple molecule such as esterified trimesic acid,[8] or pentaerythritol.[9] The selection of the reactive core is of great importance, since its size, shape and multiplicity will strongly influence the molecular geometry and specific functions of the dendrimer. New cores designed specifically for dendrimers have been produced, such as the potassium benzene-1,3,5-triyltris(ethynethiolate) core[10] synthesised by L'abbé *et al.*, but the core region has been seen mostly as an opportunity for applying dendritic methodology to other new functional materials;[11] these will be discussed later in this Thesis.

ii) The ***interior*** region contains cascading tiers of *branched cells* (monomer units) with radial connectivity to the core (each layer is individually referred to as a *generation*). The multiplicity of the core and the branch juncture directly affect the number of terminal groups, the number of branch segments, and the molar mass of the dendrimers as a function of generation. Molecular radius increases linearly with the number of generations through which the molecule has grown. The internal structure can influence the physical[12] and the chemical properties[13] of a dendrimer. For example, arylacetylenic dendrimers synthesised by Moore *et al.*[12] proved difficult to synthesise and were very insoluble. Molecular modelling showed these problems to be due to the steric constraints imposed upon the system by its rigidity. Solubility was improved after extensive investigations into the addition of functional groups at the periphery to aid solubility. Yields were improved by increasing spacer length to reduce steric interaction. It has been stated that if monomer size were to increase sufficiently, then in principle dendrimer growth could increase indefinitely.[12a]

Interior structures containing ruthenium[14] possess interesting photo-physical and electrochemical properties; polyaryl ethers are good engineering plastics.[15] It is hoped that chiral dendrimers[16] will show an ability to resolve chiral molecules when used in chromatographic experiments in the same way that poly(amidoamine) dendrimers separate neutral species in electrokinetic capillary chromatography.[17] To date, most dendrimers have been predominantly organic in nature, but the increasing

number of organometallic,[14,18] organosilicon,[12e,19] and phosphorus-containing[20] dendrimers have generated much interest, although the specific uses of these materials have yet to be assessed.

iii) The ***exterior*** region consists of terminal groups attached to the outermost generation. As mentioned earlier, the number of terminal groups depends upon the nature of the interior region of the dendrimer. The number of surface groups at the periphery is exponentially related to the number of generations through which the dendrimer has grown.

Modification of the exterior region can bring out drastic changes in the physical properties of the dendrimer, such as solubility and phase transition temperature.[21] For example, dendrimers with hydrophobic or hydrophilic peripheries behave as surfactants at liquid interfaces, and as they are macromolecules held together by covalent bonds, they are more stable than micelles which are sustained purely by non-covalent intermolecular interactions (Figure 1.2.3). These "unimolecular micelles" showed a high capacity for solvating hydrophobic pyrene in water when compared to a traditional surfactant such as sodium dodecyl sulfate.[21d] The unimolecular micelles were efficiently recycled to recover free dendrimer and free pyrene, demonstrating the potential for use of dendrimers as recyclable solublisation and extraction systems. Other approaches to the assembly of unimolecular micelles have been made by Newkome *et al.*[21c] in the construction of dendrimers with combined hydrophilic and hydrophobic characteristics.

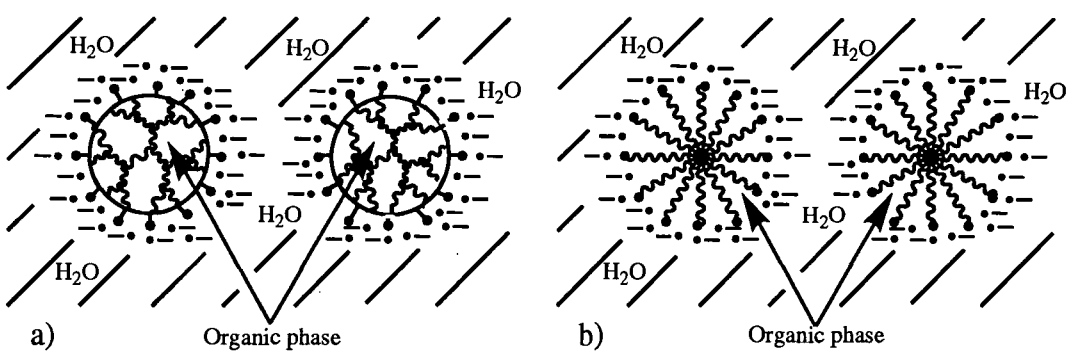


Figure 1.2.3 *Comparison of a) a Unimolecular Micelle and b) a Classical Micelle*

As the size of a dendrimer increases, the macromolecule begins to take on the characteristics of a biological entity. Small viruses contain many identical protein subunits, which are symmetrically arranged around their RNA core, providing protection and fulfilling targeting functions. The surfaces of large dendrimers can similarly provide steric protection to their interior, whilst also interacting with external reagents and solvents.[7a] Consequently, the ease with which the structural features of dendrimers can be varied and controlled has aroused interest in their potential to mimic the activities and functions of living systems at a microscopic level.[11a, 22]

At the commencement of the work contained in this Thesis, very little had been published in the area of surface functionalised dendritic systems, which is the focus for the results contained herein. By introducing redox-active substituents to this region it is possible to induce new electrochemical properties.

1.2.3 Dendrimer Synthetic Methodology

In early work, dendrimer syntheses originated from an initiator core, diverging to an exterior surface (*divergent methodology,* Figure 1.2.4). For dendrimer construction of this type, a number of criteria must be fulfilled: a suitable initiator must be found that can be converted in high yield into a reactive core, and it must be possible to execute an iterative sequence, where the initiator core, and other branch cells, are converted in high yield to branched assemblies with specific molecular surfaces. Growth commences at the central core by reaction with two or more protected branching units. The protecting groups are subsequently removed to reveal reactive functionalities, which are further coupled to branching units using the iterative growth procedure, until a dendrimer of the desired size is obtained (Figure 1.2.4). Using this procedure, molecules of high mass are rapidly obtained as the molecules grow through geometric progression (Figure 1.2.5).

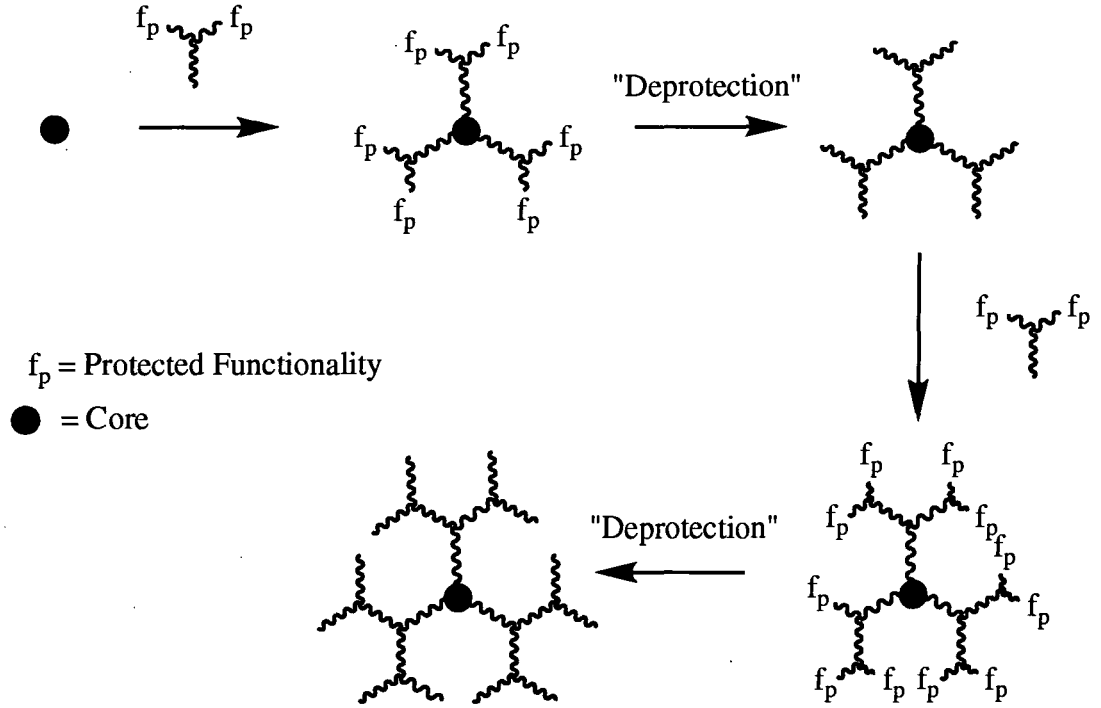
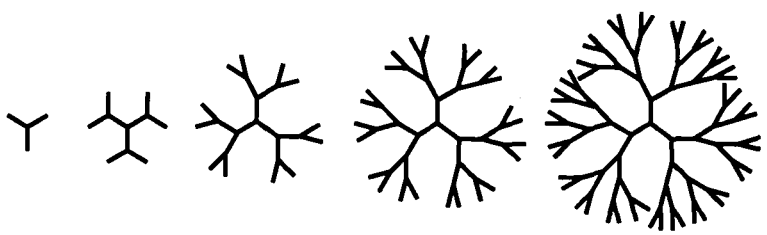


Figure 1.2.4 *A Schematic Representation of Divergent Growth Methodology*



Generation Number:	1	2	3	4	5
Terminal Groups:	3	6	12	24	48

Figure 1.2.5 *A Dendrimer Series Illustrating Growth in Size as a Function of Generation Number*

In a search for greater control over the size, shape, and surface of dendrimers, a second methodology was developed. *Convergent methodology* has been used by several groups,[8, 23] notably by Fréchet *et al.* Assembly of the dendrimers occurs from what will ultimately become the periphery, inwards to the central core, *via* assembly of a series of "dendron wedges" (W) of increasing size, which are eventually attached to a polyfunctional core (Figure 1.2.6).

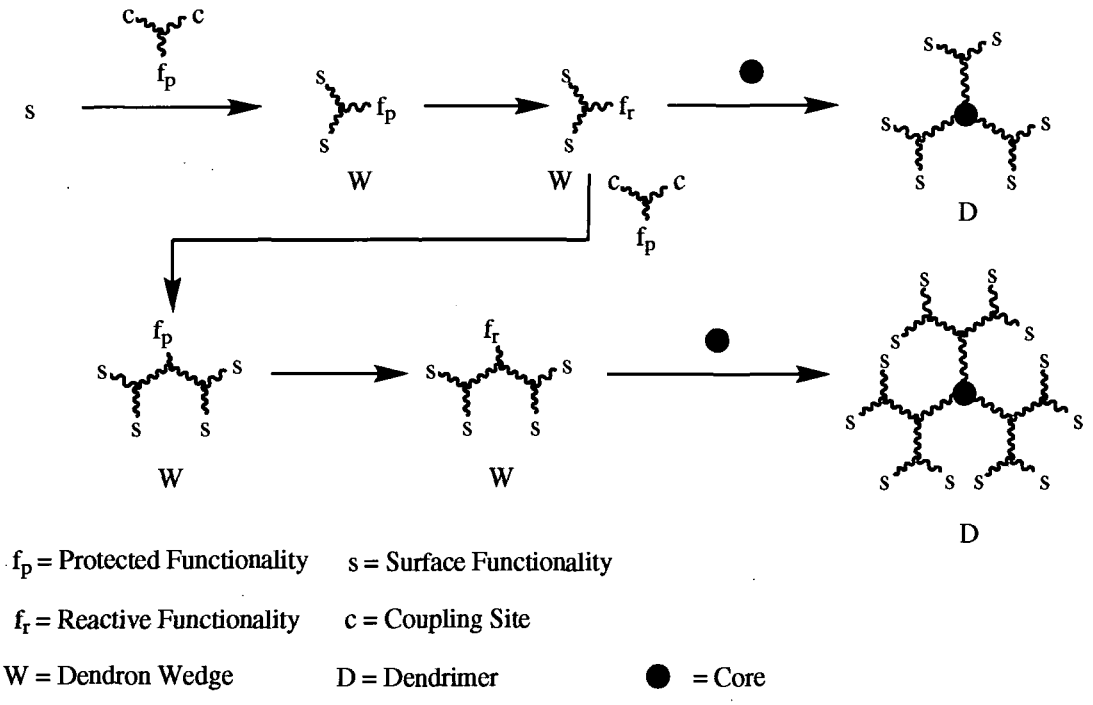
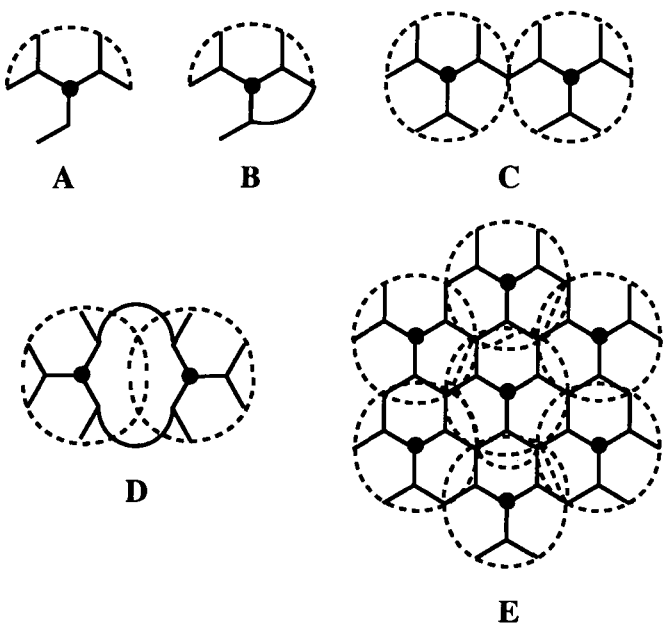


Figure 1.2.6 *A Schematic Representation of Convergent Methodology*

Convergent methodology offers many advantages over *divergent methodology*, in that the former requires the same number of reaction steps for the formation of each generation, as opposed to an increasing number of reaction steps for *divergent* growth. This overcomes the problems associated with incomplete, or undesirable reactions at congested surfaces, and results in a monodisperse product. *Convergent methodology* gives control over the exact number, nature, and placement of functional groups at the surface of the dendrimer and prevents the variety of structural abnormalities such as intra-dendrimer bridging of chains, or inter-dendrimer linking, which are both associated with *divergent methodologies* (Figure 1.2.7). These factors allow for ease of purification and characterisation of a well-defined product. The limiting factor in the use of convergent methodology is that as the number of generations increases, the ease of reaction decreases due to steric inhibition. Hence, deprotection and further reaction with branching units becomes more difficult, limiting the size and ultimately, the number of generations that can successfully be prepared.



A Branch Defective Dendrimer **B** Intra-Dendrimer Looping

C Inter-Dendrimer Bridging **D** Inter-Dendrimer Looping

E Dendrimer Cluster (Bridged/Looped)

Figure 1.2.7 *Schematic Representation of Dendrimer Defects*[7d]

In an attempt to overcome the factors which limit dendrimer growth, a number of techniques have been employed, notably the "double-stage" convergent growth technique,[24] the "two-monomer" approach,[25] and the "accelerated" growth technique.[26] High molecular weight compounds can be prepared using the "double-stage" process. Several growth steps are eliminated by the use of large dendritic core molecules called "hypercores", to which other large dendron wedges may be attached. The "two-monomer" approach allows the growth of two generations in one stage, without further purification. As a further development, the "accelerated" growth methodology utilises "branched monomers". This last technique replaces the conventional AB_2-type monomer (Figure 1.2.1) with an AB_4-type monomer, whilst preserving the convergent growth methodology.

Many different convergent methodologies have been published.[12a-d,23-26] Figure 1.2.8 illustrates the construction of two different dendron wedges utilised in

convergent dendrimer synthesis. The work in this Thesis builds upon the convergent dendritic polyester approach first published by Miller *et al.*[8]

Convergent methodology has provided the means to assemble many different polymeric species which were inaccessible by divergent techniques. For example; polyether wedges were used to end-cap free-radically polymerised poly(ethylene glycol) and polystyrene chains to yield dumbbell-like species,[27] free-radical copolymerisation of styrene with polyether dendron wedges led to the formation of a linear graft polymer with dendron wedges pendant from the styrene backbone,[28] and a combination of polyether and polyester wedges resulted in a segment copolymer, where different types of dendron wedge were coupled to the same core.[29] The flexibility that convergent techniques provide is leading to many new and different molecular assemblies, enabling dendritic fragments to be incorporated into new classes of speciality materials.

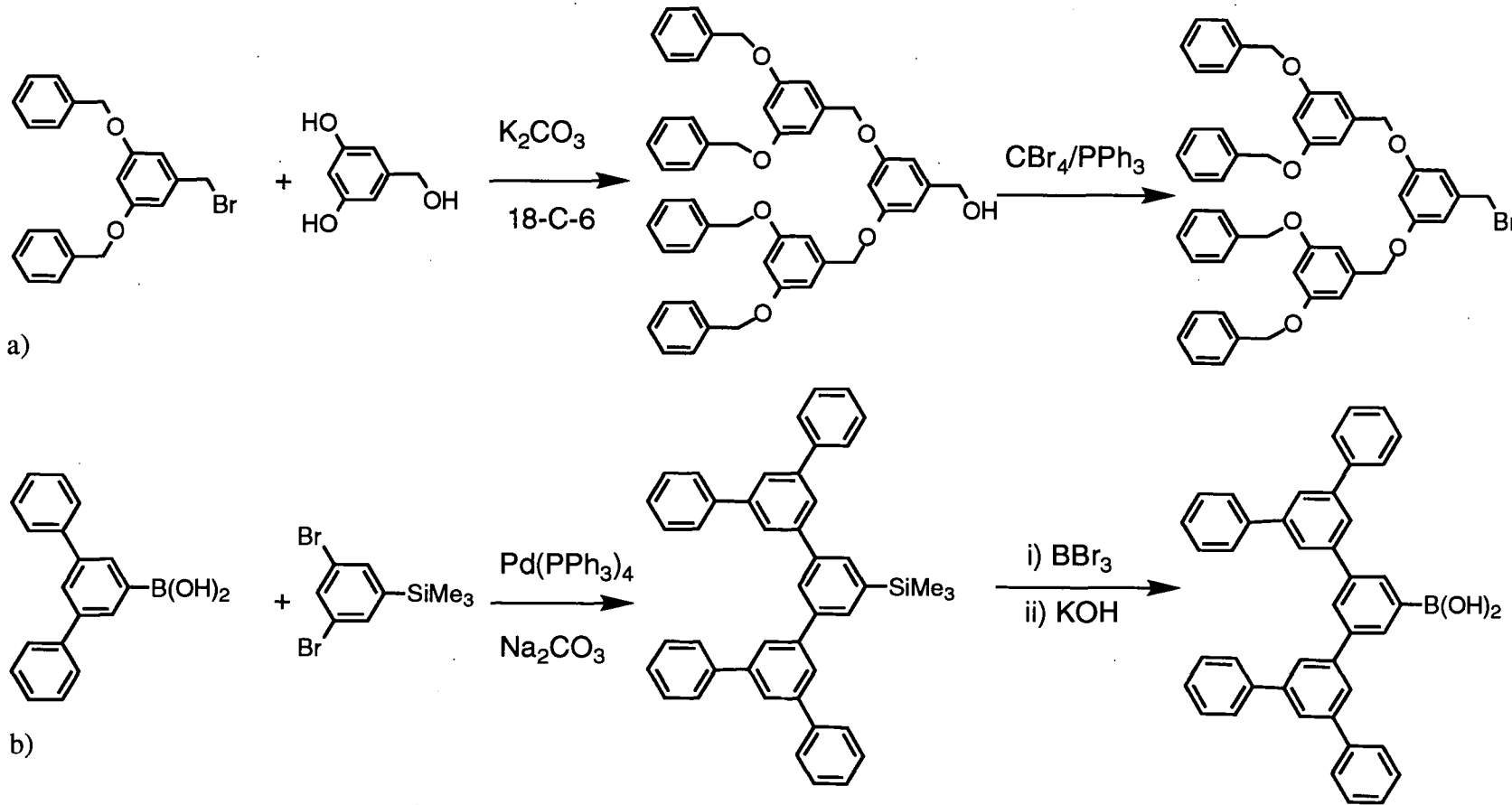


Figure 1.2.8 *Examples of Dendron Wedges for Convergent Synthesis of a) Poly(benzylether) Dendrimers*[23b] *b) Hydrocarbon Dendrimers*[23c]

1.2.4 The Concept of Limiting Generation

Computer modelling has shown that dendrimers undergo a gradual transition in shape as they grow in size. The smaller molecules change from being open, starfish-shapes, into rigid ball-shaped structures with densely packed surfaces enclosing an interior comprised of a number of voids and channels.[30] The utilisation of photochemical relaxation techniques which have probed the surface structure of polyether dendrimers, has given some credibility to this model.[31] The number of terminal groups at the dendrimer surface grows exponentially, while molecular radius grows linearly, therefore, it is clear that dendrimer growth cannot continue indefinitely. Eventually, a state will be reached where the density of the packing of the surface layer will prohibit further ideal growth, *i.e.* without defects (Figure 1.2.7). The "starburst limiting generation"[32] is an increasing function of spacer length; therefore, if a spacer is sufficiently short, the starburst limiting generation can be estimated from purely geometric and steric constraints, but as spacer length increases, that length must be taken into account. Two theoretical models attempt to predict starburst limiting generation for dendrimers:

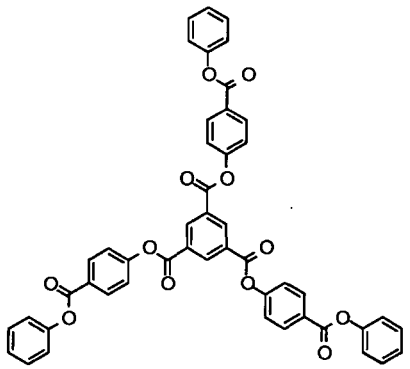
i) The model of de Gennes and Hervet[32] for PAMAM dendrimers assumes that dendrimers grow radially outwards, with all terminal groups residing at the periphery of the molecule. The model predicts the dependence of molecular radii and limiting generation on spacer length, given that all branch cells are fully reacted, and that branch length is sufficiently long that the chemical nature of the branch points is irrelevant. This model shows the dendrimers to be very flexible in the early stages of growth, but quite rigid as the radii approach the limiting generation. The model predicted PAMAM dendrimers to have a limiting generation of around 10, and shows good agreement with the experimental results obtained by Tomalia,[33] but is known to be flawed in the limitations it makes in its assumptions.

ii) Lescanec and Muthukumar[34] devised a numerical simulation of kinetic growth using a "self-avoiding walk" algorithm, which allows for folding back of branches and buried terminal groups. This model has some accuracy when applied to sufficiently flexible dendrimers,[35] but it must be stressed that insufficient studies have been carried out to be able to endorse firmly either model as being the more accurate.

1.2.5 Dendrimer Methodology Applied to Synthesis of New Speciality Materials

Most materials start life as an academic curiosity, only finding true usefulness when they can be applied to a specific application. Dendritic macromolecules are no exception to this rule. It is only recently that the deluge of publications on dendrimers has started to contain examples of systems that possess useful applications.

i) Blending studies of aryl ester dendrimers with linear polymers have shown interesting effects on the physical properties of the polymer blend.[36, 37] Karasz *et al.* demonstrated an ability of these dendrimers to reduce the glass transition temperature, T_g, of polycarbonates, showing that they were capable of plasticising the mixture.[36] Feast and Stainton showed that two successive generations of related aryl ester dendrimers (compounds **4** and **5**) with flexible spacer units when blended with poly(ethylene terephthalate) had plasticising and antiplasticising properties, respectively.[37] Compound **4** exhibited plasticising abilities by increasing the free volume of the system, and reducing chain interactions, this led to increased chain slippage and reduced chain orientation. Compound **5** was antiplasticising due to enhanced orientation of polymer chains, caused by increased interaction between the linear polymer and the dendrimer.



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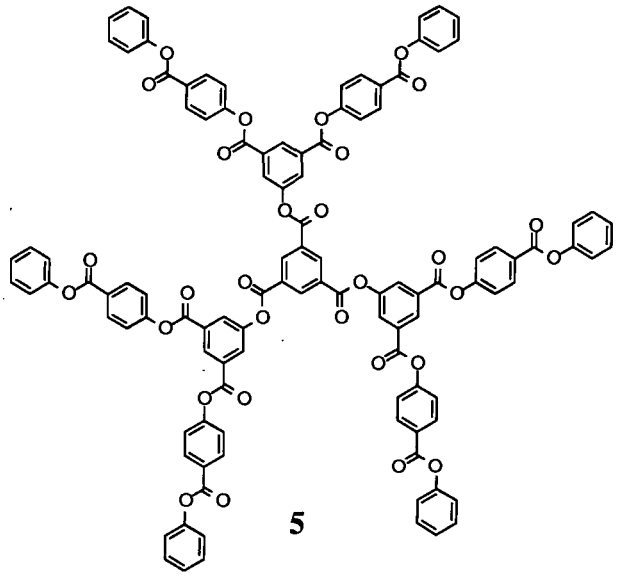

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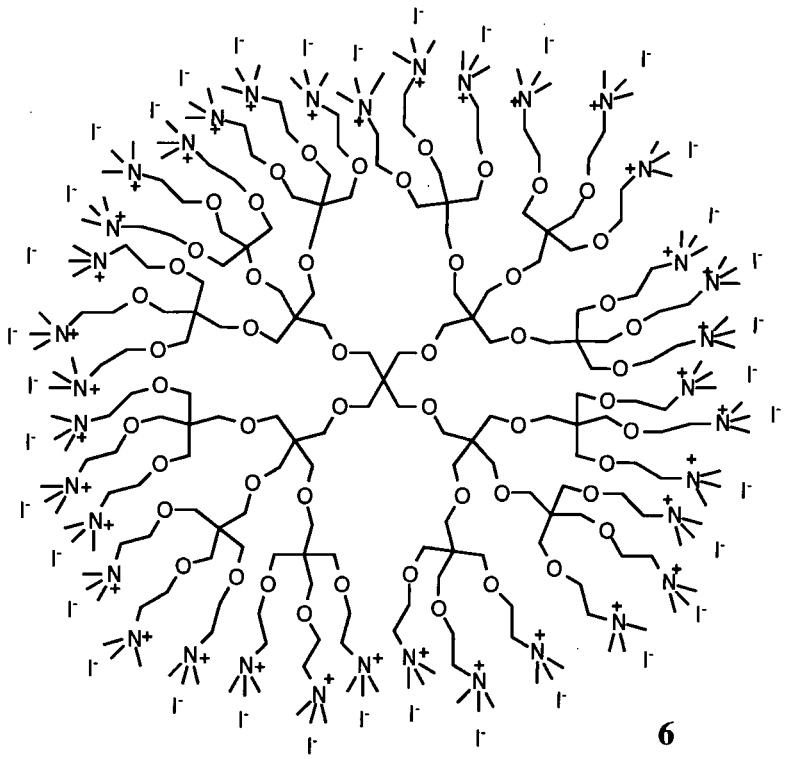
ii) The ionic quaternary ammonium dendrimer **6** synthesised by Ford *et al.* was used to catalyse well documented decarboxylation and hydrolysis reactions.[38] Compound **6** was a less efficient catalyst compared to traditional micellular catalysts, due to the increased hydrophilic nature of the dendrimer surface (as opposed to the core of a micelle where traditional catalysis would occur). The expectation is that dendrimers with a more lipophilic surface character will show increased activity in these reactions. More recently, van Koten *et al.* assembled silane dendrimers functionalised with arylnickel(II) complexes **7**.[39] These functionalised dendrimers successfully catalysed the Kharasch addition of polyhalogenoalkanes to an olefinic carbon-carbon double bond, such as the addition of carbon tetrachloride to methylmethacrylate.

iii) Dendrimer synthesis methodology has been applied to other classes of organic molecules to impart their characteristics upon the hybrid system: dendritic crown ether **8** being an example.[40] These assemblies were an attempt to produce dendritic analogues of the linear polymer sandwich complexes of caesium,[41] but binding studies showed the crown ether moieties to be acting independently, and complexing preferentially to K^+ and Na^+, analogous to their non-polymeric derivatives. As the dendritic fragments attached to the crown ether became larger, the binding capabilities of the macromolecule decreased. This was attributed to an increasing tendency towards

buried functionalities of the larger dendritic species, preventing efficient complexation occurring.



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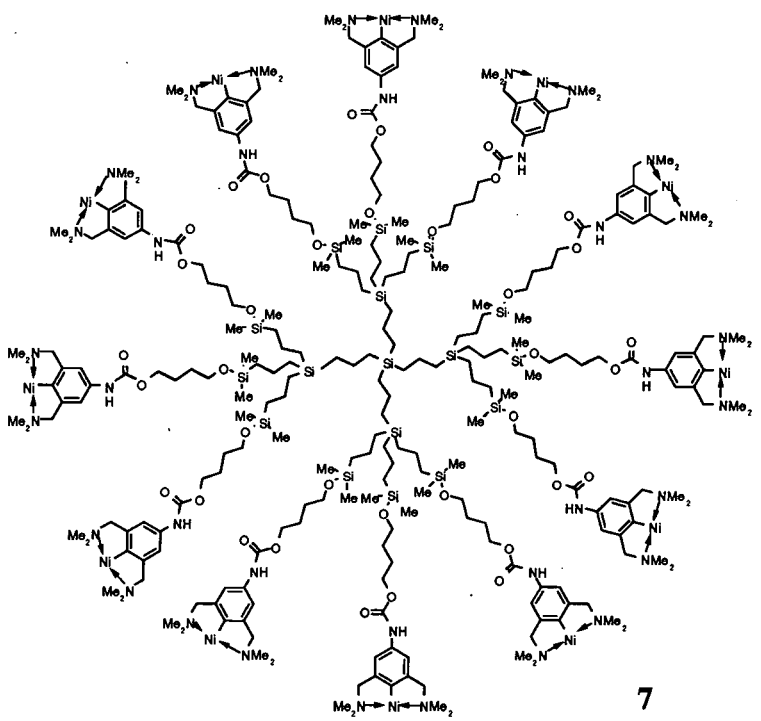

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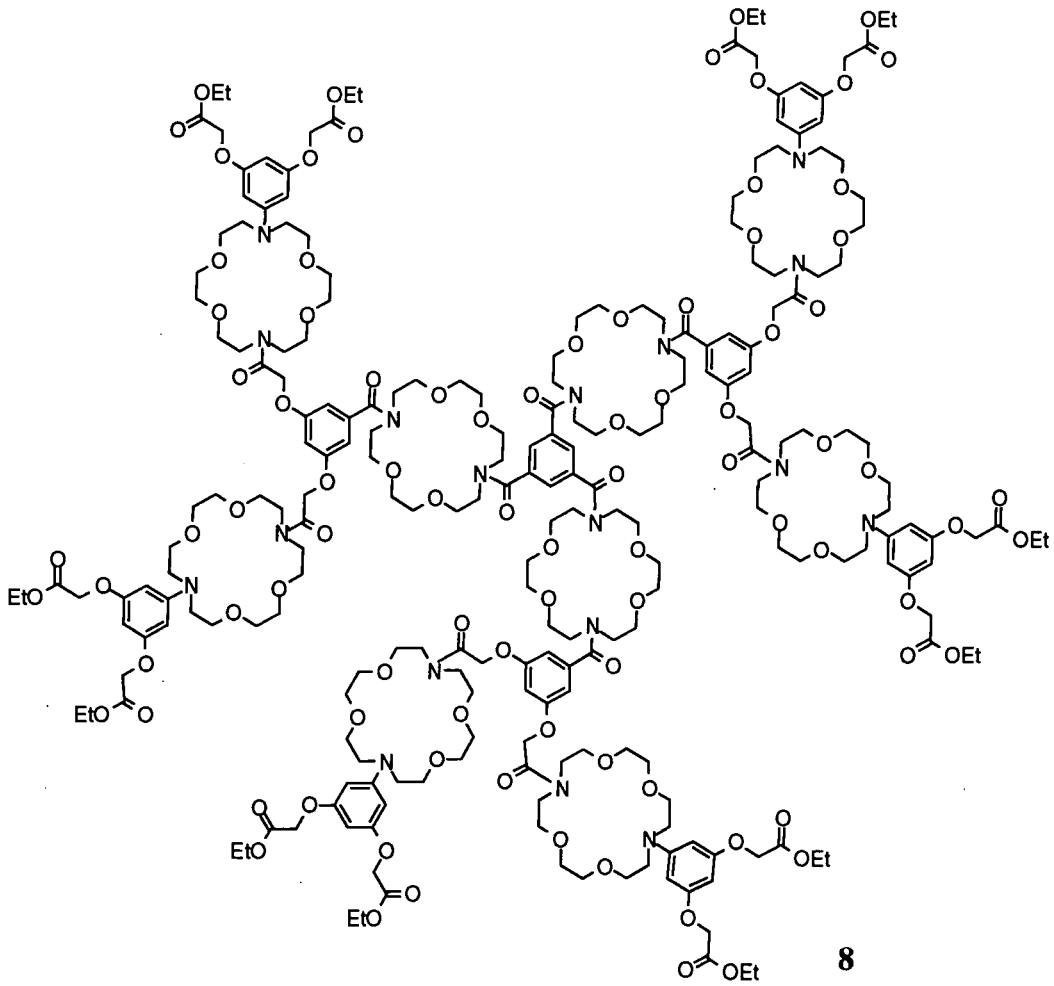
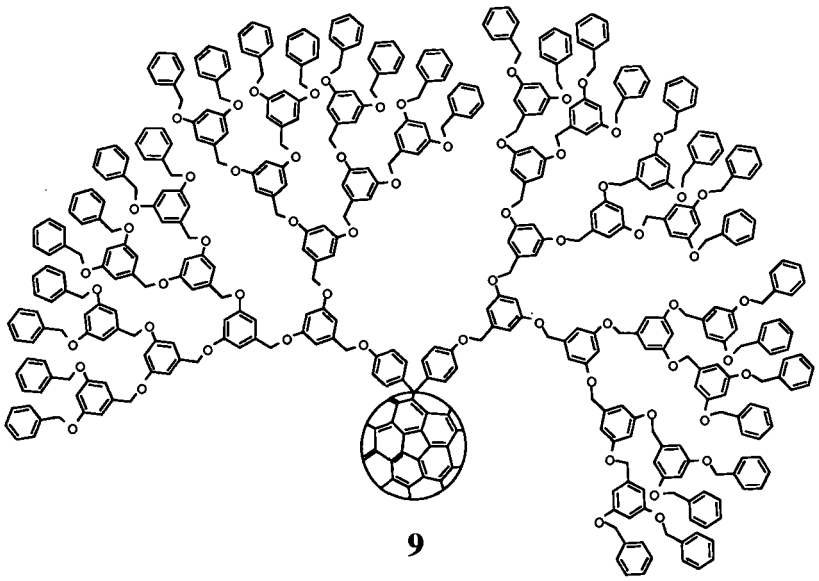


8

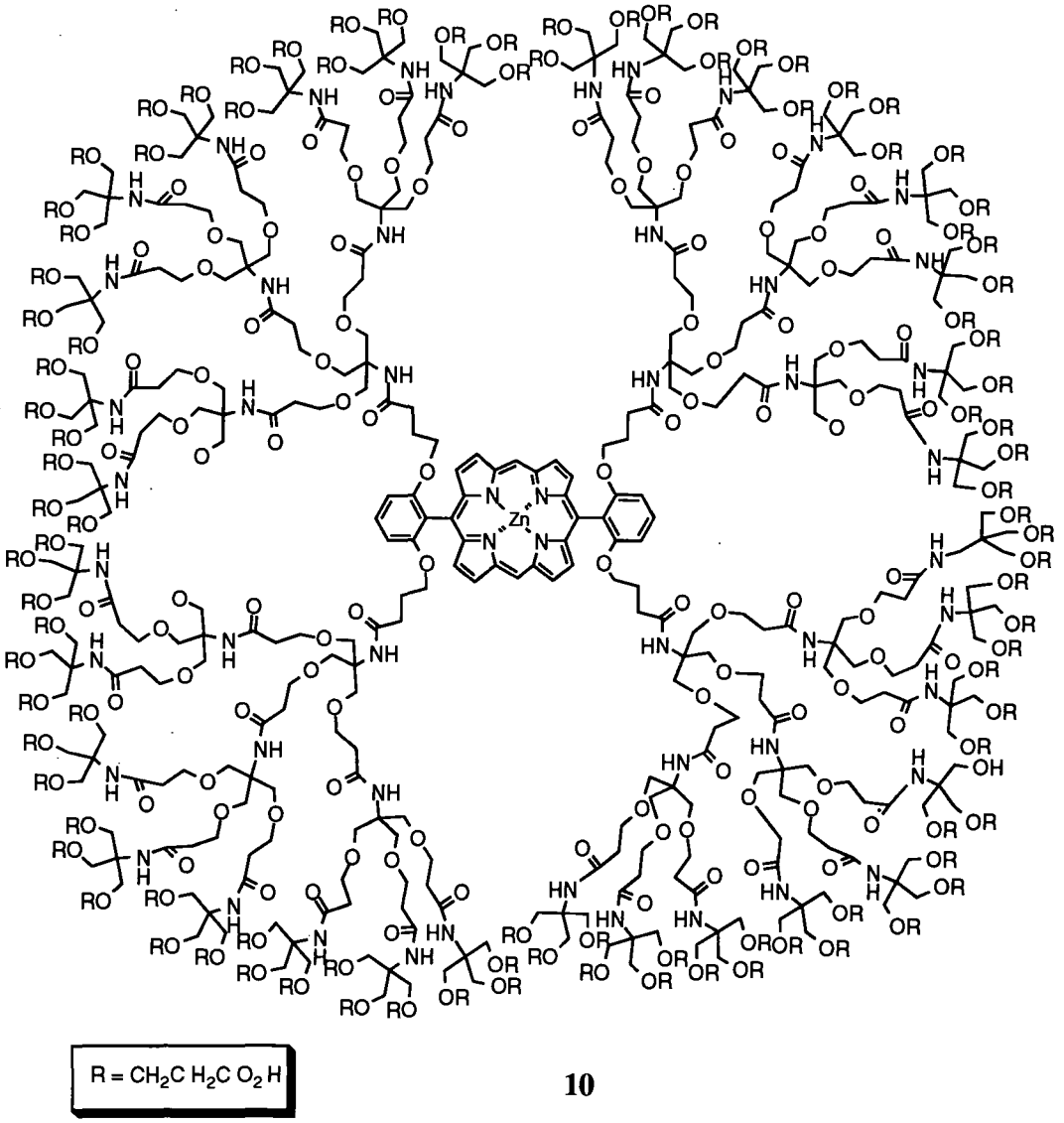
1.2.6 Redox-Active Dendritic Macromolecules

Research in dendrimer chemistry has now shifted its emphasis away from the assembly of ever larger macromolecules,[42] towards the assembly of hybrid systems. Incorporation of dendritic fragments modifies the properties of both parent species: redox-active moieties attached to dendritic macromolecules are an example. The first examples of redox-active dendritic species were the buckminsterfullerene superstructures published by Fréchet[11f, 11g] in separate collaborations with Wudl[11f] and Hawker,[11g] compound **9** is an example of this type of dendrimer. These molecules offered the possibility of conducting fullerenes encapsulated in an insulating polymeric shield.



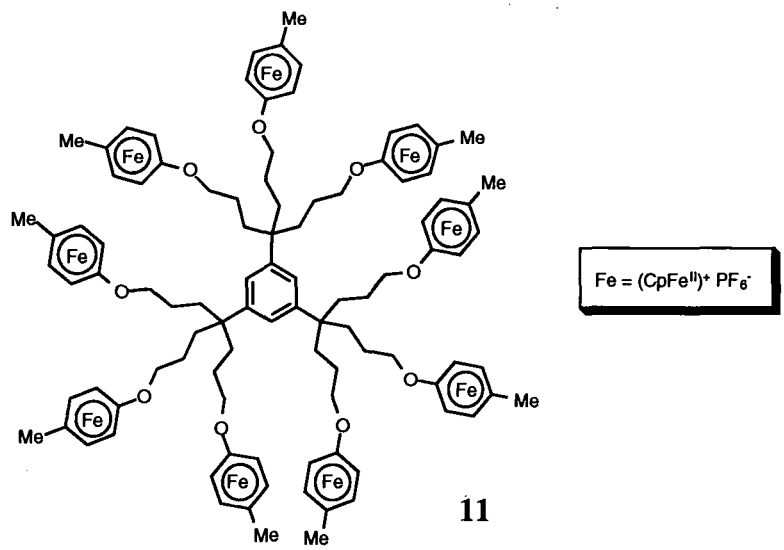
9

The first dendrimer with a complexing aza-crown core was published by Vögtle *et al.*,[43] but Inoue *et al.*[44] were the first to describe a sterically shielded metal porphyrin, surrounded by polyether dendron wedges. Diederich *et al.*[11f] investigated the influence of surface groups on the electrochemical behaviour of porphyrins. Third generation dendrimer **10** was prepared utilising the methodology devised by Newkome *et al.*,[45] which had redox chemistry contrasting greatly from non-dendritic analogues. The porphyrin nucleus was protected by a core of electronegative oxygen atoms, which hindered reduction and facilitated oxidation. Diederich suggested that the metal ion core could act as a "molecular energy collector", capable of spontaneous emission of stored energy as light, corresponding to an amplification of light intensity (a light harvesting effect).



10

Astruc *et al.* were the first to publish an assembly capable of a multi-electron transfer.[46] Cyclic voltammetry of nonairon complex **11** showed 8±1 electrons could be transferred per molecule, indicating nine quasi-equivalent and reversible Fe^{II}/Fe^{I} oxidations occurring at the surface of the dendrimer. The principle of attaching pendant redox-active substituents was shortly followed by Morán *et al.* in their divergent assembly of organometallic silicon dendrimer **12**.[47] These flexible systems containing up to eight pendant ferrocene groups showed each redox-active substituent to be capable of undergoing a single, non-interacting, reversible oxidation, as determined by the intensity of a cyclic voltammetric wave. This work, along with that contained in this Thesis, represents the first publications of multi-redox dendritic assemblies.



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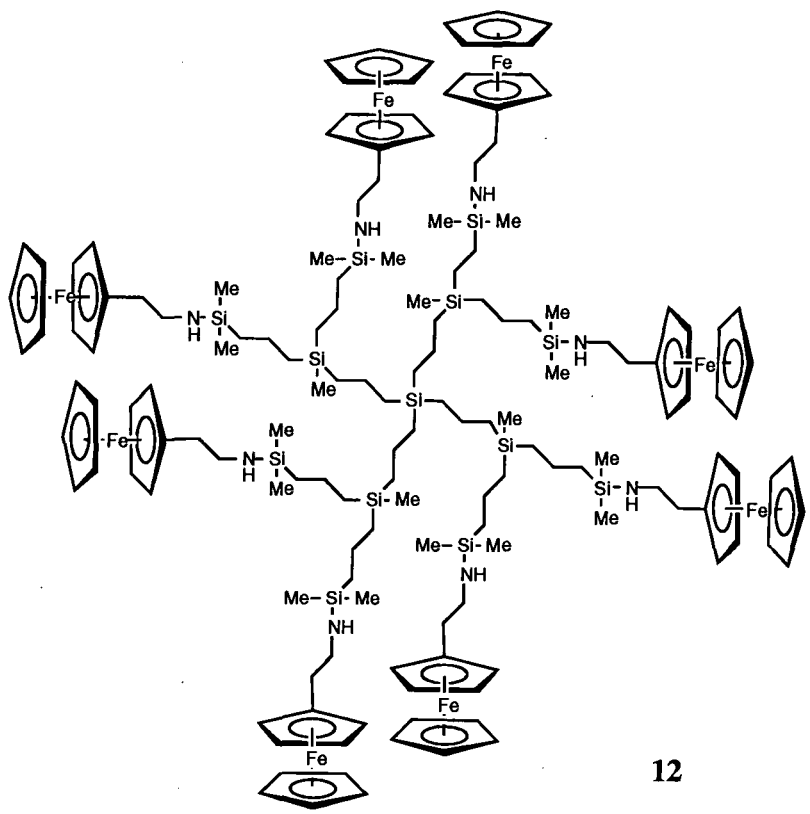
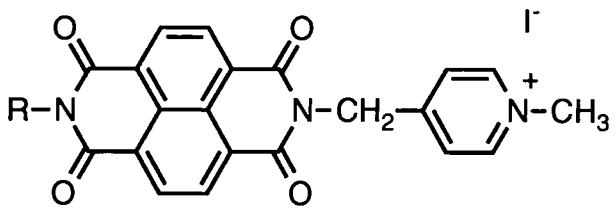


12

Recently, Miller *et al.* described a series of PAMAM dendrimers (Scheme 1.2.1) emblazoned with the imide electronophore **13**.[48] Dendrimers containing 12-192 electrophores were assembled, then reduced with sodium dithionite in D_2O, resulting in the formation of π-stacks on the surface of the dendrimer. Electrochemistry showed the all the dendrimers to exhibit similar cyclic voltammograms, corresponding to two reversible one electron reductions per surface group.



13

R = PAMAM Dendrimer

1.3 Introduction to Tetrathiafulvalene

The area of tetrathiafulvalene (TTF) chemistry is one which has also been extensively documented and its molecular properties are fully explored. Many methods for the synthesis and derivatisation of this remarkable molecule have been developed, and this text will now discuss the extension of the properties of this important π-electron donor to the supramolecular construction of new materials.

1.3.1 Tetrathiafulvalene And Its Properties

The foundation stone of TTF chemistry was laid in 1926 by Hurley and Smiles in the synthesis of dibenzotetrathiafulvalene.[49] It was not until 1970 that the synthesis of TTF was first published by Wudl *et al.*[2] TTF was shown to form a radical cation species by the action of chlorine gas on a carbon tetrachloride solution of the neutral donor, and further oxidation produces the dication; note that the dication is a 4n+2 Hückel aromatic species. The presence of the sulfur atoms on the two fused 1,3-dithiole rings makes TTF very polarizable, allowing the molecule to be a highly efficient π-electron donor. The dithiolium cation formed in the first oxidation has good resonance stabilisation and high thermodynamic stability; ESR studies[2] showed this stability to be directly attributable to the ability of the sulfur atoms to accommodate much of the spin-density of the charged species. Cyclic voltammetry (CV) shows that oxidation of the TTF to the radical cation, and its subsequent oxidation to the dication are fully reversible (Figure 1.3.1).

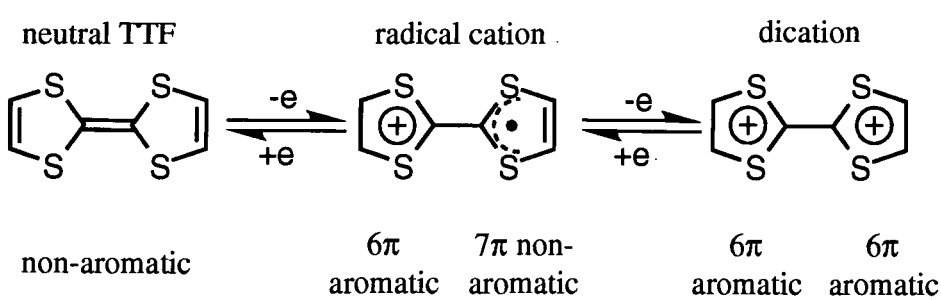
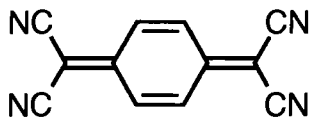


Figure 1.3.1 *The Redox Behaviour of Tetrathiafulvalene*



14

In 1973 TTF was discovered to form charge-transfer complexes with electron acceptors.[50] In particular, TTF formed a black, crystalline, 1:1 conducting charge-transfer complex with the electron acceptor, 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) **14**, which showed a room temperature electrical conductivity of σ_{rt} = 500 S cm^{-1}, rising to a maximum of $\sigma_{max} = 10^4$ S cm^{-1} (metals have conductivities of *ca* 10^6 S cm^{-1}, which rise with decreasing temperature; typical semi-conductors have values of $\sigma_{rt} = 10^{-2}$ - 10^{-8} S cm^{-1}, which fall with decreasing temperature). These values are several orders of magnitude higher than those for most organic compounds, which are usually electrical insulators. This breakthrough triggered the investigation of TTF in the context of 'organic metals'. In the formation of a 1:1 complex between TTF and TCNQ, infra-red spectroscopy[51] and X-ray scattering techniques[52] determined that there was a partial charge-transfer of 0.59 electrons from donor to acceptor, which resulted from a balance of the ionisation potential of the TTF donor and the electron affinity of the TCNQ acceptor. The crystal structure of the complex[49] showed the planar TTF and TCNQ molecules assembled into two well defined segregated stacks, one comprising partially-charged TTF molecules and the other partially-charged TCNQ molecules. The stacked moieties lie in planes which are tilted in opposite directions to each other, the so-called 'herringbone' structure (Figure 1.3.2). Strong intra-stack interactions, extensive π-electron superposition and the partially filled energy bands on the stacks enable electronic conduction to occur, predominantly in one dimension. This anisotropic conduction has led to materials of this type being termed 'pseudo-one-dimensional' conductors.

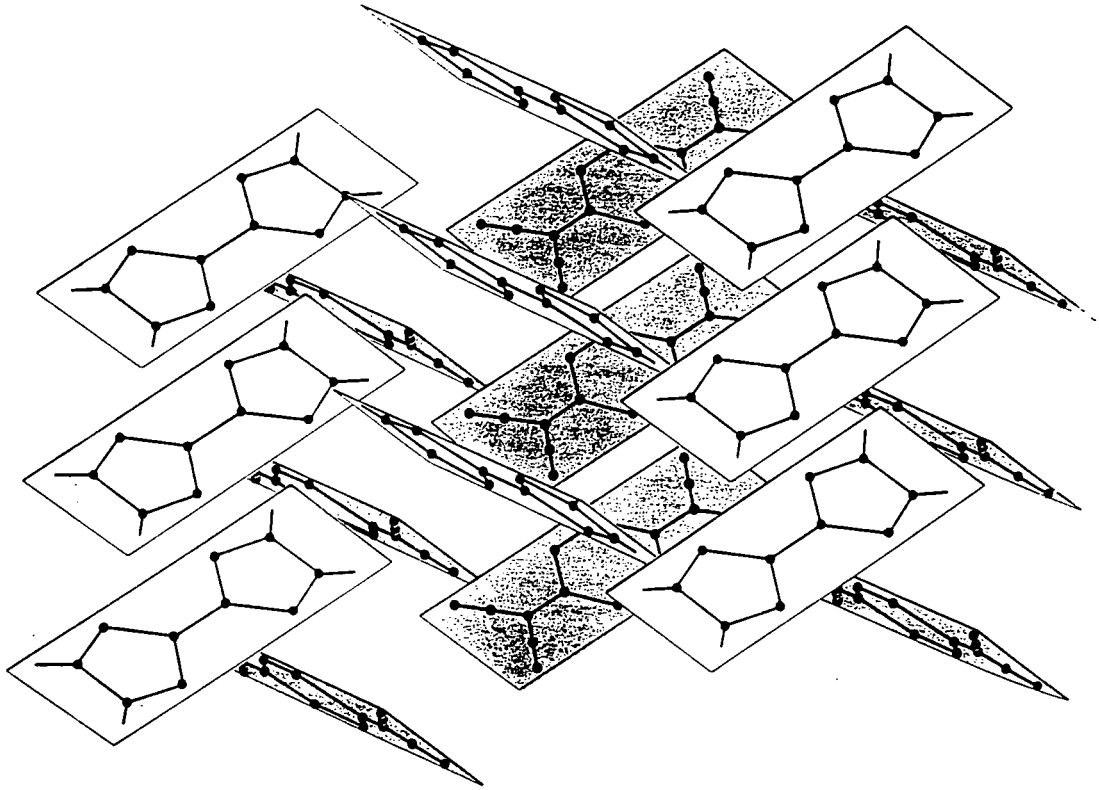
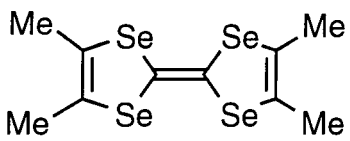


Figure 1.3.2 *The 'Herringbone' Crystal Structure of the TTF-TCNQ Charge-Transfer Complex*



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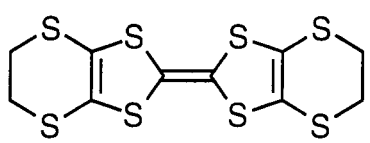


16

The redox-addressablity and conduction properties of TTF are the two main characteristics that ensured the continued propagation of research in this area. In 1980 Bechgaard *et al.* discovered a series of superconducting salts (PF_6^-, AsF_6^-, ReO_4^-, *etc.* salts) of the tetramethyltetraselenafulvalene (TMTSF) **15** radical cation, which have a superconducting transition temperature (T_c) of 1K under 12Kbar pressure.[53] This superconductivity arises from two dimensional stacking interactions in the crystal (Figure 1.3.3). Since then progress has been made with the bis(ethylenedithio) derivative of TTF (BEDT-TTF) **16**, and several superconducting salts are now known.[54] The organic superconductor in this family with the highest T_c at ambient pressure is $(BEDT\text{-}TTF)_2Cu[N(CN)_2]Br$ with T_c at 11.6K.[55] Ongoing investigations search for salts of TTF derivatives which superconduct at higher T_c.

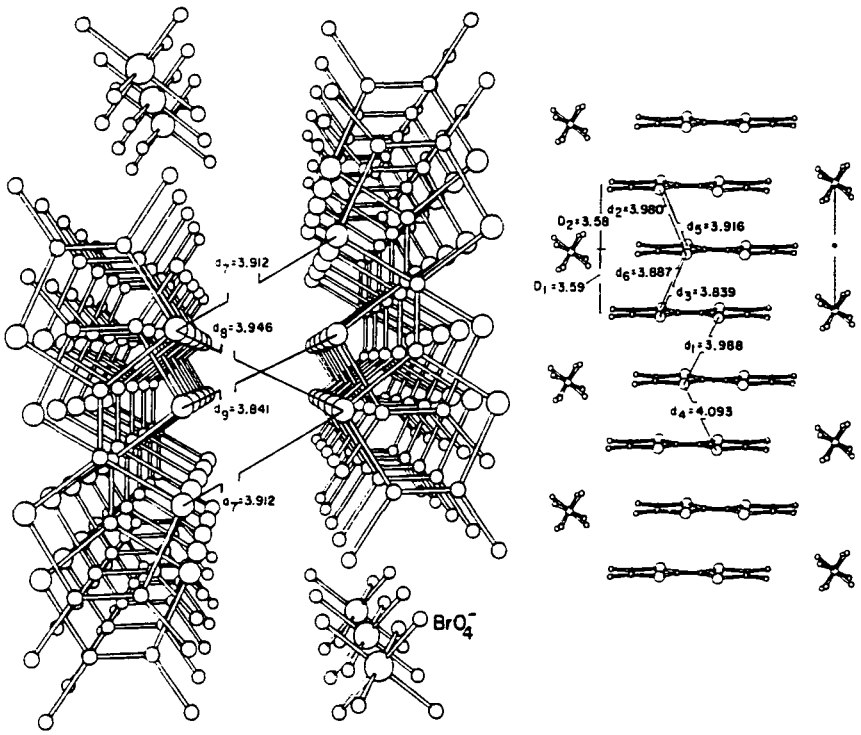


Figure 1.3.3 *Crystal Structure of* $(TMTSF)_2BrO_4$

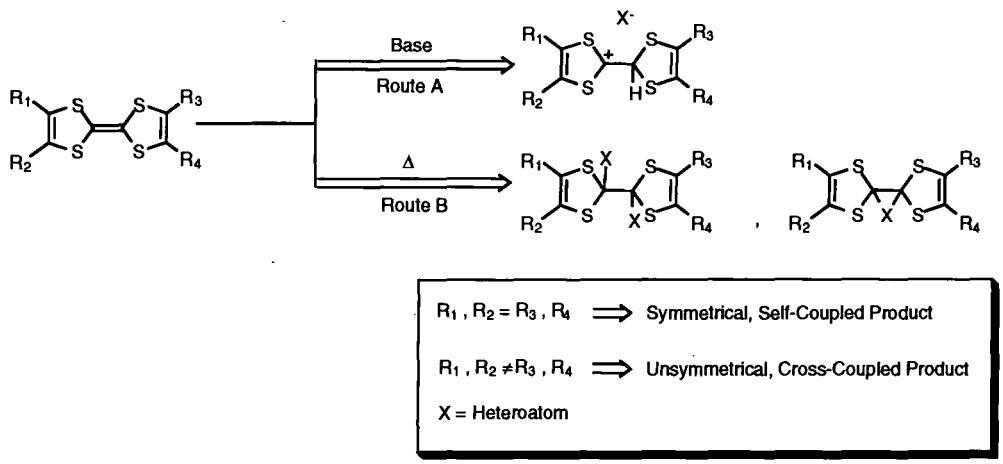
1.3.2 Synthetic Strategies Towards Tetrathiafulvalene Derivatives

Numerous synthetic approaches exist to construct TTF derivatives. This section will give an overview of the methodologies available. More comprehensive details can be found in the review articles of Narita and Pitman,[56] Fanghänel *et al.*[57] and Garín.[58] The methodologies that will be discussed include *derivatives formed by coupling reactions* and *derivatisation via the TTF anion.*

1.3.3 Tetrathiafulvalene Derivatives Formed by Coupling Reactions

Within this category of reactions several different methods are available for the formation of TTF derivatives. The premise that inter-relates them is that the central

2,2'-π-bond is formed *via* an elimination reaction, involving the loss of either protons or heteroatoms in the final step of the reaction (Scheme 1.3.1).

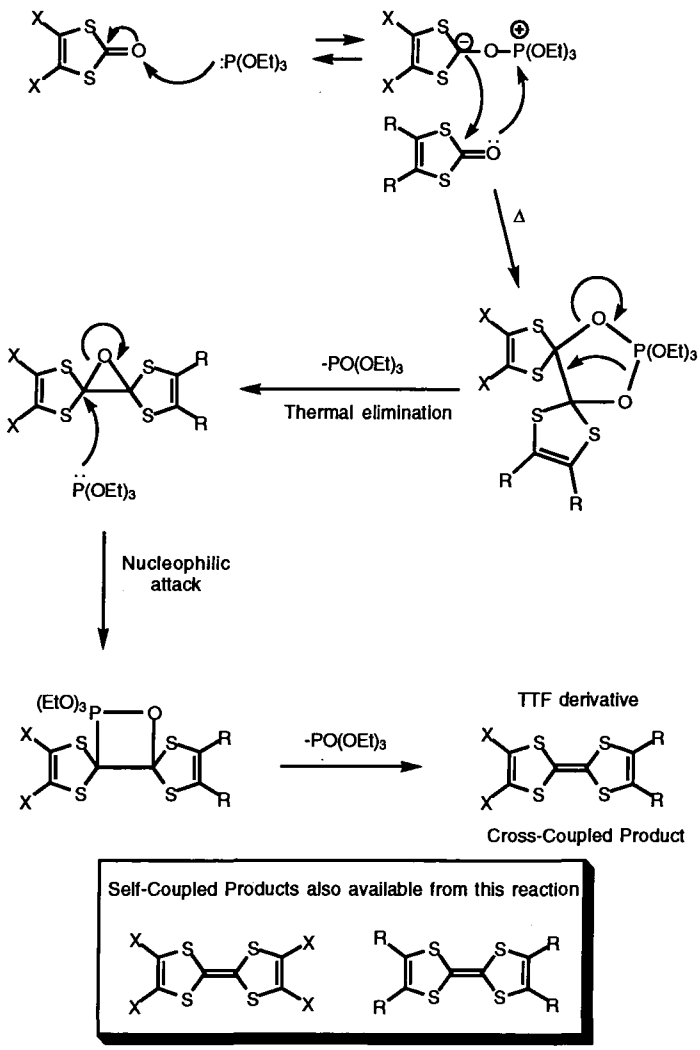


Scheme 1.3.1 *Synthesis of Tetrathiafulvalene Derivatives*

In the case where a proton is eliminated in the final step, the reaction involves the interaction of a carbene, or phosphorus ylide, with a 1,3-dithiolium salt possessing a hydrogen at C-2. The adduct formed is then transformed into a TTF derivative by the action of a suitable base (Scheme 1.3.1, Route A). The 1,3-dithiolium salt can be obtained from 1,3-dithiole-2-imminium salts,[59] or the alkylation of 1,3-dithiole-2-thiones.[60] If the reaction with the base at the final step is between two differently functionalised half-units, the formation of three products is possible: two symmetrical self-coupled products and one unsymmetrical cross-coupled product.

A powerful route to the synthesis of TTF derivatives utilises in the ability of trivalent phosphorus species to react at elevated temperature with 2-oxo-, 2-thioxo-, and 2-selenoxo-1,3-dithioles to give the corresponding fulvalenes[56] (Scheme 1.3.1, Route B, Scheme 1.3.2). This route gives access to an abundance of symmetrical and unsymmetrical derivatives containing electron donor (alkyls, cycloalkyls), electron acceptor (nitriles, esters, trifluoromethyl), or aromatic groups. Triphenylphosphine and trialkylphosphites have been used in this process as desulfurizing agents, although the latter are generally more efficient. As in Scheme 1.3.1, Route A, the products

obtained from the reaction are a mixture of cross- and self-coupled fulvalenes, the separation of which can be problematic.

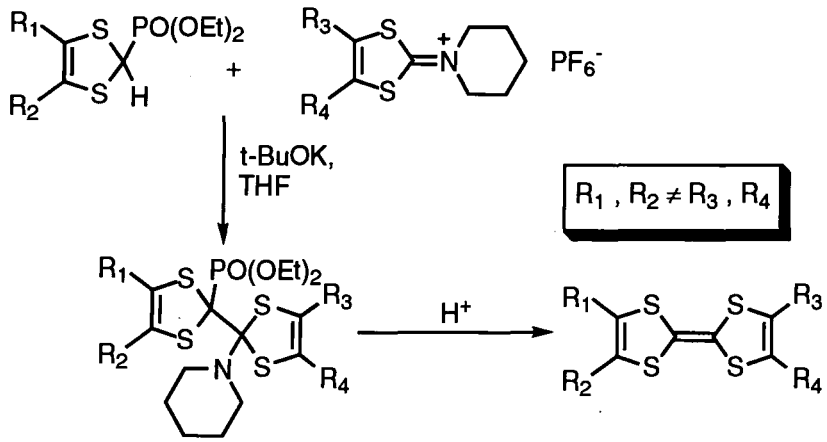


Scheme 1.3.2 *Mechanism for Synthesis of Tetrathiafulvalene Derivatives via Phosphite-Induced Coupling*

Selectivity in cross-coupling can be obtained by the reaction of a phosphorus ylide with a 1,3-dithiolium salt, in the presence of a base at low temperature.[61] This method has provided numerous unsymmetrical tetrathiafulvalenes, but instability of the starting materials under the reaction conditions leads to formation of variable amounts of symmetrical TTF derivatives. The most successful route to date for exclusive formation of one unsymmetrical derivative in a reaction is that developed by Lerstrup *et al.*,[62] where phosphonate esters of unsubstituted dithioles were reacted with iminium

compounds (Scheme 1.3.3) in modest yield. The starting materials are stable under reactions conditions and couple to produce one unsymmetrical TTF derivative.

Other coupling reactions exist, such as the treatment of 1,3-dithiole-2-thiones with dicobalt octacarbonyl, but they provide modest yields and are not widely used.[63]



Scheme 1.3.3 *Synthesis of Tetrathiafulvalene Derivatives by Reaction of Phosphonate Esters and Iminium Salts*

1.3.4 Derivatives *via* the TTF Anion

This strategy involves derivatisation of the parent TTF molecule **1**. The first monofunctionalised TTF derivatives were prepared by Green, *via* the formation of tetrathiafulvalenyllithium **17**, generated by the use of butyllithium.[64] Further investigation by Green showed that the TTF anion could be generated by the action of either *n*-BuLi or lithiumdiisopropylamine (LDA) at -78°C, and trapped with a wide variety of electrophiles, to give monosubstituted derivatives (Figure 1.3.4).[65]

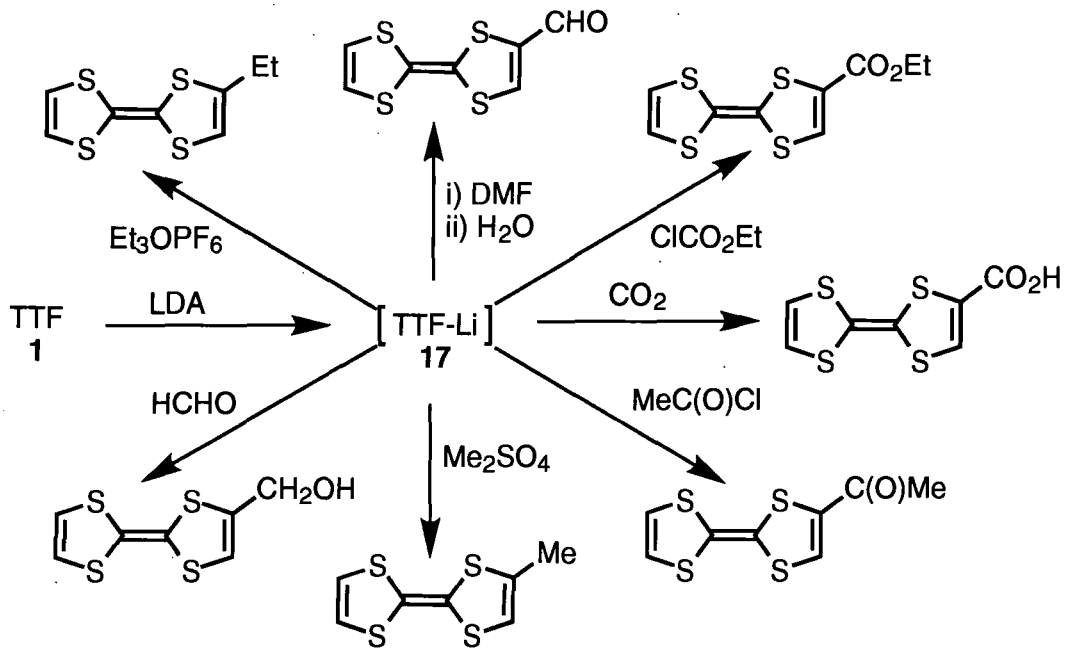
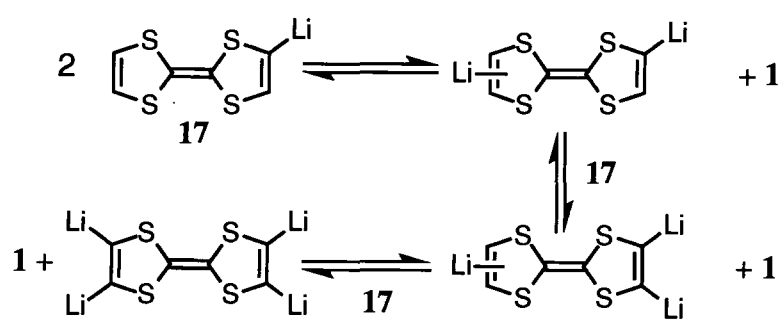


Figure 1.3.4 *Substituted Tetrathiafulvalenes via the TTF Anion*

The tetrathiafulvalenyl anion **17** is very reactive, even at -78°C. Unless strict controls are made on temperature, a wide variety of by-products can be formed due to the generation of multi-lithiated species, which are created by the disproportion of the monolithiate **17** at higher temperatures (Scheme 1.3.4).[64] Green also showed that on the addition of just one equivalent of LDA, even at -78°C, the formation of small quantities of disubstituted products cannot be avoided.[64]

The metallation technique has been successfully used to produce a capacious range of TTF derivatives, which have been comprehensively described in the review by Garín.[58]

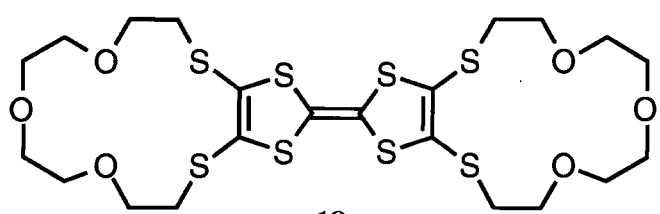


Scheme 1.3.4 *Multi-Lithiated Species Formed by the Action of LDA on Tetrathiafulvalene*

1.3.5 Tetrathiafulvalenes in Supramolecular Chemistry

Tetrathiafulvalene has developed since the early 1970's from being a donor constituent in organic metals, to recently becoming an important redox-active component in many supramolecular systems, for example: *molecular sensors*, *molecular switches* and *molecular wires*. A few selected examples will now be presented.

In 1985 the first TTF derivative incorporating two crown ether moieties was assembled by Otsubo *et al.*, providing the first TTF-based *molecular sensor* **18** (defined as a molecule capable of selectively binding an anion, cation, or organic substrate), which selectively binds alkali metals.[66] Since then, many attempts have been made to construct TTF-based molecular sensors.[67] Becher *et al.*[68] showed the oxidation potential of a TTF-macrocycle to be an indication of the complexation status of the system. A complexed metal ion in the crown ether cavity would withdraw electrons from the system, and consequently modify the oxidation potential of the tetrathiafulvalene unit towards more anodic (positive) potentials. Only the first oxidation potential of TTF is affected by the complexation of a metal, presumably due to the metal being expelled from the crown ether cavity by the formation of the TTF radical cation. This phenomenon confirms the suitability of the TTF derivatised crown ethers as molecular sensors. As a modification on this theme, TTF-cryptand sensors were synthesised[69] and shown to have stronger binding constants, and therefore are potentially better sensor devices.



18

Stoddart *et al.* have pioneered a wide range of *molecular switching devices*, most notably catenanes and rotaxanes.[70] These devices show considerable promise for

application in the field of *molecular electronics*. Their first venture into the area of tetrathiafulvalene chemistry came in the guise of [2]pseudorotaxane **19**. TTF was complexed with a cyclobis(paraquat-*p*-phenylene) tetracationic cyclophane to produce crystalline charge-transfer complex **19** (Figure 1.3.5),[71] where TTF occupied the cavity of the cyclophane. In an extension of this work Stoddart *et al.* incorporated TTF into the self-assembly of [2]rotaxane **20**.[72] ^{1}H NMR investigations revealed that the cyclophane was forced to shuttle onto one of the hydroquinol units on oxidation of the TTF to the radical cation. This was as a result of the positive charge of the radical cation repelling the tetracationic cyclophane away from the TTF unit, thus providing a remarkable quality of being an electro-addressable redox-switch.

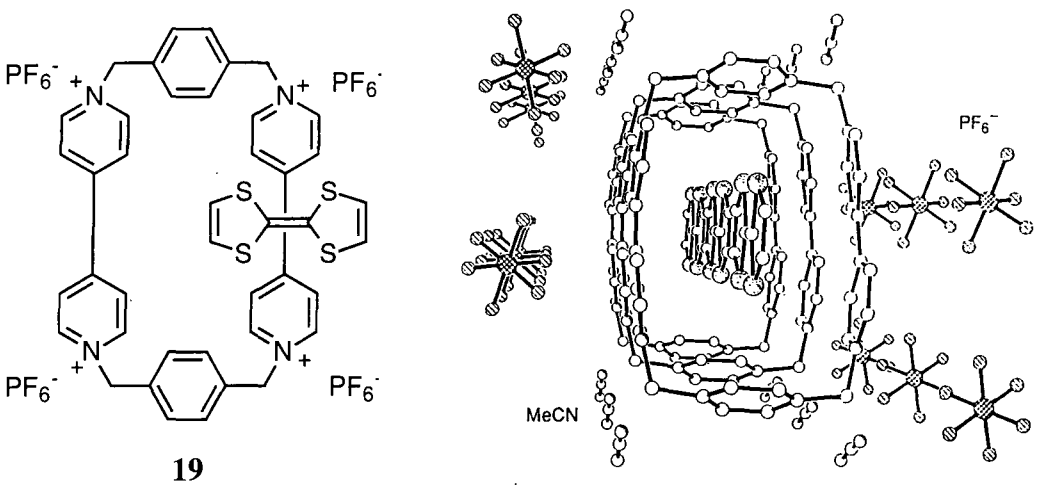


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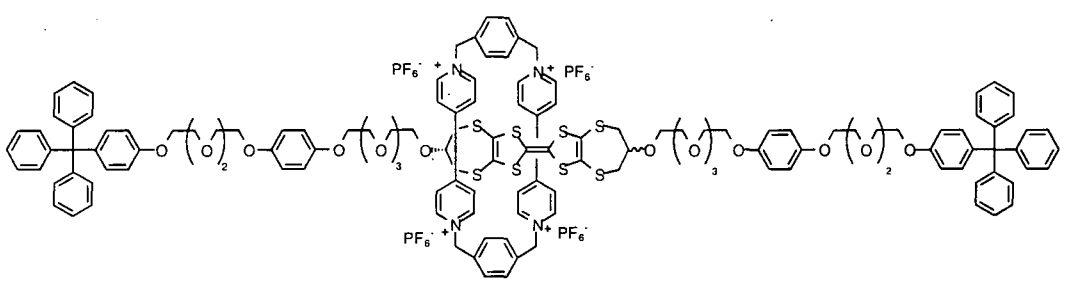
Figure 1.3.5 *A Schematic Representation & X-Ray Crystal Structure of a [2]Pseudorotaxane Incorporating Tetrathiafulvalene*



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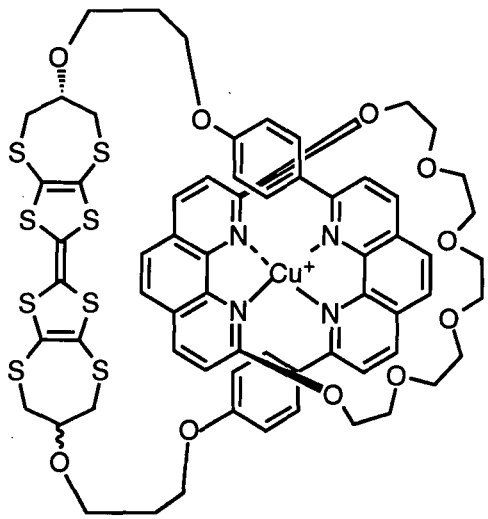
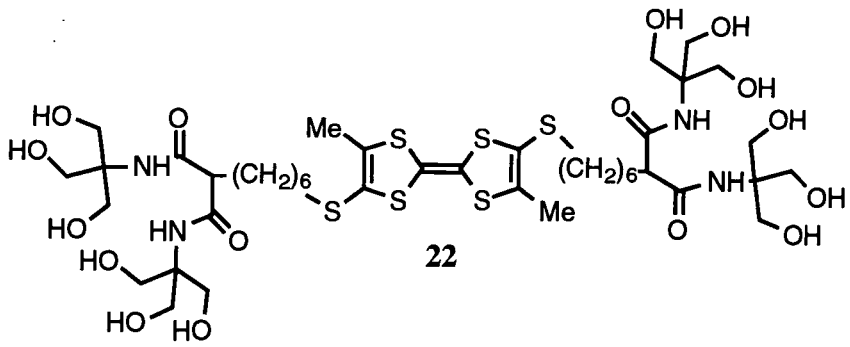
Becher *et al.*[73] recently assembled copper(I) [2]catenate **21**, incorporating a tetrathiafulvalene unit, which has the possibility of acting as a redox-switching light emitter. The working component of the catenate is the copper(I) complex formed with two 2,9-diphenyl-1,10-phenanthroline units, which has been shown to be a strong light

emitter and reductant in the excited states,[74] and is therefore a good candidate as a photoactive component. It is hoped that when the TTF unit is in the neutral state the catenate will complex copper(I) and perform the function of a photoemitter; the photoemission properties will be lost once the TTF unit is oxidised resulting in the copper(I) ion being ejected from the cavity.



21

Molecular wires may eventually find application in molecular electronic circuits. Bechgaard *et al.* used self-assembly techniques to produce TTF-based molecular wire **22**, where a TTF derivative was attached to a lipophilic chain and capped with large hydrophilic end groups.[11c] The aim was to achieve conductivity through the π-π interactions of the partially oxidised TTF groups. By analogy to conventional wires the hydrophilic groups would provide the "insulation" to the "copper core" of the TTF units. Phase-contrast and cross-polarised microscopy revealed the materials to be ordered, string-like assemblies with lengths of several microns, having a gross morphology in accordance with that of a wire-type structure.



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1.4 Summary

In recent years, the areas of TTF and dendritic polymer chemistry have received much attention and have been well documented. TTF has demonstrated its chemical versatility, producing a plethora of redox-active derivatives, including supramolecular assemblies.

Dendrimer chemistry has rapidly evolved from being an amateur tree-farmer's dream[75] into a major area of research. Many varieties of dendrimer now exist and it is possible to achieve almost any structural variation that could be required to tailor physical and chemical characteristics to the need of the designer.

In an era when the trend is towards ordered supramolecular structures, the union of tetrathiafulvalene and dendrimer chemistry is a marriage which promises a new and exciting venture into a class of hitherto unexplored speciality materials. This Thesis details new studies on macromolecular, multi-redox-active systems containing tetrathiafulvalene, including the first TTF-dendrimers. These materials have good potential in a number of technological applications, ranging from catalysis, to organic conductors and molecular electronics.

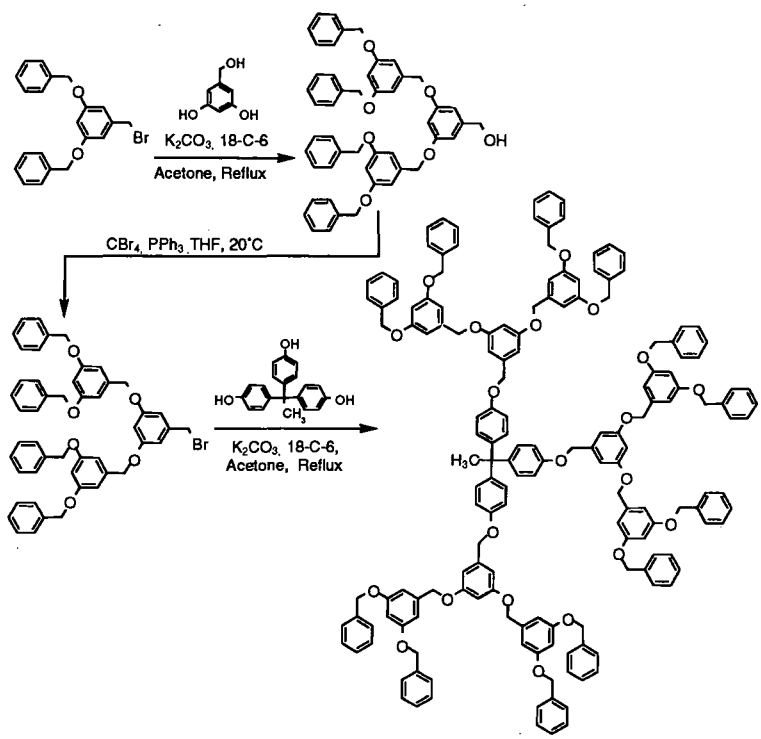
CHAPTER TWO

DENDRITIC MACROMOLECULES INCORPORATING TETRATHIAFULVALENE

2.1 Introduction

The synthesis of multi-TTF systems has long been an aim of many research groups in their quest for novel organic metals and superconductors. At the time this project was initiated there were no examples of dendritic, multi-redox-active systems; examples of subsequently published works are discussed in Section 1.2.5. The inspiration for the work in this Thesis came from Tomalia's 1990 review paper,[7d] where the advances in the relatively new field of dendritic polymers were chronicled. Later that year Fréchet *et al.*[23a] published a new *convergent methodology* that we recognised could enable the placement of redox-active substituents on the surface of dendrimers in a controlled manner (Scheme 2.1.1). This work provided the initial foundation to our design of redox-active dendritic macromolecules.

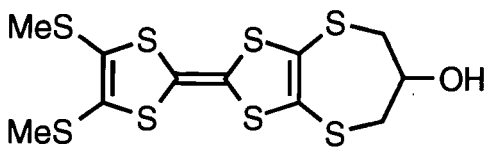
The Fréchet synthetic pathway involved the iterative reaction of substituted benzylic bromides with 3,5-dihydroxybenzyl alcohol, followed by subsequent activation of the benzyl site by bromination using CBr_4/PPh_3. For tetrathiafulvalene to be applied to this methodology an alcohol derivative was needed that could be functionalised with a good leaving group.



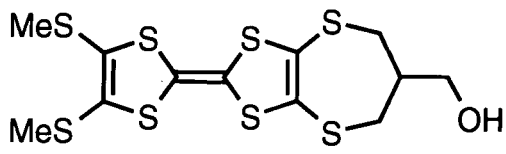
Scheme 2.1.1 *The Fréchet Convergent Methodology*

2.2 Tetrathiafulvalene Derivatives for Functionalisation into Supramolecular Assemblies

Previous investigations by Bryce *et al.*[76] had shown compound **23** to be unsuitable for functionalisation, because, although the tosyl derivative could be obtained, it was too sterically hindered to undergo nucleophilic displacement reactions.



23



24

Compound **23** was one of the first TTF derivatives to incorporate a potential 'reactive handle', and the thiomethyl groups provided good solubility. Further investigations, initially in conjunction with G.J. Marshallsay,[77] led to the development of the analogue of alcohol **23**, 4,5-di(methylthio)-4',5'-[2-(hydroxymethyl)propylene-1,3-dithio]tetrathiafulvalene **24**, as a potential building block for poly(benzylether) dendrimers, decorated with tetrathiafulvalene derivatives. It was hoped that the hydroxymethyl groups would overcome the steric problems associated with compound **23**

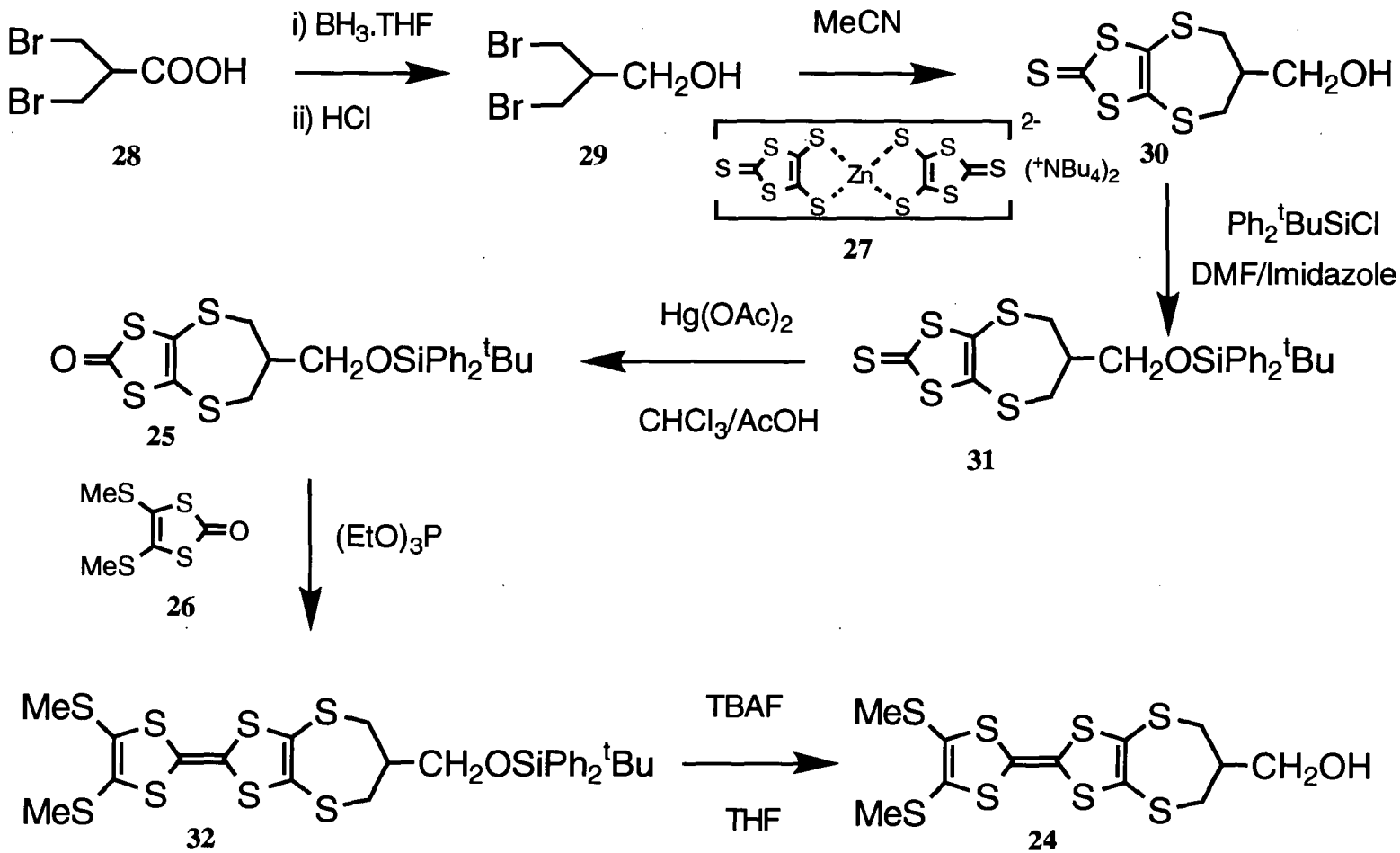
2.2.1 Synthesis of Di(methylthio)-4',5'-[2-(hydroxymethyl) propylene-1,3-dithio]tetrathiafulvalene

Compound **24** was assembled from ketone half-units **25** and **26** (Scheme 2.2.1), both of which are derived from zincate salt **27**. The pathway to ketone **25** starts with the reduction of commercially available 3-bromo-2-(bromomethyl)propionic acid **28** with borane-THF complex in dichloromethane to afford alcohol **29** in *ca.* 95% yield.[78] Thione **30** was prepared by reaction of alcohol **29** with zincate salt **27** in refluxing acetonitrile in 85% yield. The hydroxyl functionality was protected by

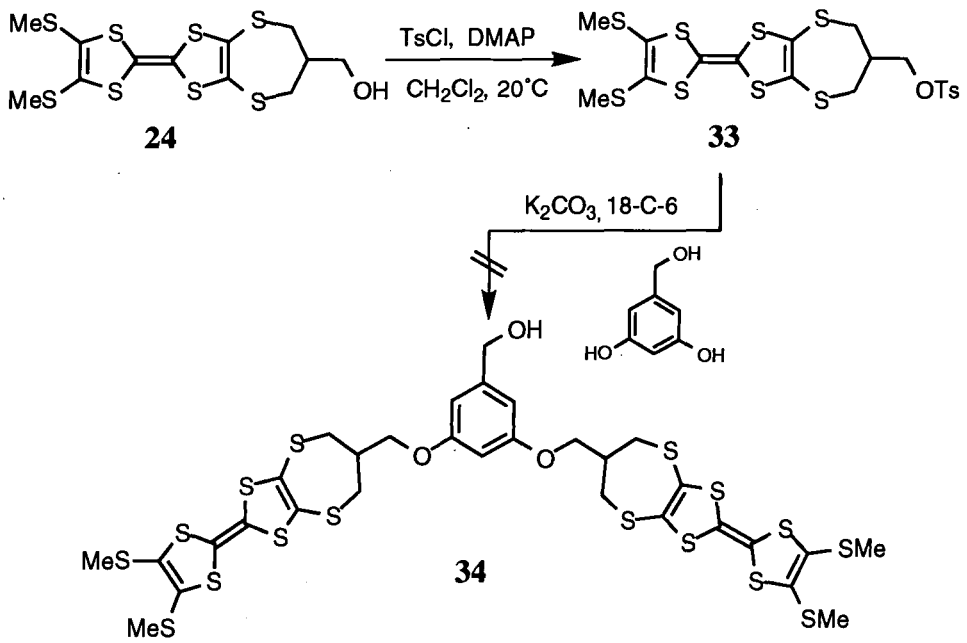
formation of the *tert*-butyldiphenylsilyl ether derivative in DMF, in the presence of imidazole, affording thione **31** in 84% yield. The thione functionality was then oxidised to the corresponding ketone **25** using mercuric acetate in chloroform/acetic acid, in 87% yield.

Ketone **26** was produced from zincate **27** by stirring in acetone with excess methyl iodide in 87% yield, followed by oxidation to the ketone using a procedure analogous to the formation of compound **25**.[79] Ketones **25** and **26** were then cross-coupled in the presence of triethylphosphite at 130°C, to yield compound **32**, which, on deprotection with tetrabutylammonium fluoride (TBAF) in tetrahydrofuran (THF) yielded alcohol **24** in 31% overall yield for the two steps. ^{1}H NMR revealed that alcohol **24** exists as a mixture of two conformational isomers,[77] where the hydroxymethyl group at C-2 can be directed up, or down with respect to the conformation of the seven-membered ring.

Reaction of alcohol **24** with *p*-toluenesulfonyl chloride at 20°C in the presence of 4-dimethylaminopyridine (DMAP), afforded tosylate **33** in 95% yield (Scheme 2.2.2).



Scheme 2.2.1 *Synthesis of 4,5-Di(methylthio)-4',5'-[2-(hydroxymethyl) propylene-1,3-dithio]tetrathiafulvalene*



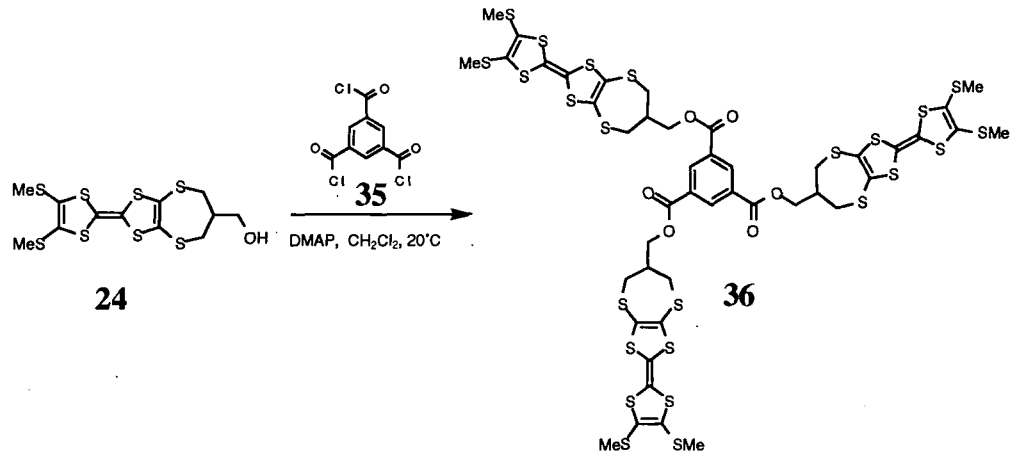
Scheme 2.2.2 *Attempted Reaction of Tosylate 33 with 3,5-dihydroxybenzyl alcohol*

Attempts were made to functionalise tosylate **33** by reaction with 3,5-dihydroxy benzyl alcohol (Scheme 2.2.2), using the conditions of Fréchet,[21e] but no reaction was observed. Further investigation to vary the quantity of base, solvent and reaction temperature failed to produce the desired compound **34**. Attempts to produce compound **34** from the mesylate of alcohol **24**[77] also failed. The failure of this synthetic strategy can be attributed to the general lack of reactivity of the tosylate and mesylate of alcohol **24**.[77] At this juncture it was decided to employ compound **24** in a different convergent methodology in future syntheses.

2.3 Dendritic Macromolecules Derived from 5-Hydroxyisophthalic Acid

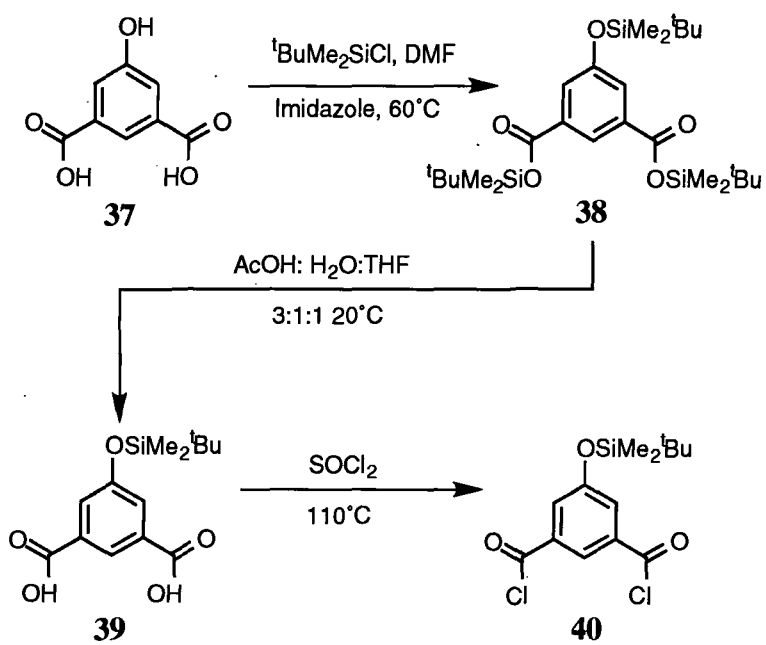
The suitability of alcohol **24** in Miller's acid chloride/alcohol methodology[8] was first tested by reacting it with commercially available 1,3,5-benzenetricarbonyl chloride **35** in dichloromethane, with DMAP as base (Scheme 2.3.1). After 18h triester **36** was obtained as an orange solid in 57% yield, which was stable for several

days at 20°C. The success of this reaction encouraged the use of alcohol **24** in the synthesis of derivatives using this methodology.



Scheme 2.3.1 *Reaction to Produce Model Compound 36*

5-(*Tert*-butyldimethylsiloxy)isophthloyl dichloride **40** was synthesised in three high yielding reactions[8] (Scheme 2.3.2) and employed in an iterative protection/ deprotection scheme, building dendron wedges of increasing size that could be coupled to a central core.



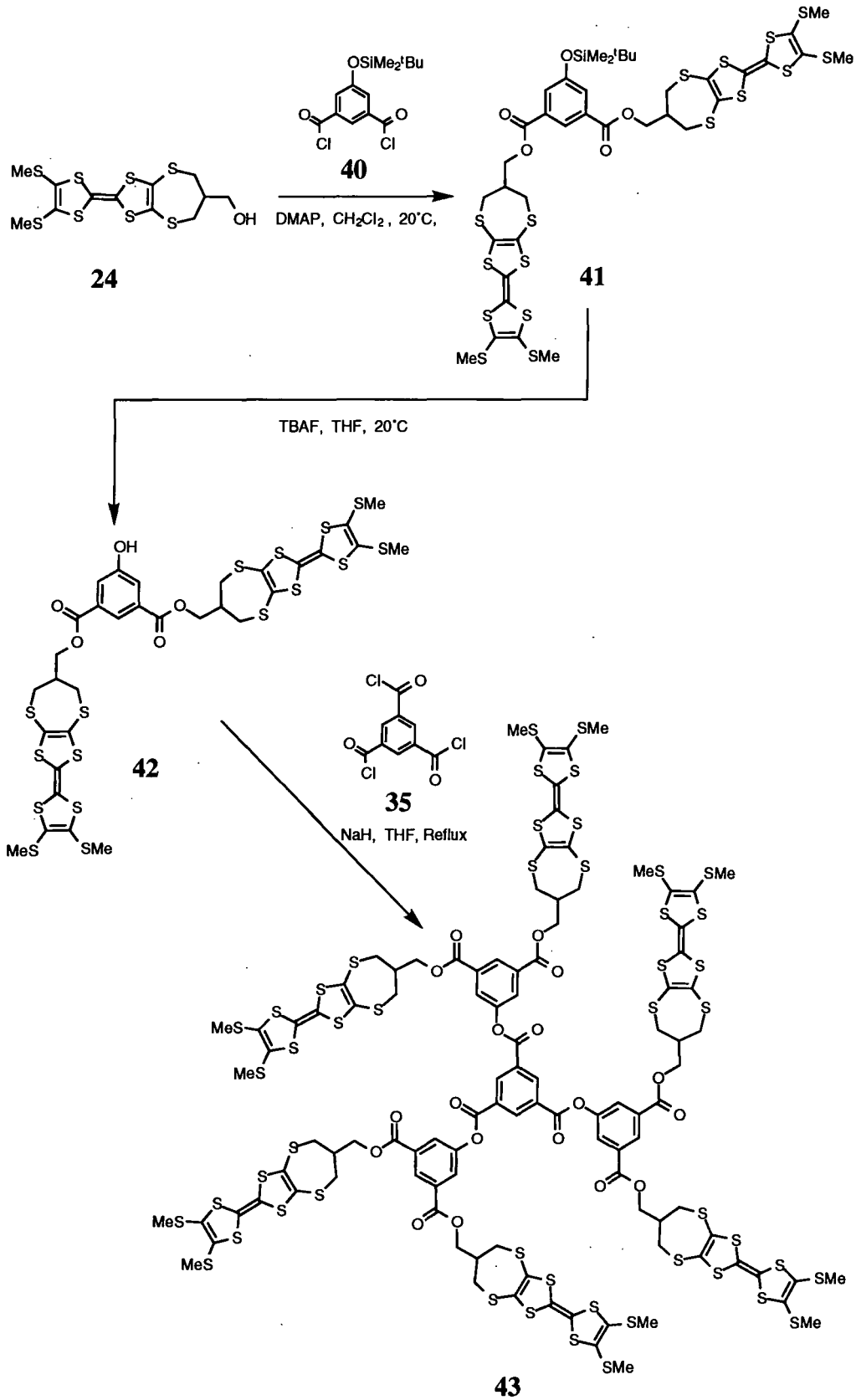
Scheme 2.3.2 *Synthesis of Dendritic Monomer 40*

Reaction of alcohol **24** with diacid chloride **40** in dichloromethane, in the presence of DMAP, afforded diester **41** in 96% yield. Subsequent deprotection of

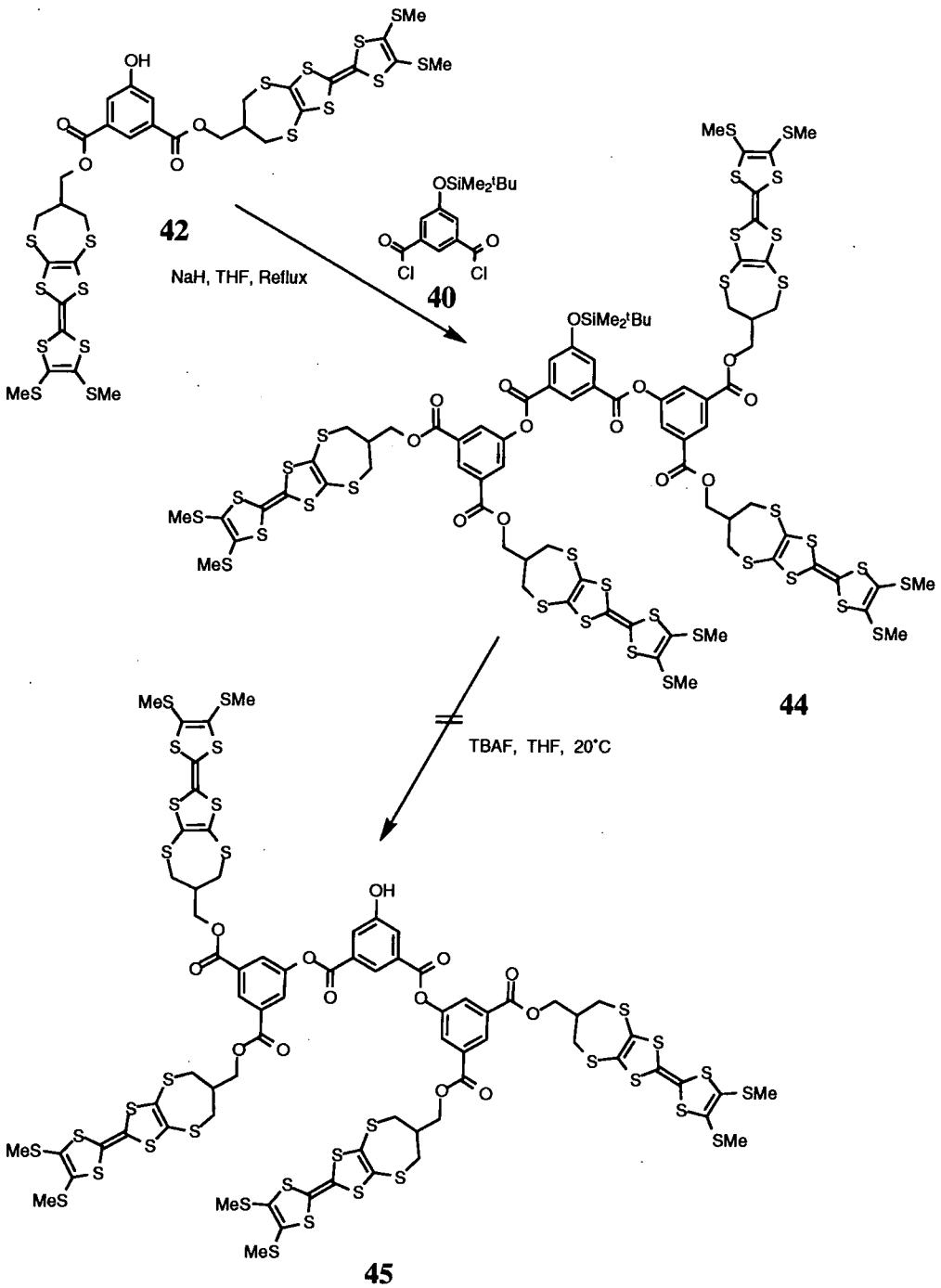
compound **41** with TBAF in THF afforded first generation dendron wedge **42** in 66% yield (Scheme 2.3.3). Compound **42** showed a sensitivity towards fluoride deprotection, which, unless dilute conditions were utilised, resulted in the rapid formation of a dark brown, uncharacterised oil, suggesting decomposition or oxidation of the TTF moiety.

Reactions of alcohol **42** with 1,3,5-benzenetricarbonyl chloride **35**, in dichloromethane at either 20°C, or at reflux in the presence of DMAP, proved unsuccessful, affording only unreacted starting material from the reaction mixture. Deprotonation of alcohol **42** was achieved with sodium hydride in refluxing THF, and the resulting alkoxide reacted with 1,3,5-benzenetricarbonyl chloride **35** to afford dendrimer **43** as an orange oil in 69% yield. This methodology, using compound **40**, assembled silyl ether **44** in 50% yield (Scheme 2.3.4). Numerous attempts to deprotect dendron wedge **44** to yield alcohol **45** proved unsuccessful. Decomposition of the TTF system occurred in the presence of TBAF, even in dilute solution .

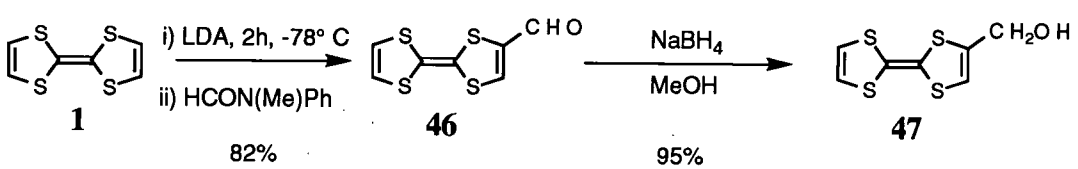
The instability of the dendritic species decorated with alcohol **24** in fluoride deprotection conditions, led us to explore a different TTF derivative in these reactions. Concurrent with this investigation, the efficient syntheses of 4-formyl-tetrathiafulvalene **46**, and 4-(hydroxymethyl)tetrathiafulvalene **47** were achieved in our laboratory (Scheme 2.3.5).[80] The availability of multi-gram quantities of compound **47** prompted it to be used in subsequent reactions.



Scheme 2.3.3 *Reaction Pathway to Assemble Second Generation Dendrimer* ***43***



Scheme 2.3.4 *Attempted Synthesis of Dendron Wedge* ***45***



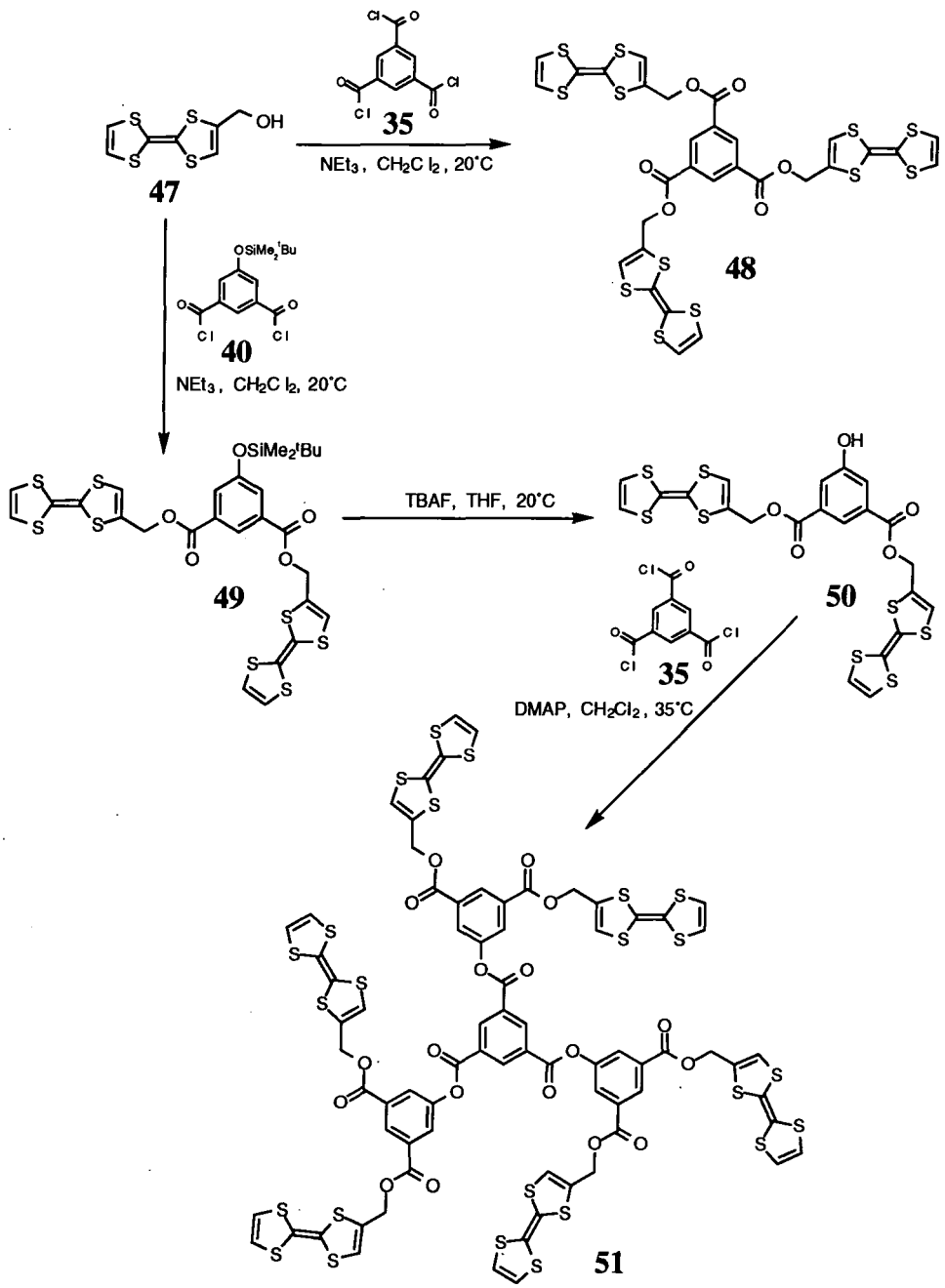
Scheme 2.3.5 *Synthesis of 4-(Hydroxymethyl)tetrathiafulvalene* ***47***

Experience gained from esterifications of alcohol **47**,[80] indicated that a milder base than DMAP should produce the first generation dendron wedges *via* esterification reactions. Consequently, triester **48** was obtained in 85% yield by the reaction of alcohol **47** with 1,3,5-benzenetricarbonyl chloride **35**, in the presence of triethylamine. This method was also successful in assembling dendron wedge **49** in 83% yield by the reaction of alcohol **47** with diacid chloride **40** (Scheme 2.3.6). Reaction of silyl ether **49** with TBAF in THF afforded alcohol **50** in 95% yield, which, when subsequently reacted with 1,3,5-benzenetricarbonyl chloride **35** in the presence of DMAP, resulted in the formation of hexakis(TTF) dendrimer **51** in 75% yield. On repetition, this reaction proved capricious, being strongly influenced by temperature, concentration and base strength. Optimum yields were obtained on heating the solution at 35°C for three days, in the presence of a ten-fold excess of DMAP. Characterisation of this second generation molecule **51** proved slightly problematical due to its low solubility in common organic solvents and its sensitivity to prolonged exposure to acidic conditions. Although the materials functionalised with 4-(hydroxymethyl)tetrathiafulvalene **47** show tolerance to silica gel during purification, they are sensitive to even dilute acid and acidic solvents such as chloroform, rapidly decomposing to a brown, oily material.

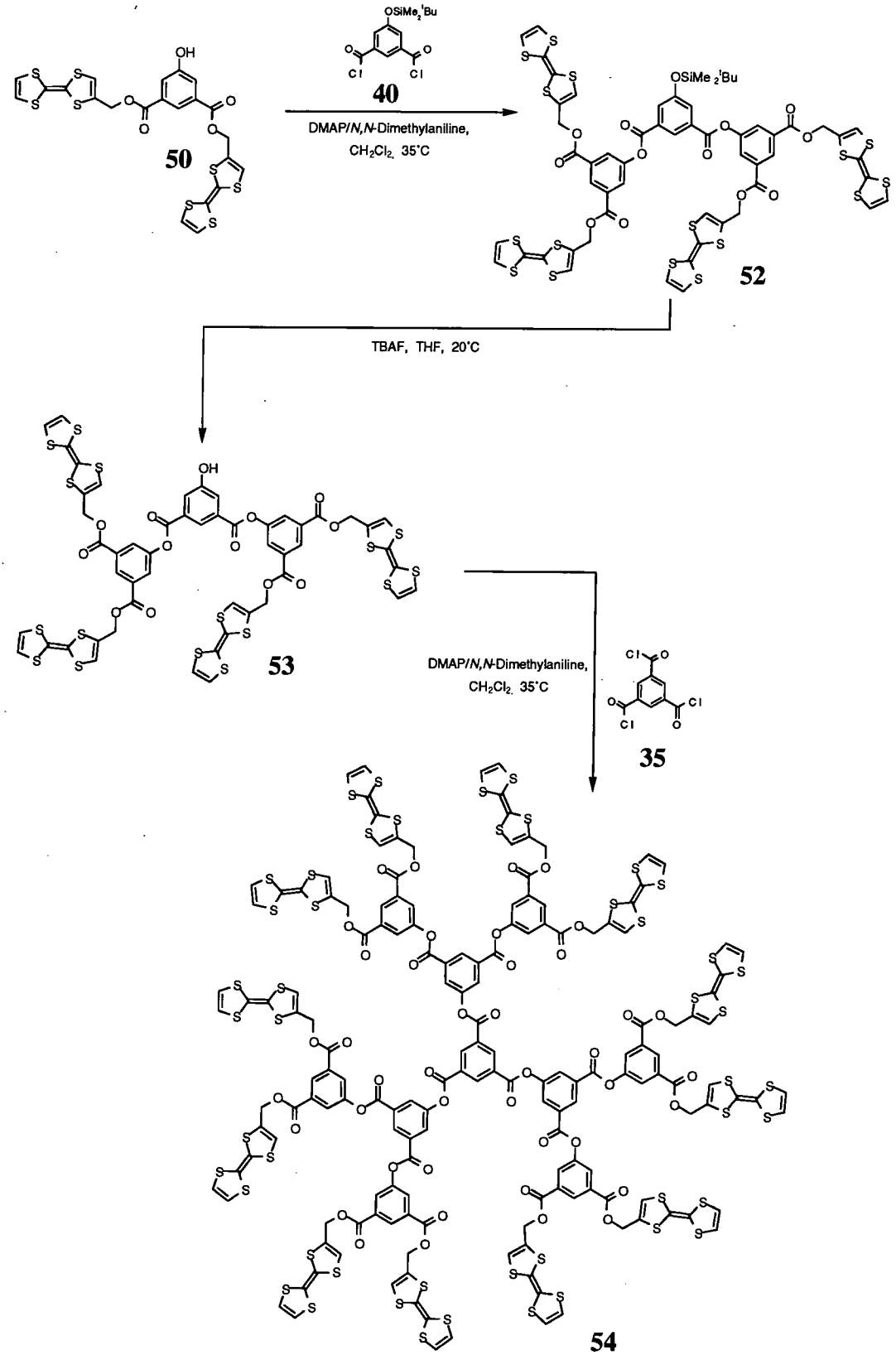
Alcohol **50** was next reacted with diacid chloride **40** in the presence of DMAP/*N,N*-dimethylaniline (1:1 $^{v}/_{v}$) to afford the second generation dendron wedge **52** in 76% yield (Scheme 2.3.7), which was subsequently deprotected by TBAF to afford compound **53** in 95% yield. Experiments to produce compound **52** using DMAP and *N,N*-dimethylaniline as sole base were unsuccessful. A careful study of base ratio and concentration confirmed the discovery that a 1:1 $^{v}/_{v}$ mixture is the optimum condition. These experiences with iterative esterifications, demonstrated the importance of carefully selecting the base for a specific reaction, as noted previously by Miller *et al.*[8]

Repetition of the base conditions used to form compound **52** were also successful in the reaction between alcohol **50** and 1,3,5-benzenetricarbonyl chloride, affording dodeca(TTF) dendrimer **54** in 48% yield. Reaction of alcohol **53** with diacid

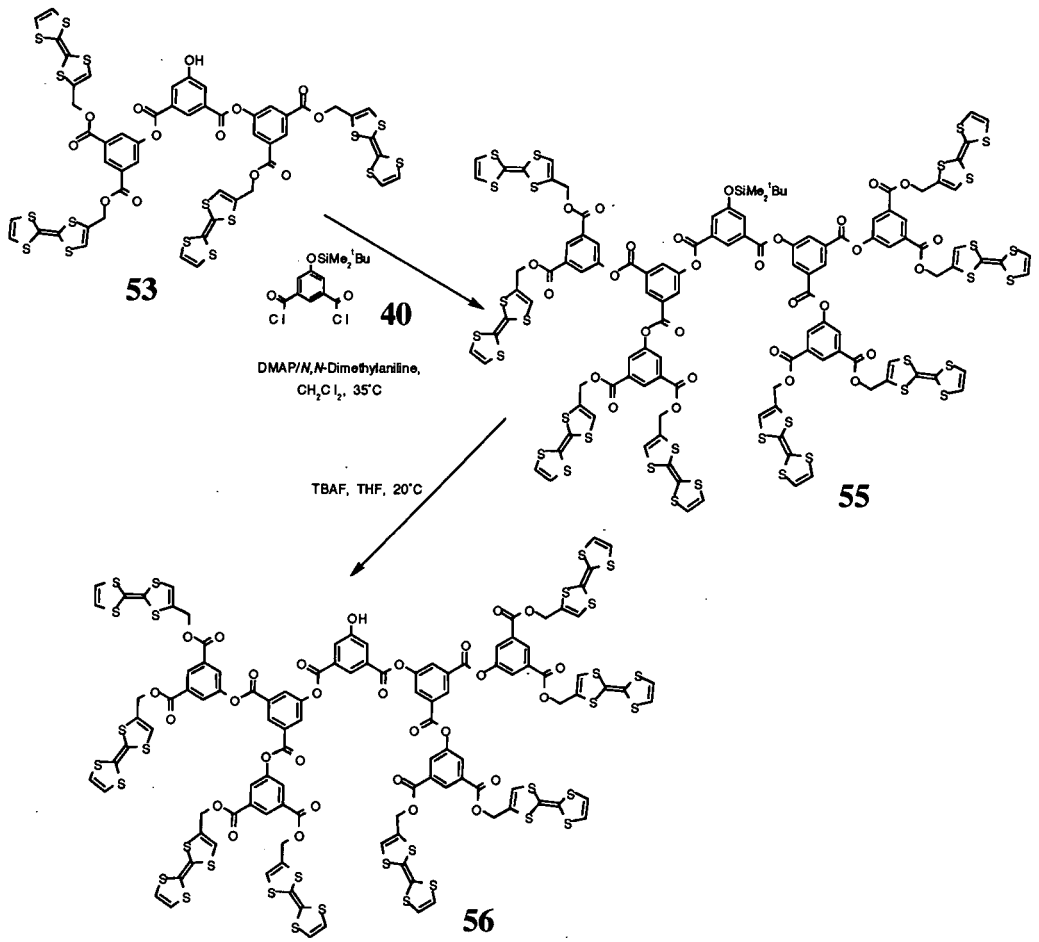
chloride **40** in the presence of DMAP/*N,N*-dimethylaniline (1:1 $^{v}/_{v}$) afforded third generation protected wedge **55** in 76% yield, this was subsequently deprotected with TBAF to yield alcohol **56** in 50% yield (Scheme 2.3.8). Figures 2.3.1, 2.3.2 and 2.3.3 show ^{1}H NMR spectra for second generation silyl ether **52**, second generation alcohol **53**, and second generation dendrimer **51**. These spectra are representative of dendrimers incorporating alcohol **47**.



Scheme 2.3.6 *Synthetic Pathway to Second Generation Dendrimer 51*



Scheme 2.3.7 *Synthetic Pathway to Third Generation Dendrimer 54*



Scheme 2.3.8 *Synthetic Pathway to Third Generation Dendron Wedge* ***56***

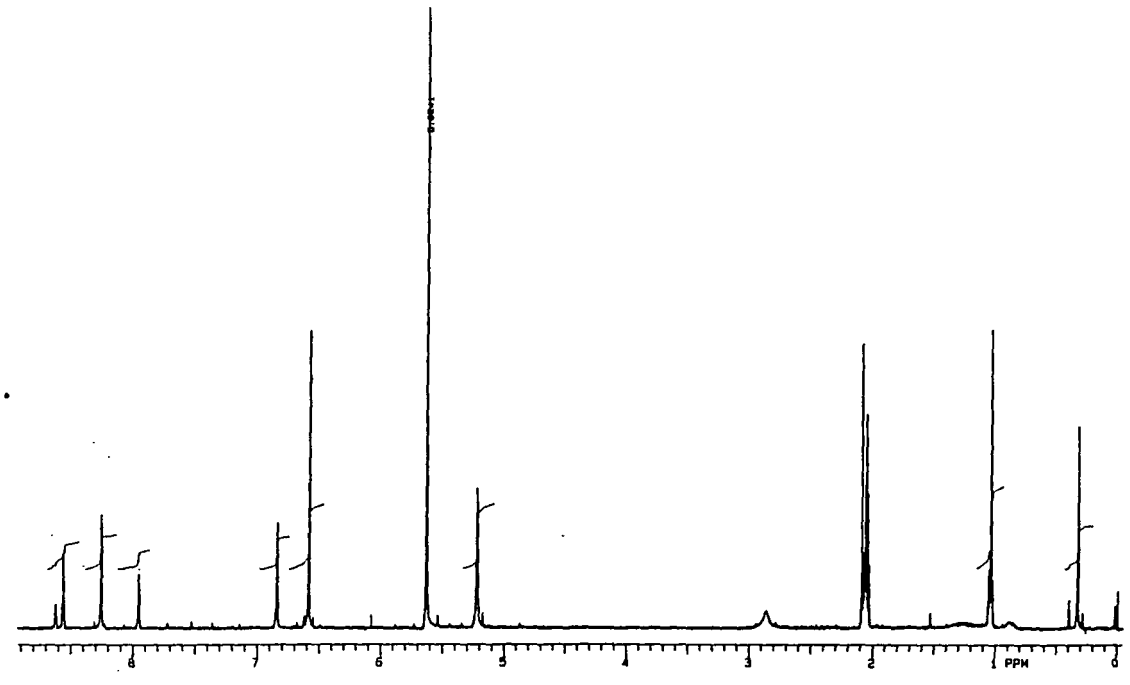


Figure 2.3.1 *^{1}H NMR Spectrum of Second Generation Silyl Ether 52*

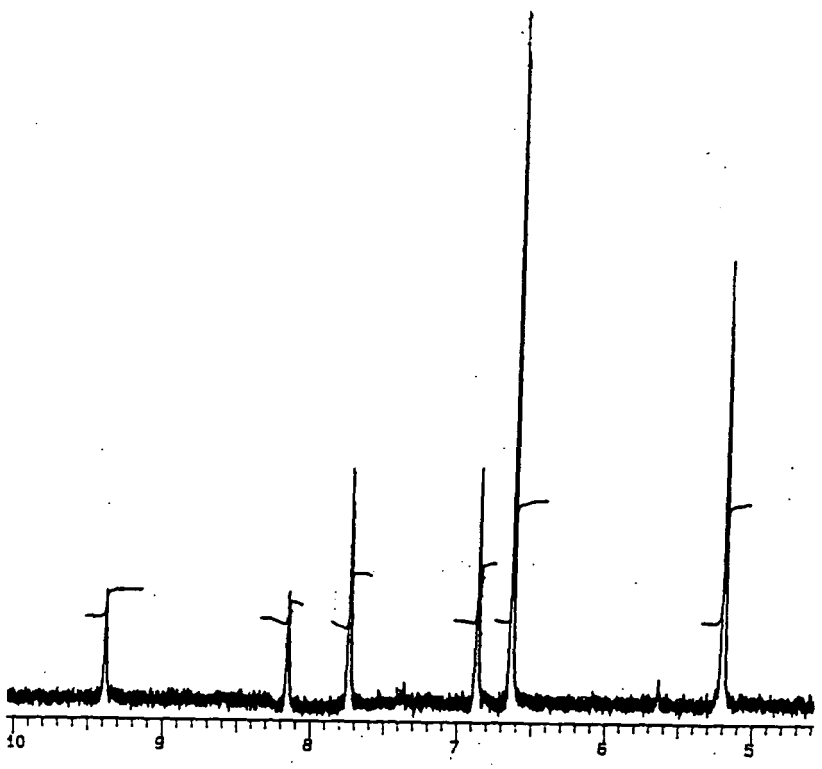


Figure 2.3.2 *^{1}H NMR Spectrum of Second Generation Alcohol 53*

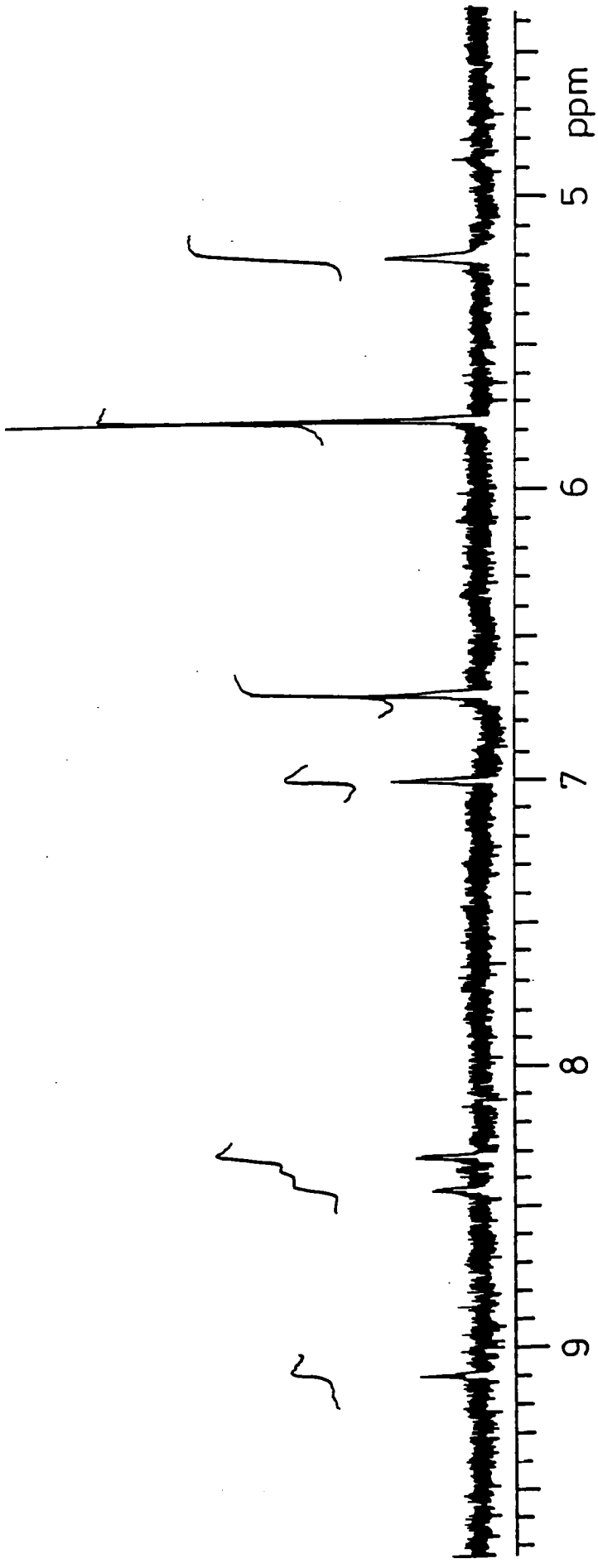
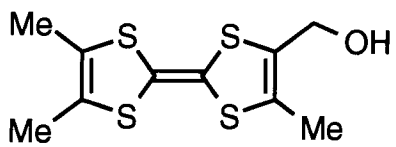


Figure 2.3.3 *^1H NMR Spectrum of Second Generation Dendrimer 51*

A notable feature of the molecules in this series of macromolecules is their decreasing stability to air and dilute acid with increasing molecular weight. Whereas first generation molecules **48**, **49** and **50** were stable at room temperature in the dark, under argon atmosphere for several weeks, second generation molecules **51**, **52** and **53** were stable for only a week under these conditions, and third generation molecules **54**, **55**, and **56** decomposed after only a few days. Storage was best achieved at 0°C in the dark. This instability discouraged us from assembling molecules of higher generation, which would most likely be increasingly difficult to purify, handle and characterise. Instead, we have used branched entities **50** and **52** in the assembly of molecules with different core units, which will be discussed in Chapter 3.



57

The use of 4-(hydroxymethyl)-4',5,5'-trimethyl-tetrathiafulvalene **57** was briefly explored in the assembly of dendritic species, as some other recently synthesised derivatives[81] showed remarkable stability, despite having lower oxidation potentials when compared to analogous TTF derivatives (Table 2.3.1).

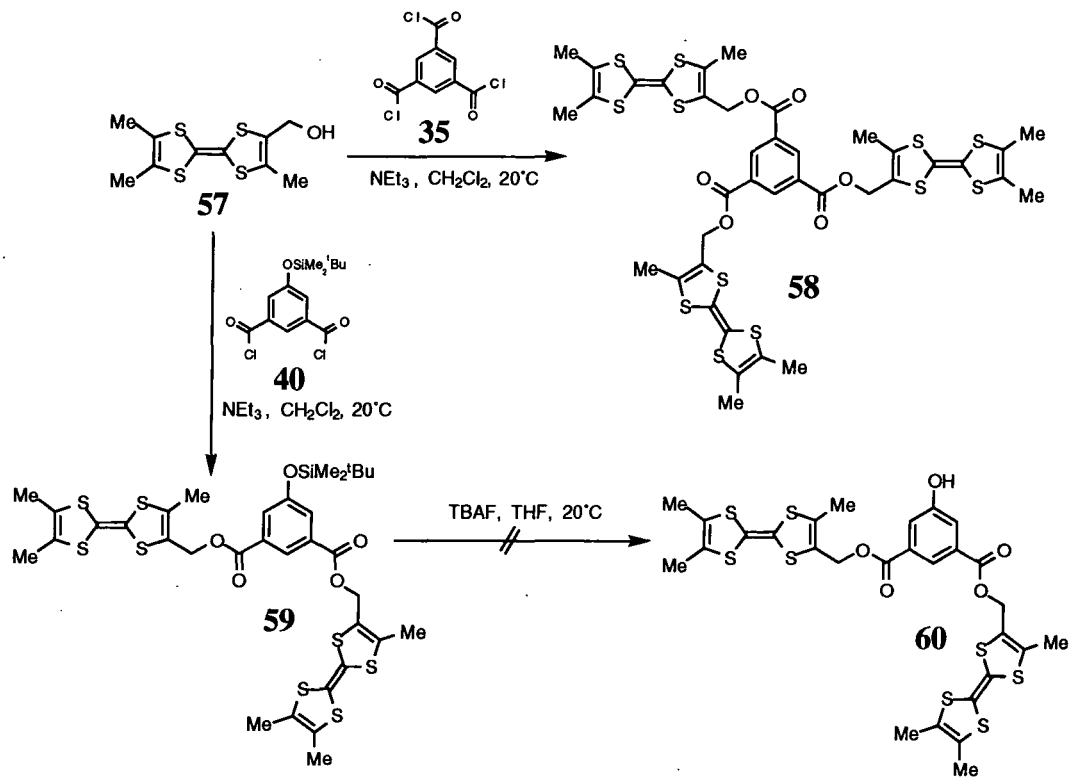
Compound	$E_1^{1/2}$ /V	$E_2^{1/2}$ /V
TTF 1[50a]	0.34	0.71
47[65]	0.41	0.79
57[81]	0.29	0.69

Data were obtained at 20°C versus Ag/AgCl, in dry MeCN under argon using a platinum wire counter electrode.

Table 2.3.1 *Oxidation Potentials of Selected TTF Derivatives*

Two model derivatives of alcohol **57** were prepared. Reaction with 1,3,5-benzenetricarbonyl chloride **35** in the presence of triethylamine afforded tri-ester **58** in 48% yield. Analogously, alcohol **57** was reacted with diacid chloride **40** in the

presence of triethylamine, affording silyl ether **59** in 90% yield (Scheme 2.3.9). We were disappointed to discover that not only were compounds **58** and **59** more sensitive to acidic media than compounds **48** and **49**, but also the trimethyl-TTF systems showed significant decomposition after four weeks when stored in the dark, under argon, at 4°C. An attempt was made to produce alcohol **60**, using the previous fluoride deprotection procedures, but this proved unsuccessful, affording an inseparable reaction mixture of decomposition products. As there were no apparent stability advantages in utilising trimethyl-TTF system **57**, these derivatives were not explored further.

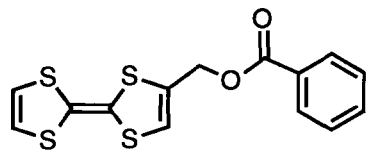


Scheme 2.3.9 *Attempted Synthesis of Dendron Wedge 60*

2.4 Electrochemical Analysis of Dendrimers Derived from 5-Hydroxyisophthalic Acid

An important aspect of this work was to evaluate the solution electrochemical properties of the materials produced. Assemblies containing up to twelve TTF units have been synthesised (Scheme 2.3.7) and a variety of electrochemical techniques were employed to assess their behaviour, when subjected to an applied potential. Classical cyclic voltammetry (CV), cyclic voltammetry using ultra-micro electrodes (UME CV) and chronoamperometry (CA) were employed in this study. Table 2.4.1 shows the redox potentials of the dendron wedges and dendrimers studied, along with model TTF derivatives for comparison. All the multi-TTF derivatives display two, reversible, multi-electron oxidation waves, typical of the parent TTF system. There is no apparent broadening of either of the two oxidation waves, suggesting that there are no significant intra- or inter-molecular Coulombic interactions between charged TTF units and that the TTF moieties are electronically independent. The multi-TTF species described below each show redox waves at very similar potentials to their alcohol precursors, and to ester **61**.

Classical voltammetry, cyclic voltammetry with ultra-micro electrodes and chronoamperometry were used to determine the number of electrons involved in the multi-electron oxidations by comparing the response of each compound with that of a reference compound (*viz.* 2,3-dichloronaphthoquinone) exhibiting a one electron reversible reduction (Table 2.4.1). It was noted during this study that silyl ether derivatives (compounds **41**, **44**, **49**, **52**, and **55**) exhibited an increased tendency for adsorption onto the electrode, resulting in a broadened voltammogram, therefore, care had to be taken to ensure thorough cleaning of electrode surfaces after each successive measurement.



61

Compound	$E_1^{1/2}$ / V	$E_2^{1/2}$ / V	Number of TTF Units	Electrons Measured in Oxidation 1	Electrons Measured in Oxidation 2
TTF **1**	0.34	0.71	1	0.94	1.07
61	0.48	0.86	1	[a]	[a]
36	0.52	0.83	3	2.58	1.88
41	0.52	0.84	2	1.51	1.48
42	0.50	0.82	2	1.69	1.27
43	0.52	0.83	6	4.03	2.69
44	0.51	0.81	4	2.10	1.66
48	0.42	0.84	3	2.08	1.78
49	0.42	0.81	2	1.82	2.14
50	0.42	0.81	2	2.06	1.82
51	0.45	0.86	6	2.33	3.01
52	0.43	0.81	4	1.96	1.96
53	0.42	0.81	4	2.76	2.47
54	0.43	0.86	12	5.72	5.72
55	0.44	0.82	8	3.89	5.35
56	0.43	0.84	8	3.51	2.77

Data were obtained at 20°C versus Ag/AgCl, in dry MeCN/CH_2Cl_2 (1:1 $^v/_v$) under argon using a platinum wire counter electrode, ca. 5 x 10^{-4} M compound, 0.1 M tetrabutylammonium hexafluorophosphate, scan rate 100 mV s^{-1}; [a] Data were not obtained.

Table 2.4.1 *Electrochemical Data and Coulometric Study of TTF Derivatives*

CV and UME CV data obtained by the author at the Université d'Angers, showed good agreement in determining the number of electrons involved in the first oxidation reaction, but the slow scan speed at steady state of UME CV means that the fast reduction from the dication, to the radical cation is either hardly observed, or

shows a very low number of electrons participating in the oxidation reaction. The study revealed that the lower mass multi-TTF systems (*viz.* compounds **36**, **41**, **42**, **49**, **50**) exhibited almost full oxidation to the radical cation and subsequent oxidation to the dication. As the size of the molecule increased there was a decrease in the number of electrons recorded as removed, with a tendency towards 50% oxidation, for compounds **43**, **44**, and **51-56**. This phenomenon suggested that a diffusion effect was influencing the number of electrons being recorded, because an assumption of this technique is that the reference compound and species under examination will travel to the working electrode at the same speed. To correct for this anomaly, attempts were made to estimate the diffusion coefficient using chronoamperometry and introduce this factor into the calculations. The results obtained showed no correlation between the diffusion coefficient and the size of the dendrimer, whereas larger molecules would be expected to diffuse to the electrode at a slower rate than the reference compound. Further attempts were made in Durham to improve on these measurements,[82] but they only served to verify the results obtained in the original study. Astruc *et al.*[46] observed full oxidation of their flexible ferrocene functionalised dendrimers and star-shaped assemblies by cyclic voltammetry. We suggest that our dendritic TTF macromolecules described in this chapter are too inflexible and are likely to have buried redox-groups, which will not be oxidised at the surface of an electrode. Figures 2.4.1 and 2.4.2 show the classical and UME voltammograms of dendrimer **54**.

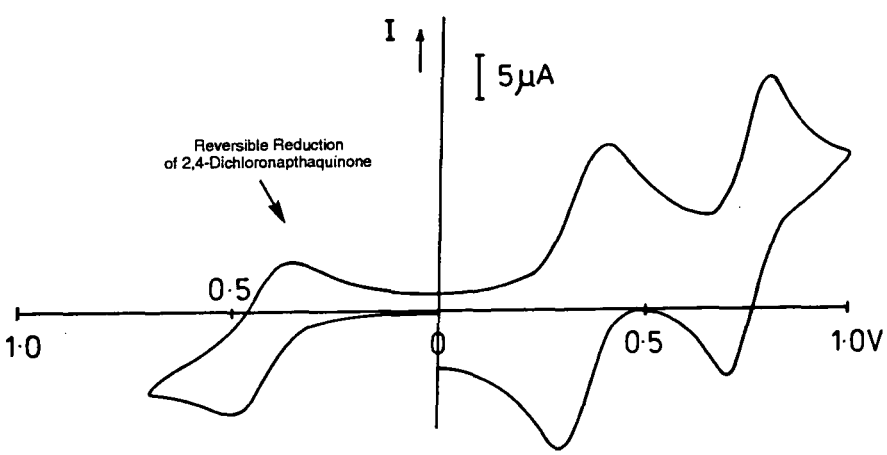


Figure 2.4.1 *Classical Voltammogram of Dendrimer 54*

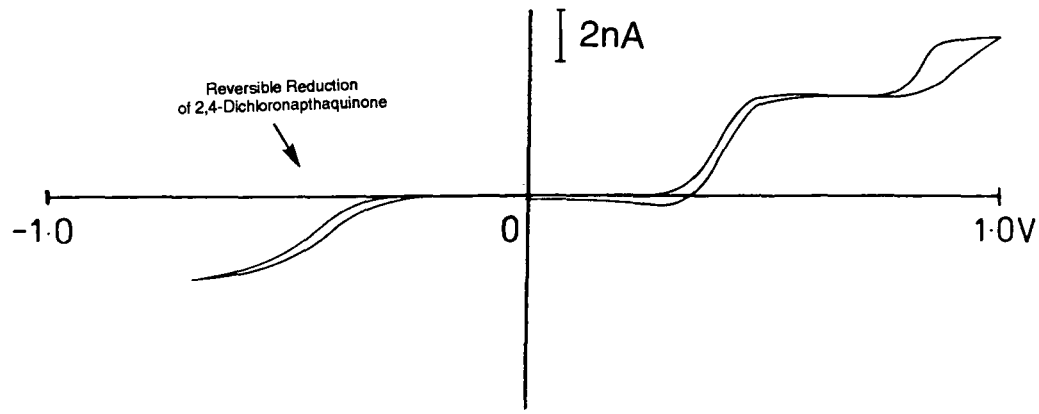
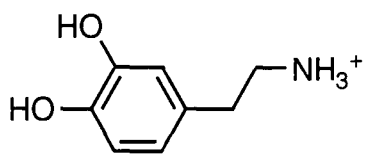


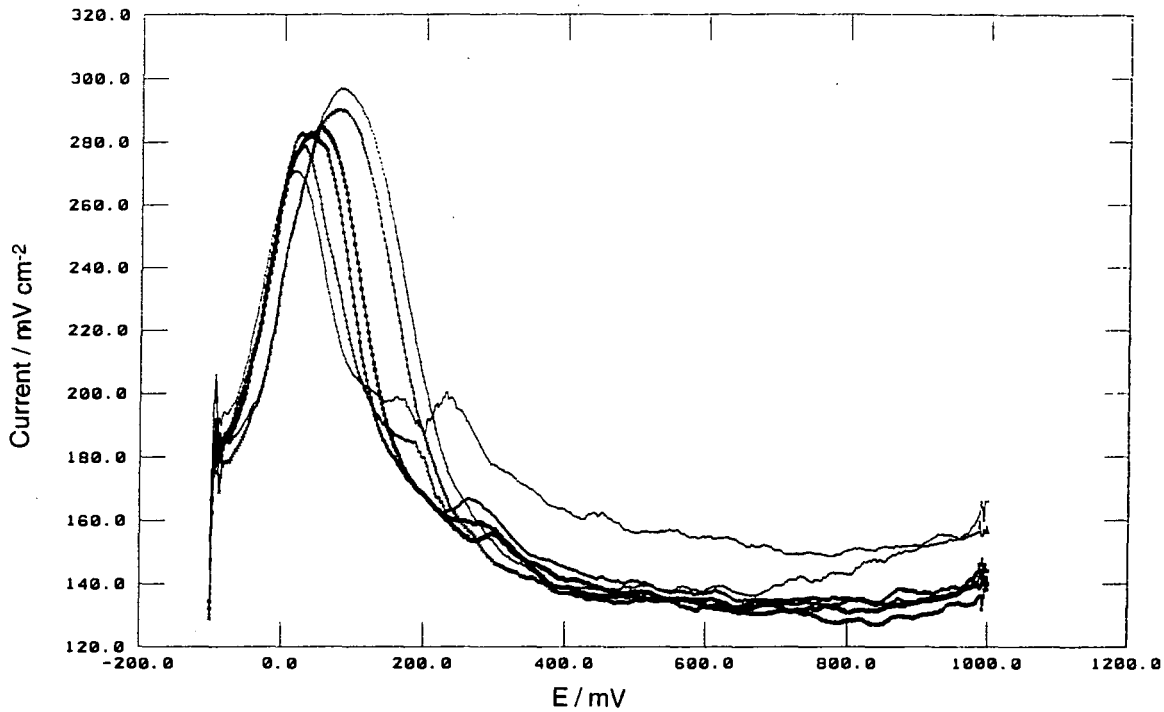
Figure 2.4.2 *UME Voltammogram of Dendrimer 54*



62

Preliminary results obtained from differential pulse voltammetry (DPV), indicated that alcohol **50** could be used as an ionophore, facilitating electron mediated transport in an electrochemical detector for dopamine **62** in phosphate buffered solutions (pH 7.0). Dopamine plays an important role in the regulation of heart rate and blood pressure in the body. Alcohol **50** was shown to detect dopamine **62** at concentrations *ca.* 5 x 10^{-5} mol L^{-1} and exhibited a proportional current response to increasing amounts of dopamine **62** (Figure 2.4.3 and Figure 2.4.4), up to an upper limit of 10^{-2} mol L^{-1}, at which point the electrode became saturated and detector response decreased. TTF **1** and ester **61** failed to detect dopamine **62** in the concentration range of 10^{-5} to 10^{-2} mol L^{-1}, this suggested that the ammonium ion of the dopamine species was residing within a cavity created by the 3,5-diester groups of alcohol **50**, facilitating the pre-concentrating and electrocatalytic oxidation of the dopamine (Figure 2.4.5). Alcohol **50** acted as a mediator between the carbon electrode and the dopamine, lowering the oxidation potential from *ca.* 300mV to *ca.* 50mV, by

donation of π-electrons. Further work to vary the size of the cavity in the mediator species would establish if other drugs could be detected in this way.



Data were obtained at 20°C versus Ag/AgCl, in phosphate buffered aqueous solution using a platinum wire counter electrode.

Figure 2.4.3 *Differential Pulse Voltammogram with Increasing Concentration of Dopamine* ***62***

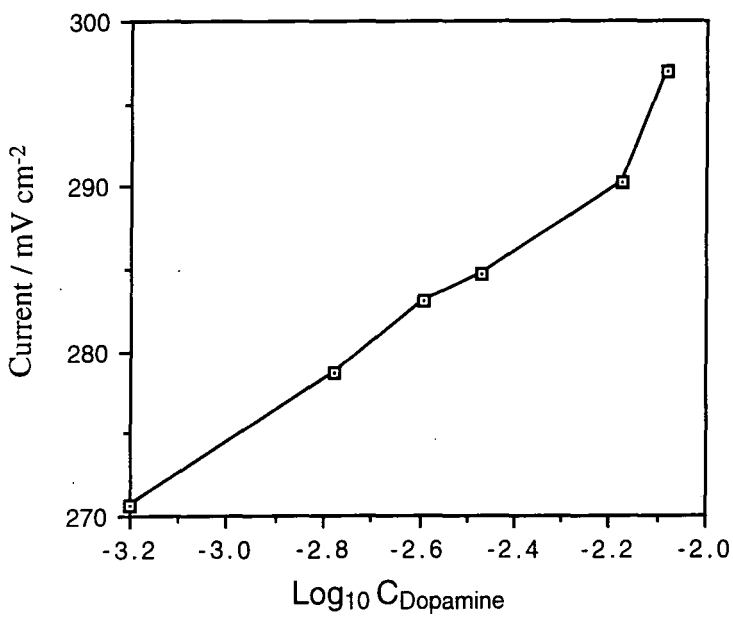


Figure 2.4.4 *Graph of Current Response as a Function of Dopamine* ***62*** *Concentration*

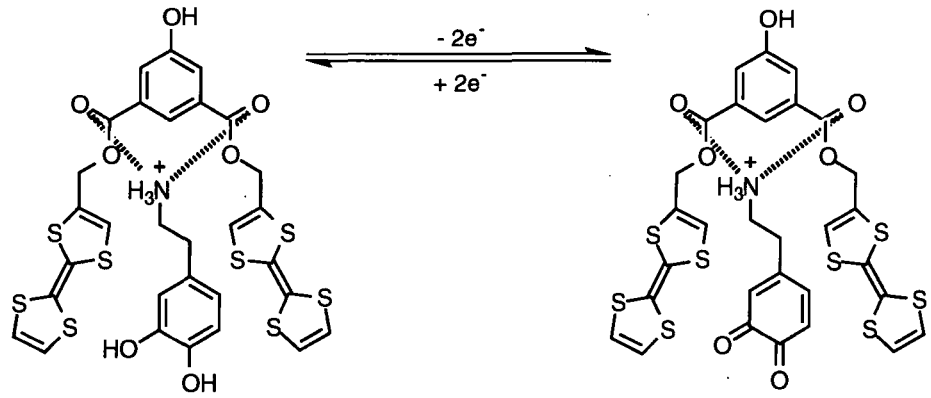


Figure 2.4.5 *Reversible Oxidation of Dopamine* **62**

2.5 Charge-transfer Complexes of Redox-Active Dendrimers

Tetrathiafulvalene forms conducting charge-transfer complexes with electron acceptors,[50a] suggesting interesting properties for dendrimers with incorporated TTF units. UV-visible spectroscopic studies in the presence of iodine were conducted on the multi-TTF species synthesised, to establish the potential of these materials to form charge transfer salts. All the TTF derivatives studied exhibited a charge-transfer band in the UV-visible region at *ca.* 590nm when complexed with iodine, suggesting chemical oxidation by iodide to form a tetrathiafulvalenyl radical cation charge-transfer salt with iodide ions at the surface of the dendrimers. Table 2.5.1 collates the UV-visible spectroscopic data for compounds **36**, **43**, **48**, **50**, and **54**, before and after addition of iodine to the solution. The band in the 820nm region seen with compounds **36** and **43** suggests the presence of aggregated TTF species.[83]

Compound	λ_{max} (CH_2Cl_2) Without I_2	λ_{max} (CH_2Cl_2), After Addition of I_2
36	233, 272, 335, 392	233, 290, 359, 815
43	233, 263, 311, 335, 440	230, 296, 335, 476, 827
48	220, 307, 365	225, 363, 439, 590
50	220, 263, 305	222, 294, 363, 590
54	221, 296, 363	223, 262, 291, 363, 590

Table 2.5.1 *UV-Visible Spectroscopic Data for Redox-Active Dendrimers*

Attempts were made to form complexes of dendrimers **48**, **51**, and **54**, with only limited success. The product obtained upon admixture of acetonitrile solutions of dendrimer and TCNQ **14** was a black solid (probably a charge-transfer salt), mixed with crystals of TCNQ and uncomplexed dendritic material. Further studies leading to electronically conducting charge-transfer systems are discussed in Chapter 3.

2.6 Computer Modelling of Redox-Active Dendrimers

Computer modelling using the Insight II computer program was used to explore the conformation of the dendritic species and explain their behaviour in the previous studies. Figure 2.6.1 shows compound **48**, in an apparent C_3, rotor conformation, the TTF units pointing in the directions of the *x*, *y*, and *z* axis. Figure 2.6.2 shows compound **51** in a variation of the conformation exhibited by compound **48**, but in this case the TTF units extend orthogonally away from each other. Figure 2.6.3 shows compound **54** adopting a more open shape in space; the aromatic rings are rotated away from each other and the TTF units are positioned as far apart as possible. It can be seen from this structure that there is increased possibility for entanglement and burial of surface groups as the molecules become ever larger, which helps to explain the results obtained in the solution electrochemistry experiments and the inability of the dendrimers to form stoichiometric charge-transfer salts. The limits of this technique are fully recognised; the models shown do not represent an exact conformation in solution nor solid state, but they serve as a rough indication of minimum energy conformations.

Figure 2.6.1 *Molecular Model of Tris(TTF) Ester* ***48***

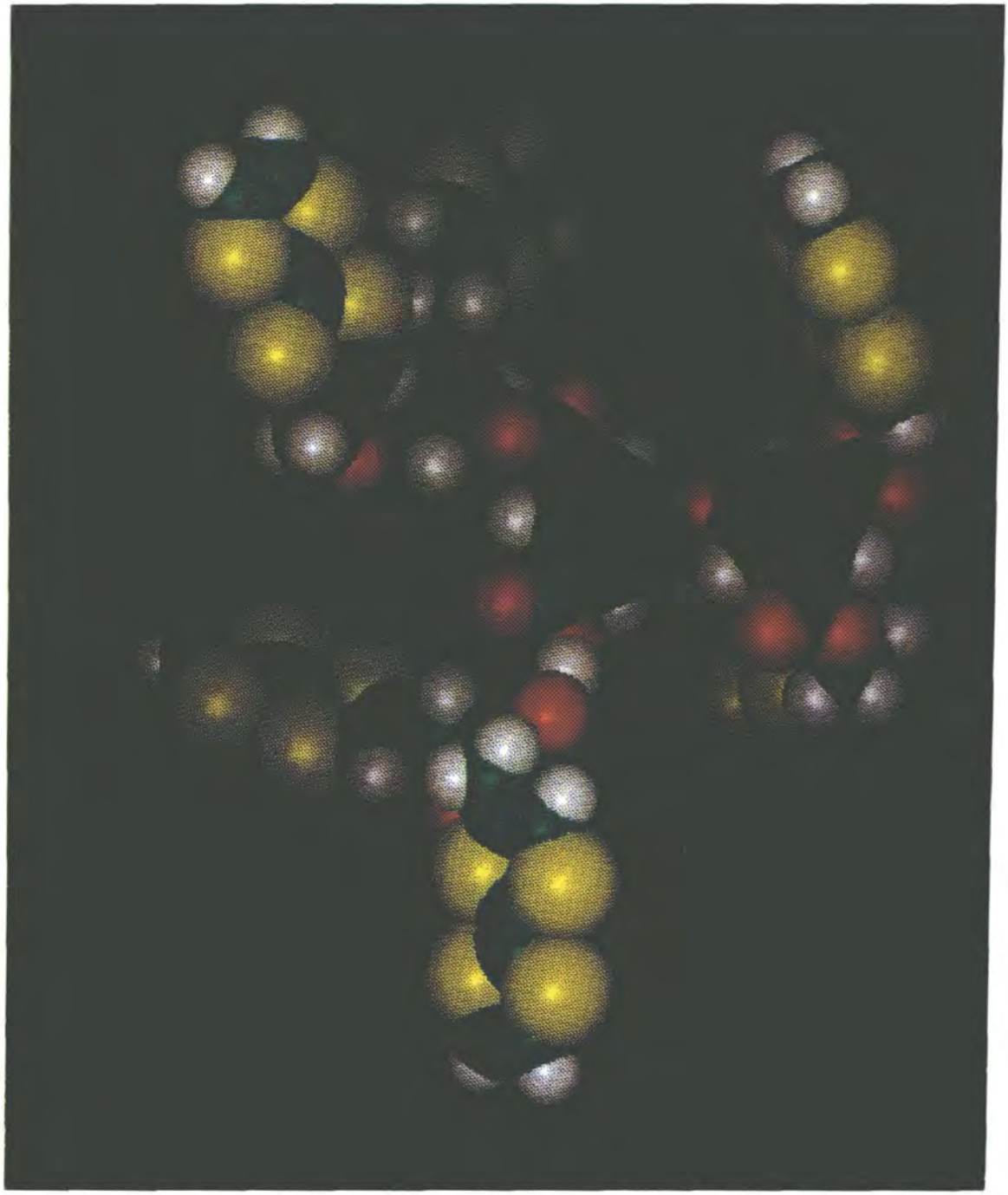


Figure 2.6.2 *Molecular Model of Hexakis(TTF) Ester* ***51***

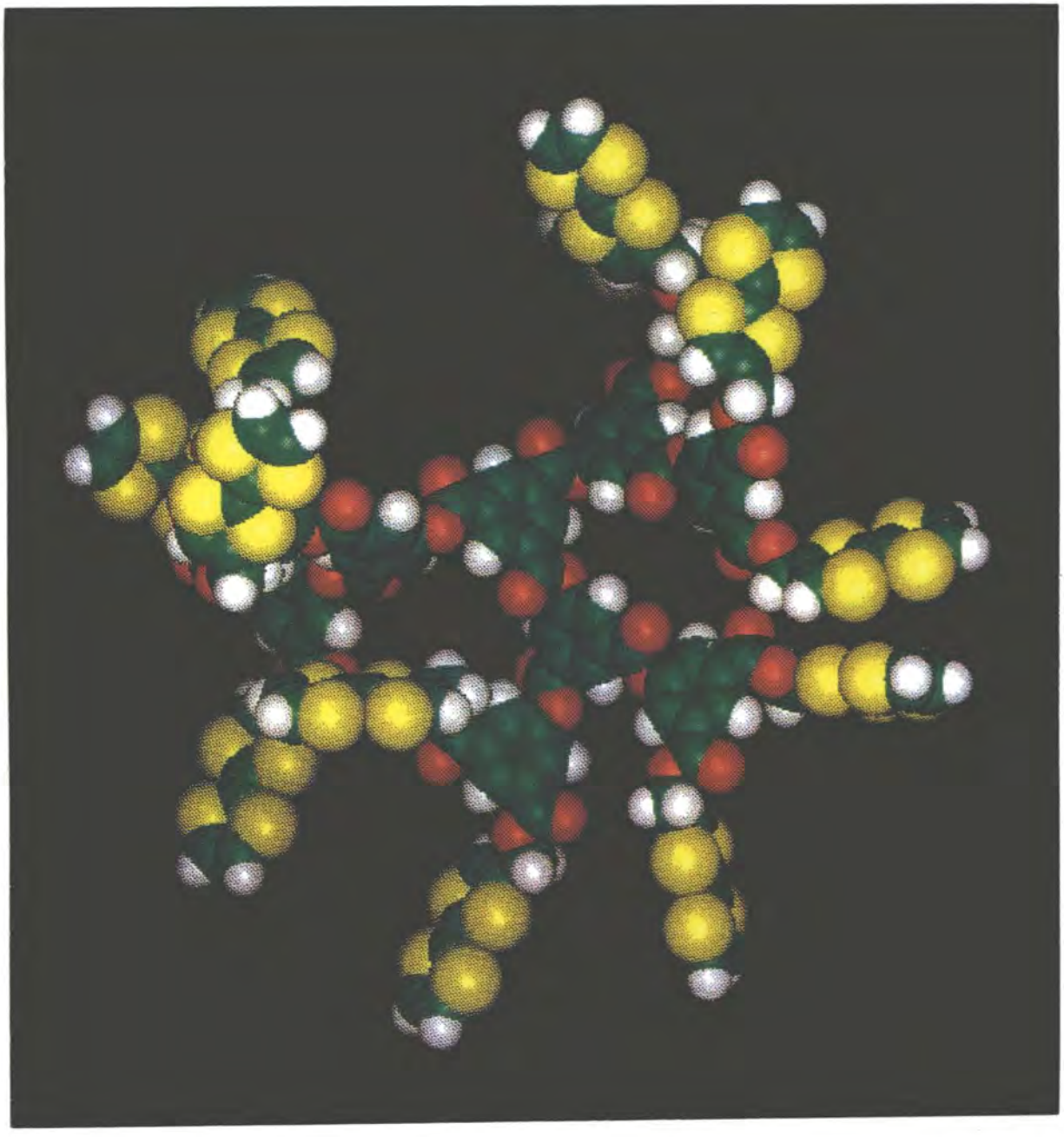


Figure 2.6.3 *Molecular Model of Dodeca(TTF) Ester* ***54***

2.7 Conclusions

A range of dendron wedges and dendritic species have been assembled by *convergent methodology*. This work sets the framework for the assembly of a wide variety of multi-TTF systems derived from branched poly-esters. Dendron wedges **42, 50, 53**, and **56** are now, for the first time, readily available in viable quantities for endowment of redox-activity to many supramolecular assemblies. Compounds **36, 43, 48, 51**, and **54** represent an important advance in the assembly of TTF on a macromolecular scale. The electrochemical properties of these species have been explored and the redox activity of TTF is not impaired by its assembly into a larger array of redox-active units. Alcohol **50** has been used to detect dopamine **62** and has opened the way for the use of these multi-TTF compounds as electrochemical detectors. The formation of solution state charge-transfer complexes has been exhibited by these compounds and this will hopefully lead to the formation of conducting dendritic species in the future.

CHAPTER THREE

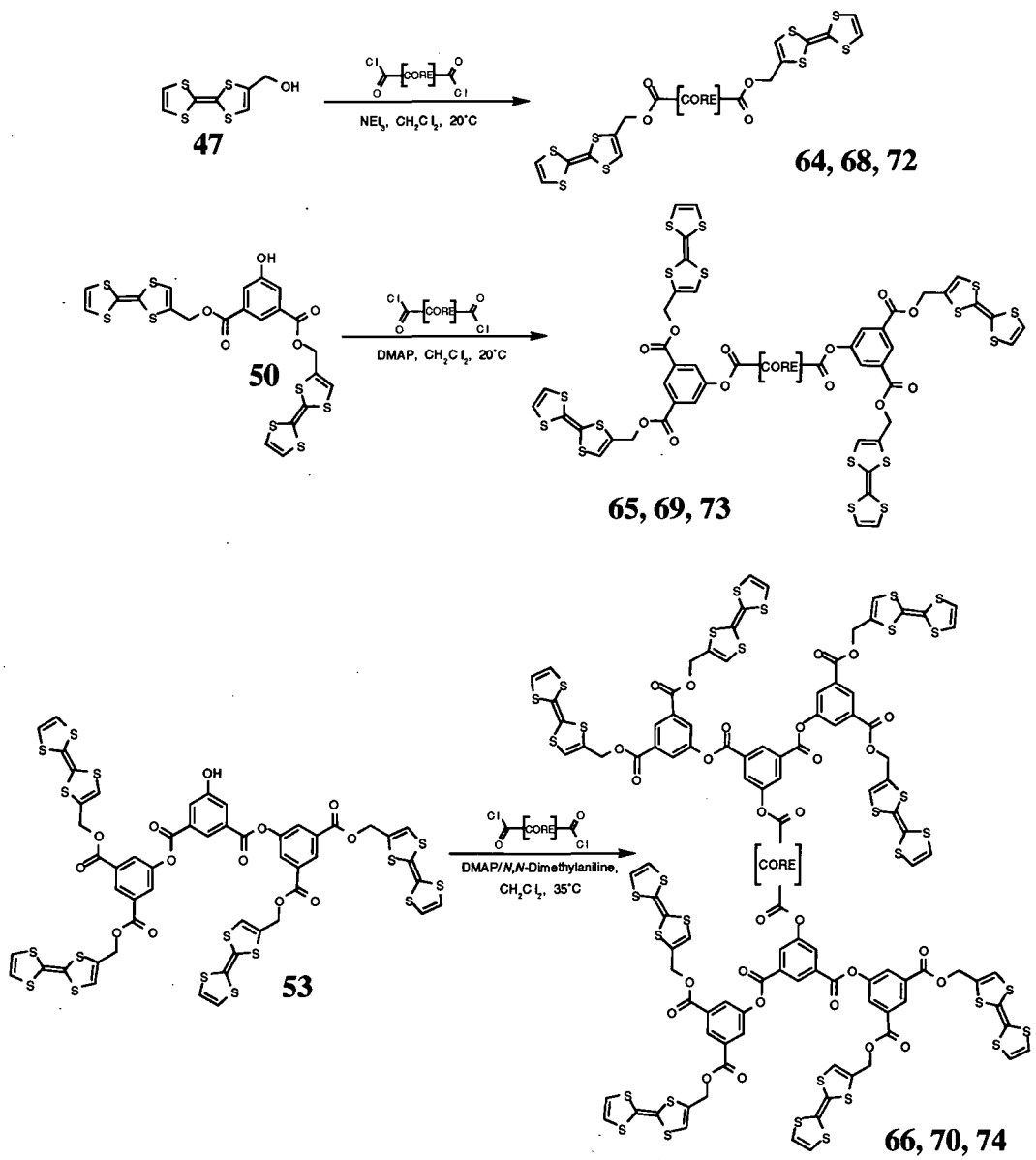
OLIGOMERIC ESTERS INCORPORATING TETRATHIAFULVALENE

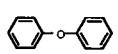
3.1 Introduction

Dendritic macromolecules incorporating tetrathiafulvalene offered many possible properties: electro-addressability, interacting redox-functionalities, conducting salts, and redox-catalysis, but the instability observed in these molecules severely limits their application. The lower generation dendrimers **48**, **51**, and **54** that have already been assembled, demonstrated no significant interaction between redox-functionalities; this is expected to occur at higher generations, but the increasing instability with increasing molecular weight makes these very difficult synthetic targets. Instead of forging ahead to higher generation of macromolecule, it was decided that we would aim to increase stability. Despite having slightly higher oxidation potentials than their mono-TTF analogues (Table 2.4.1), TTF-dendrimers exhibited less stability. Our hypothesis was that the decreased stability was due in part, to the crowded nature that a tri-functionalised core imparted. To counteract this we moved to a more open, bi-functionalised core, hence, retaining the multi-TTF system, whilst hopefully attaining greater stability.

3.2 Oligomeric Tetrathiafulvalenes with Bifunctional Cores

Our initial work focused on the use of commercially available terephthaloyl chloride **63** as a core. Alcohol **47** reacted with diacid chloride **63** in the presence of triethylamine to afford diester **64** in 59% yield. The second and third generation members of this series were assembled using conditions analogous to those of compounds **51** and **54**. Tetrakis(TTF) ester **65** was furnished from the reaction of diacid chloride **63** with alcohol **50** in 59% yield, and subsequently, octakis(TTF) ester **66** was assembled by reaction of diacid chloride **63** with alcohol **53** in 15% yield (Scheme 3.2.1). Compounds **64**-**66** were sparingly soluble in acetone and dichloromethane and proved problematic in characterisation.



64, 65, 66	[CORE] =		**63**
68, 69, 70	[CORE] =		**67**
72, 73, 74	[CORE] =		**71**

All cores are *para*-substituted diacid chlorides

Scheme 3.2.1 *Oligometric Tetrathiafulvalenes with Bifunctional Core Units* ***63, 67, 71***

In an attempt to improve the poor solubility experienced with compounds **64**, **65**, and **66**, a more flexible core, biphenyldiacid chloride **67**[84] was employed. Diester **68** was assembled in 55% yield, by reaction of alcohol **47** with diacid chloride **67** in the presence of triethylamine. Reaction of alcohol **50** with diacid chloride **67**, with DMAP as base, produced tetrakis(TTF) polyester **69** in 83% yield. A mixture 1:1 $^{v}/_{v}$ of DMAP/*N,N*-dimethylaniline was used as base in the reaction between alcohol **53** and diacid chloride **67**, furnishing octakis(TTF) polyester **70** in 35% yield. However, this series of polyesters also suffered from the same solubility problems encountered with compounds **64**, **65**, and **66**.

In a final attempt to induce solubility from a bifunctional aromatic core, diacid chloride **71**,[85] with a flexible ether linkage at the centre, was employed in the assembly of a third series of compounds analogous to **64-66**, and **68-70**. Reaction of alcohol **47** with diacid chloride **71** in the presence of triethylamine afforded compound **72** in 73% yield. Second generation tetrakis(TTF) polyester **73** was produced in 52% yield by the reaction of diacid **71** with alcohol **50** in the presence of DMAP. The formation of octakis(TTF) polyester **74** in 16% yield was achieved by reaction of alcohol **53** with diacid chloride **71** in the presence of DMAP and *N,N*-dimethylaniline (1:1 $^{v}/_{v}$). Numerous attempts using different reaction times and temperatures were made to improve upon this yield, but all were unsuccessful. Compounds **72**, **73**, and **74** were considerably more soluble than their analogues with cores **63** and **67**.

These oligoesters were initiated with the desire to obtain multi-TTF derivatives with greater stability than their dendritic counterparts; this was achieved, but at the cost of decreased solubility. The compounds described in this chapter show excellent stability at 20°C in air and daylight for several months; they also show increased stability to acid. Compounds **72**, **73**, and **74** show good solubility in most organic solvents, for example, acetone and dichloromethane, whilst retaining the good stability of their insoluble counterparts. The ability of compounds **70** and **74** to produce visible PDMS molecular ion peaks at 2954.7 and 2971.1 mass units, respectively, demonstrated their improved stability when compared to their dendritic analogues **51**

and **54**. Figures 3.2.1 and 3.2.2 show PDMS spectra for compounds **70** and **74** and are representative of mass spectra of this type.

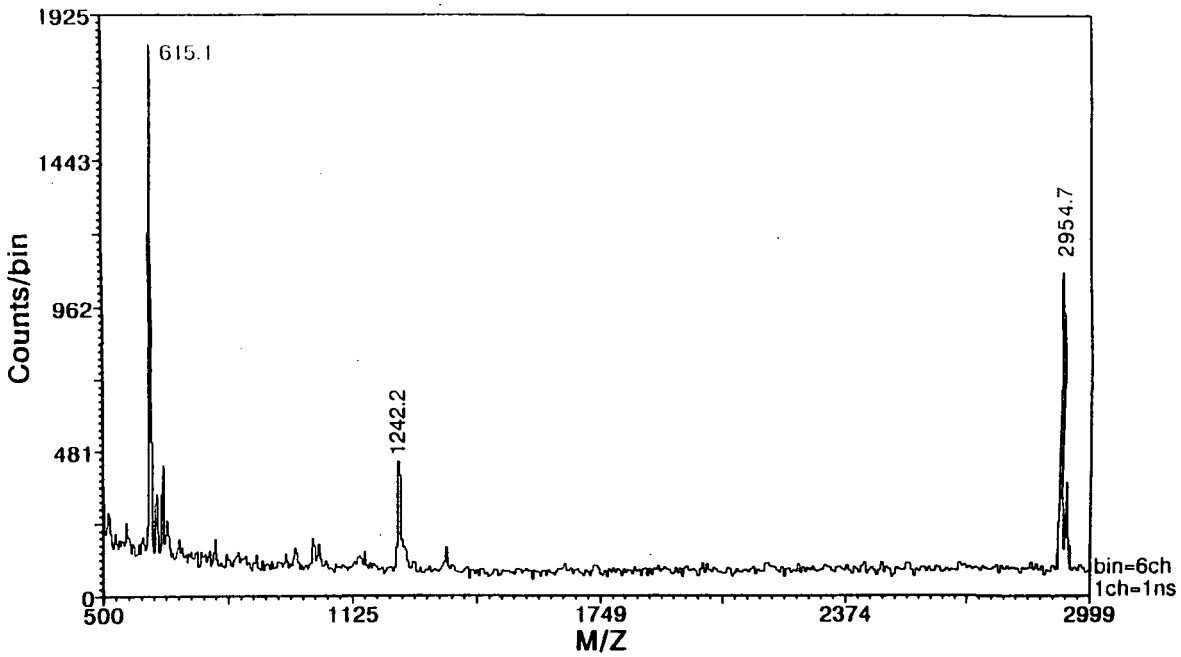


Figure 3.2.1 *PDMS Spectrum of Compound 70*

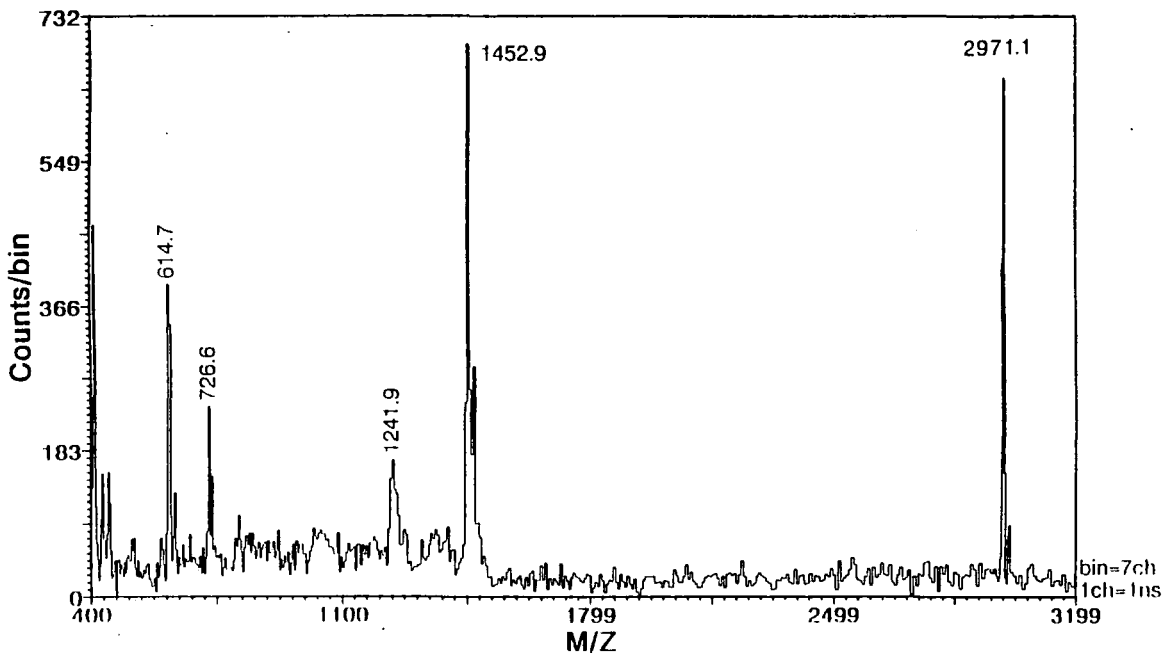


Figure 3.2.2 *PDMS Spectrum of Compound 74*

3.3 Electrochemical Study of Oligomeric Multi-TTF Systems

The poor solubility of compounds **64-70** made analysis problematic. A variety of solvents were examined for use in solution state analysis, for example, acetonitrile, acetone, dichloromethane, carbon disulfide, dimethyl sulfoxide (DMSO) and *N,N*-dimethylformamide (DMF). After careful study, DMSO was chosen as the most suitable solvent in terms of solubility and compatibility with solution state analysis techniques.

All compounds displayed two, reversible, multi-electron oxidation waves, typical of systems incorporating TTF. The $E_1^{1/2}$ and $E_2^{1/2}$ values are comparable with the multi-TTF species discussed in Section 2.4. There is no apparent broadening of either of the two oxidation waves, suggesting that there are no significant inter- or intra-molecular interactions between the individual charged TTF units and that they are electronically independent. Table 3.3.1 shows the redox potentials for these multi-TTF species.

Compound	$E_1^{1/2}$/V	$E_2^{1/2}$/V
64 [a]	0.41	0.84
65 [a]	0.42	0.83
66 [a]	0.44	0.86
68 [a]	0.40	0.81
69 [a]	0.43	0.85
70 [a]	0.41	0.82
72 [b]	0.40	0.83
73 [b]	0.40	0.84
74 [b]	0.41	0.82

Data were obtained at 20°C versus Ag/AgCl, under argon using a platinum wire counter electrode, ca 5 x 10^{-4} M compound, 0.1 M tetrabutylammonium hexafluorophosphate, scan rate 100 mV s^{-1}. [a] Solvent: DMSO. [b] Solvent : $MeCN/CH_2Cl_2$ (1:1 $^v/_v$)

Table 3.3.1 *Electrochemical Data for Oligomeric-TTF Derivatives*

3.4 Charge-Transfer Complexes of Multi-TTF Species

Multi-TTF systems based around 'open' bifunctional cores were designed to produce systems which were less sterically crowded than their dendritic counterparts and therefore, should more easily form stoichiometric charge transfer complexes in solution. UV-visible spectroscopic studies in the presence of iodine were conducted on the multi-TTF species, to establish the potential of these materials to form charge transfer salts. The TTF derivatives studied exhibited charge-transfer bands in the UV-visible region between 516 and 580nm, or *ca.* 830nm when complexed with iodine, suggesting chemical oxidation by iodine to form a tetrathiafulvalenyl radical cation. The 830nm band is diagnostic of aggregated TTF radical cation species.[83] Table 3.4.1 collates the UV-visible spectroscopic data for these multi-TTF species before and after addition of iodine to the solution.

Attempts to complex compounds **72-74** with one equivalent of TCNQ per TTF unit resulted in the formation of black charge-transfer materials. The formation of these products, uncontaminated by starting materials, demonstrates the benefits of utilising a bifunctional core at the centre of our oligo-TTF species. Although the complexes were non-crystalline, they exhibited conductivity values comparable to semiconductors at room temperature (Table 3.4.2). Solid-state infra-red spectra of the charge-transfer complexes of TCNQ with compounds **72**, **73**, and **74** exhibited a peak at *ca.* 2180 cm^{-1}, consistent with the presence of the TCNQ radical anion.

Compound	λ_{max}, Without I_2	λ_{max}, After Addition of I_2
64	222, 242, 302, 370	222, 295, 362, 516
65	222, 250, 300, 362	221, 294, 365, 516
66	222, 250, 300, 362	221, 294, 365, 516
68	223, 291, 363	221, 291, 365, 517
69	198, 294, 354	198, 302, 386, 588, 810
70	229, 306, 370	233, 296, 368, 836
72	222, 308, 363	222, 280, 363, 578
73	223, 307, 364	222, 287, 363, 828
74	233, 281, 314, 362	233, 281, 314, 830

Table 3.4.1 *UV-Visible Spectroscopic Data for Multi-TTF Species*

Donor	Number of TTF Units	Stoichiometry Donor:Acceptor	Conductivity S cm^{-1}
TTF 1	1	1:1	500[86]
72	2	2:1	3 $x10^{-3}$
73	4	1:1	3 $x10^{-3}$
74	8	*ca.* 1:3	1.5 $x10^{-3}$

Two Probe Measurement on Compressed Pellets[87]

Table 3.4.2 *Conductivity Data for TCNQ Charge-Transfer Complexes*

3.5 Computer Modelling of Multi-TTF Species

Molecular modelling studies of the three series of molecules (Scheme 3.2.1) were carried out to gain insight into the likely conformations of the multi-TTF systems. The studies indicated that compounds **64-66** and compounds **68-70** had rigid aromatic backbones, from which the TTF units arranged themselves in a minimum energy conformation. This rigid backbone could explain the low solubility of the compounds in common organic solvents. Figures 3.5.1 - 3.5.3 show computed conformations of compounds **68**, **69**, and **70**. The ether linkage at the centre of the compounds **72-74** allows for greater flexibility and a less rigid structure, resulting in greater solubility.

The bifunctionality of the core at the centre of these molecules allows for more open, less crowded structures; this factor is likely to be very important in the increased stability that these molecules exhibit.

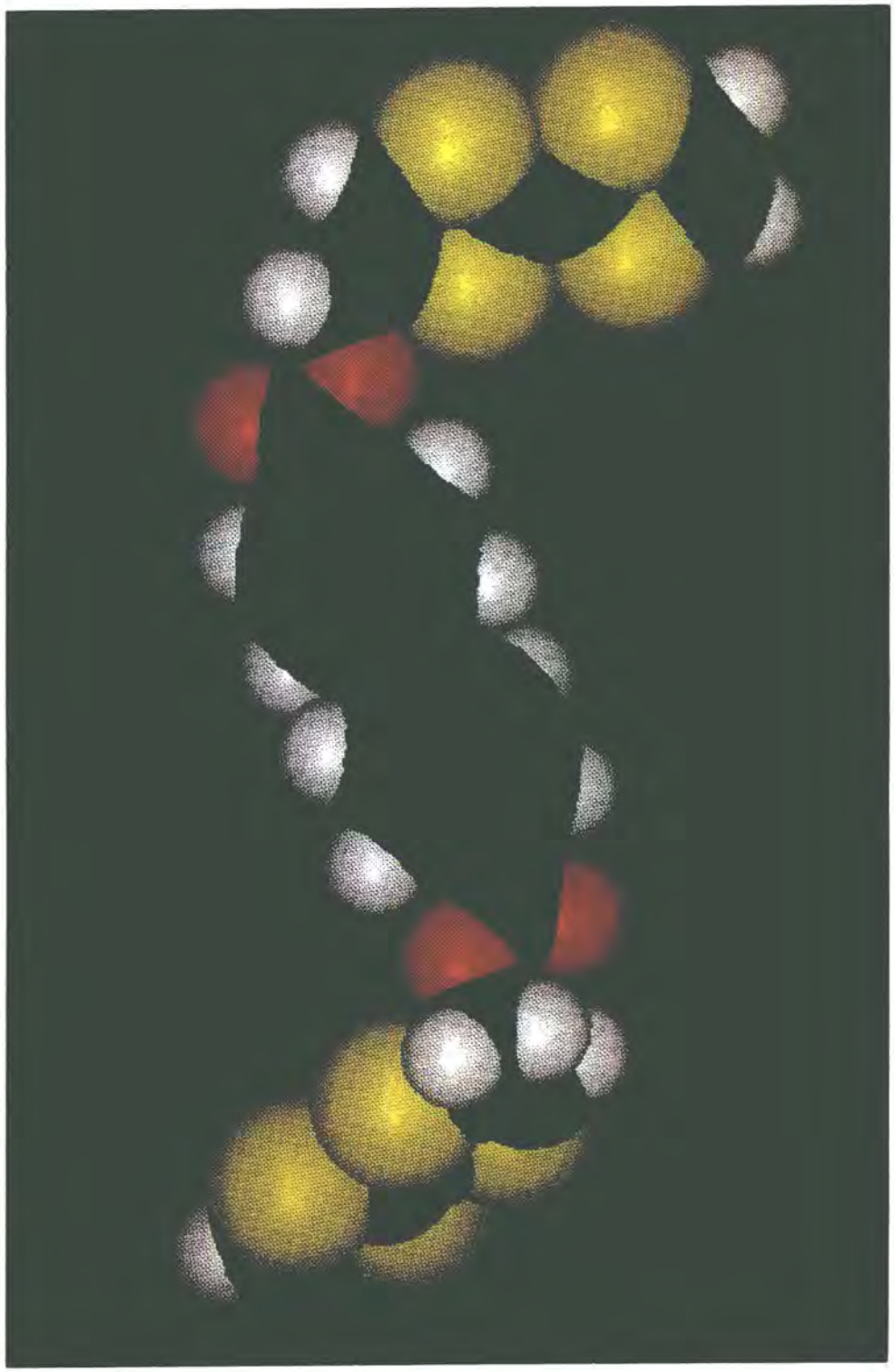


Figure 3.5.1 *Molecular Model of Bis(TTF) Ester 68*

Figure 3.5.2 *Molecular Model of Tetrakis(TTF) Ester* ***69***

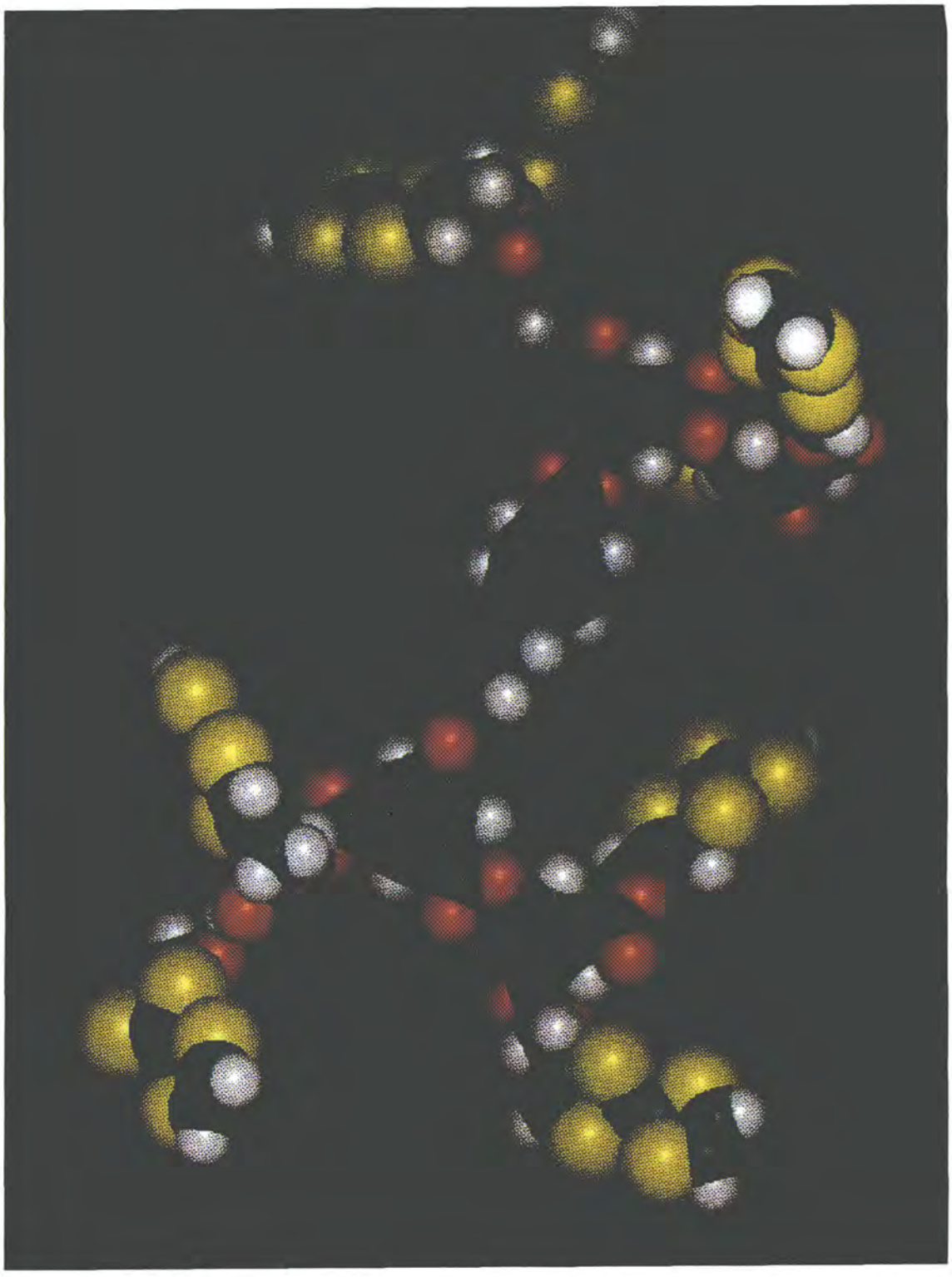


Figure 3.5.3 *Molecular Model of Octakis(TTF) Ester* ***70***

3.6 Conclusions

Three series of multi-TTF species, assembled around a bifunctional core have been constructed, using the acid chloride/alcohol methodology refined for the assembly of redox-active dendritic macromolecules. The instability problems associated with their dendritic analogues in Chapter 2 have been overcome, producing new materials with good thermal and acid stability, which, using PDMS have produced the highest mass molecular ions for molecules of their type. Initially the use of a bifunctional core produced materials with very poor solubility in organic solvents, but this was overcome by the introduction of a flexible linkage into the core unit in compounds **72-74**. The electrochemical properties of these species have been explored and the redox activity of the TTF units is not significantly changed from that of TTF, or their dendritic analogues. Charge-transfer complexes with TCNQ have been isolated and shown to exhibit conduction values in the semi-conductor regime.

CHAPTER FOUR

[2]PSEUDOROTAXANES INCORPORATING TETRATHIAFULVALENE

4.1 Introduction

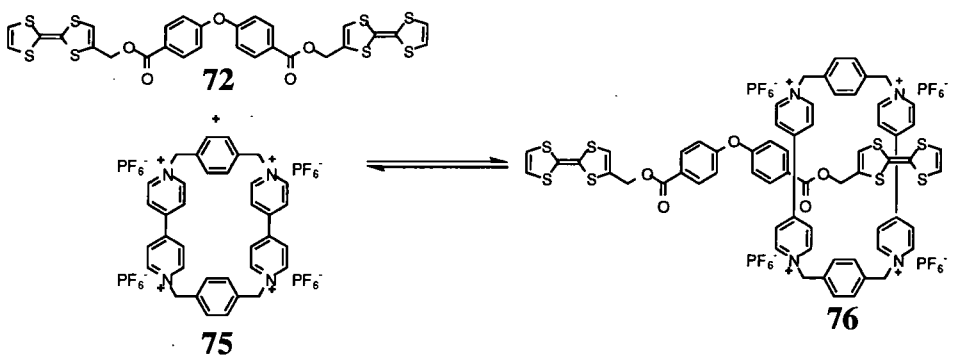
The development of strategies[1,88] for the assembly of large, well-defined molecular arrays (nanostructures), which are endowed with controllable functions, is a fascinating challenge for chemists who are aiming to synthesise materials for applications in nano-scale molecular devices.[89] Several recent studies have focused on the assembly and characterisation of rotaxanes[72, 90] and pseudorotaxanes[71] which are stabilised by virtue of intermolecular π-donor and π-acceptor interactions, typically involving π-rich hydroquinol derivatives, and the π-deficient receptor cyclophane cyclobis(paraquat-*p*-phenylene) **75**.[90] In this context, it became our target to incorporate our multi-π-electron donor species into these classes of compounds, building upon the pseudorotaxane **19**,[71] and rotaxane **20**,[72] assembled by Stoddart *et al.*, which incorporate TTF units as π-electron rich building blocks.

4.2 Assembly and Characterisation of a Bis(Tetrathiafulvalene)[2]Pseudorotaxane

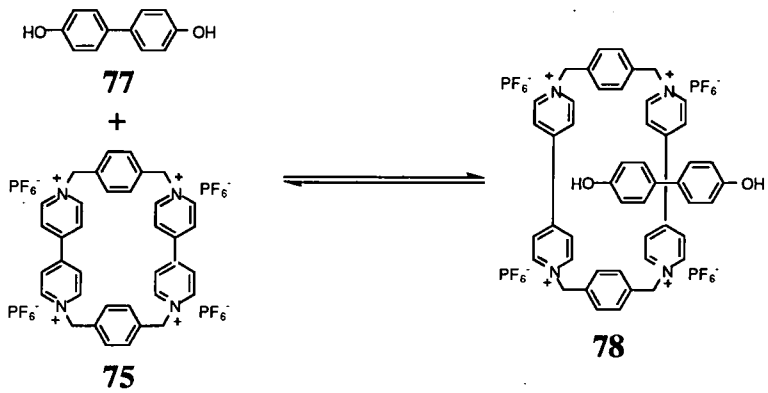
Pseudorotaxane **76** was self-assembled by admixture of equimolar amounts of diester **72** and cyclophane **75** in acetone at 20°C (Scheme 4.2.1), resulting in the immediate formation of an emerald green solution, which upon evaporation *in vacuo* afforded a green solid. Analysis of this solid by FAB mass spectrometry revealed peaks at m/z 1645 and 1500 corresponding to $(M\text{-}PF_6)^+$ and $(M\text{-}2PF_6)^{2+}$, resulting from the loss of one, and two PF_6^- counterions respectively, from a complex of **72** and **75**. No evidence was discovered for the formation of the complex with 2 molecules of cyclophane **75** and one molecule of diester **72**, which would be a [3]pseudorotaxane. The green colour is diagnostic of charge-transfer complexation between components **72** and **75**: an associated broad absorption band at λ_{max} 854nm appeared in the UV-visible spectrum of the solution. It is known that titration[91] or dilution[92] methodology can be used to calculate the association constant; dilution methodology is known to be more accurate and gave a k_a value of 3300 $dm^3\ mol^{-1}$ for complex **76**, which corresponds to

a free energy of complexation of 4.73 kcal mol^{-1}. Based on the work of Stoddart *et al.*, the charge-transfer absorption found at 854nm strongly suggests the formation of a 1:1 inclusion complex of a TTF unit of **72** within the cavity of the charged cyclophane **75** (*cf.* the charge-transfer absorption band for the complex of TTF **1** and **75** occurs at 854nm in acetonitrile, and the X-ray crystal structure of this complex establishes unequivocally that TTF resides within the macrocycle in a pseudo-rotaxane like way).[71] For comparative purposes, a spectrophotometric dilution analysis was performed at 854nm for the complex formed by the admixture of an equimolar amount of TTF **1** and cyclophane **75** (resulting in formation of complex **19**) in acetone solution at 21°C, which yielded a similar k_a value of 2600 dm^3 mol^{-1}, corresponding to a free energy of complexation of 4.59 kcal mol^{-1}: these data are in strong contrast with the values of 51 dm^3 mol^{-1}, and 2.34 kcal mol^{-1}, reported by Stoddart *et al.* for the same complex in acetonitrile. Due to this anomaly we repeated the studies on complex **19**, using both acetone and acetonitrile as the solvent, and also using both dilution and titration techniques for the determination of the association constant: the data are summarised in Table 4.2.1. Our ability to repeat the values published for non-TTF systems is shown by the complexation of 4,4'-biphenol **77** (Scheme 4.2.2) with cyclophane **75** to form complex **78**; the values we obtained for this system are in good accordance to those published by Stoddart *et al.*[90b] Our studies suggest that the original data for **19** are erroneous. Our data are consistent with the good π-electron donor ability of TTF. It should be noted that no appreciable binding has been observed between the biphenyl ether core of **72** and cyclophane **75**, primarily because of the non-planar structure and weak donor ability of the former.†

† Note added in proof. After communicating our results to Prof. Stoddart, repetition of this experiment in his laboratory revealed binding constants for complex **19** with the following values: k_a = 2680 dm^3 mol^{-1} (titration experiment in acetone) and k_a = 8030 dm^3 mol^{-1} (titration experiment in acetonitrile): J.F. Stoddart, personal communication, July 1995.



Scheme 4.2.1 *Formation of [2]Pseudorotaxane* ***76***



Scheme 4.2.2 *Model [2]Pseudorotaxane* ***78***

Complex	Technique	Solvent	Temp /°C	k_a /dm^3 mol^{-1}	ΔG° /kcal mol^{-1}
78	dilution	acetonitrile	27	123#	2.87*
76	dilution	acetone	21	3300	4.73
76	dilution	acetonitrile	21	2900	4.66
19	dilution	acetone	21	2600	4.59
19	dilution	acetonitrile	26	1400	4.30
19	titration	acetonitrile	27	1100	4.17

#cf. Data published by Stoddart et al.[90b]: 140 dm^3 mol^{-1}
**cf. Data published by Stoddart et al.[90b]: 2.95 kcal mol^{-1}*

Table 4.2.1 *Binding Data for TTF-Cyclophane Complexes*

^{1}H NMR spectroscopic data for complex **76** clearly suggest the [2]pseudorotaxane to be an inclusion complex, with a TTF unit inserted into the host cavity of cyclophane **75**. The changes in chemical shifts upon complexation are small,

but nonetheless, they are entirely reproducible on different samples and they are significant. The changes are quantitatively very similar to the data reported for the inclusion complex of TTF **1** and cyclophane **75**,[71] indicating a similar binding geometry for underivatised TTF **1** and for the substituted TTF ring of thread **72**. The displacements, $\Delta\delta$, in the ^{1}H NMR spectra of thread **72** and receptor **75** after their admixture in a 1:1 molar ratio in d_6-acetone are collated in Table 4.2.2. The largest changes in chemical shift, $\Delta\delta$, are experienced by the C_6H_4 protons of the cyclophane (+0.17 ppm), the 4',5'-TTF protons (-0.12 ppm) and the phenyl ether protons (+0.15 and 0.11 ppm, for the α and the β protons, respectively). The upfield (towards lower ppm values) shift of the TTF protons indicates a complex in which the TTF ring system is approximately coplanar with the bypyridinium (bipy) aromatic rings (*i.e.* the TTF ring is included inside the cavity). Meanwhile, the phenyl ether protons are shifted downfield indicating that this unit is located close to the edge of the bipy units, and outside the cavity.

Component	αCH (Ph)	βCH (bipy)	C_6H_4	NCH_2	4-TTF	4',5'-TTF	TTF-CH_2O	αCH (Ph)	βCH (Ph)
Cyclophane **75**	+0.07	-0.09	+0.17	-0.03	/	/	/	/	/
Guest **72**	/	/	/	/	-0.08	-0.12	+0.03	+0.15	+0.11

Table 4.2.2 *Chemical Shift Displacements $\Delta\delta$ (ppm)* at 20°C in the 400MHz NMR Resonances of Guest 72 and Receptor 75 after their Admixture In a 1:1 Molar Ratio in d_6-acetone*
* $\Delta\delta = \delta_{complex} - \delta_{free}$

Further data to support a [2]pseudorotaxane structure for complex **76** were obtained by variable temperature ^{1}H NMR spectra between +40°C and -80°C (Figure 4.2.1 and 4.2.2). Upon cooling the sample, the signals corresponding to guest **72** broaden, and at -80°C they are split into two sets of signals of equal intensity, arising from the complexed and uncomplexed TTF moieties of **72**. Larger chemical shift displacements occur for the TTF protons of **72** than for the biphenyl ether protons, which clearly implies that complexation is associated with a TTF unit (Table 4.2.3).

The symmetry of the cyclophane resonances of complex **72** at -80°C indicates that both 'sides' of the cyclophane are equivalent in the complex. The TTFC**H**$_2$O proton resonances broaden to two singlets at -80°C, corresponding to one TTFC**H**$_2$O group inside the host and one group outside the host; to achieve this splitting, both protons on the TTFC**H**$_2$O group must be equivalent, which provides additional evidence that one TTF unit is located within, rather than alongside the cyclophane. These data strongly support the [2]pseudorotaxane geometry represented by the structure **79**, in preference to the extended array, represented by structure **80** (Figure 4.2.3). An array such as **80** is most unlikely because it would not only require a large loss of entropy upon association, but would also need to remain stable up to +40°C

	4-TTF	4',5'-TTF	TTFC**H**$_2$O	α**CH**(Ph)	β**CH**(Ph)
Δν (ppm)*	-0.45	-0.51	-0.12	0.22	/

Table 4.2.3 *Chemical Shift Displacements, Δν (ppm)* at -80°C in the 400MHz ^{1}H NMR Resonances of Complex **76** arising from Complexed and Uncomplexed TTF Units of **72**.*

*$\Delta\nu = \nu_{complexed\ TTF\ unit} - \nu_{uncomplexed\ TTF\ unit}$

The solution electrochemical properties of bis(TTF) derivative **72** have been studied by cyclic voltammetry, which reveals two reversible oxidation waves at $E_1^{1/2}$ = +0.40V and $E_2^{1/2}$ = +0.83V in acetonitrile, which are typical values for esters of 4-(hydroxymethyl)TTF (Table 2.4.1), *i.e.* the oxidation potential is raised slightly, relative to TTF **1**, by attachment of the ester substituent (*cf.* values of +0.34 and +0.71 were obtained for TTF **1** under identical conditions). As expected for a bis(TTF) derivative possessing a lengthy spacer unit between the two TTF systems, there is no observable interaction between the TTF units.[93] The cyclic voltammogram of **72** is not changed by the addition of an equimolar amount, or an excess of cyclophane **75** to the solution (scan rates 50-1500mV sec^{-1}); the voltammogram of cyclophane **75** is also unchanged by complexation ($E_1^{1/2}$ = -0.24V and $E_2^{1/2}$ = -0.66V).[90b] This result suggests that the complexation/decomplexation process for **72** and **75** occurs too rapidly to be detected by cyclic voltammetry.

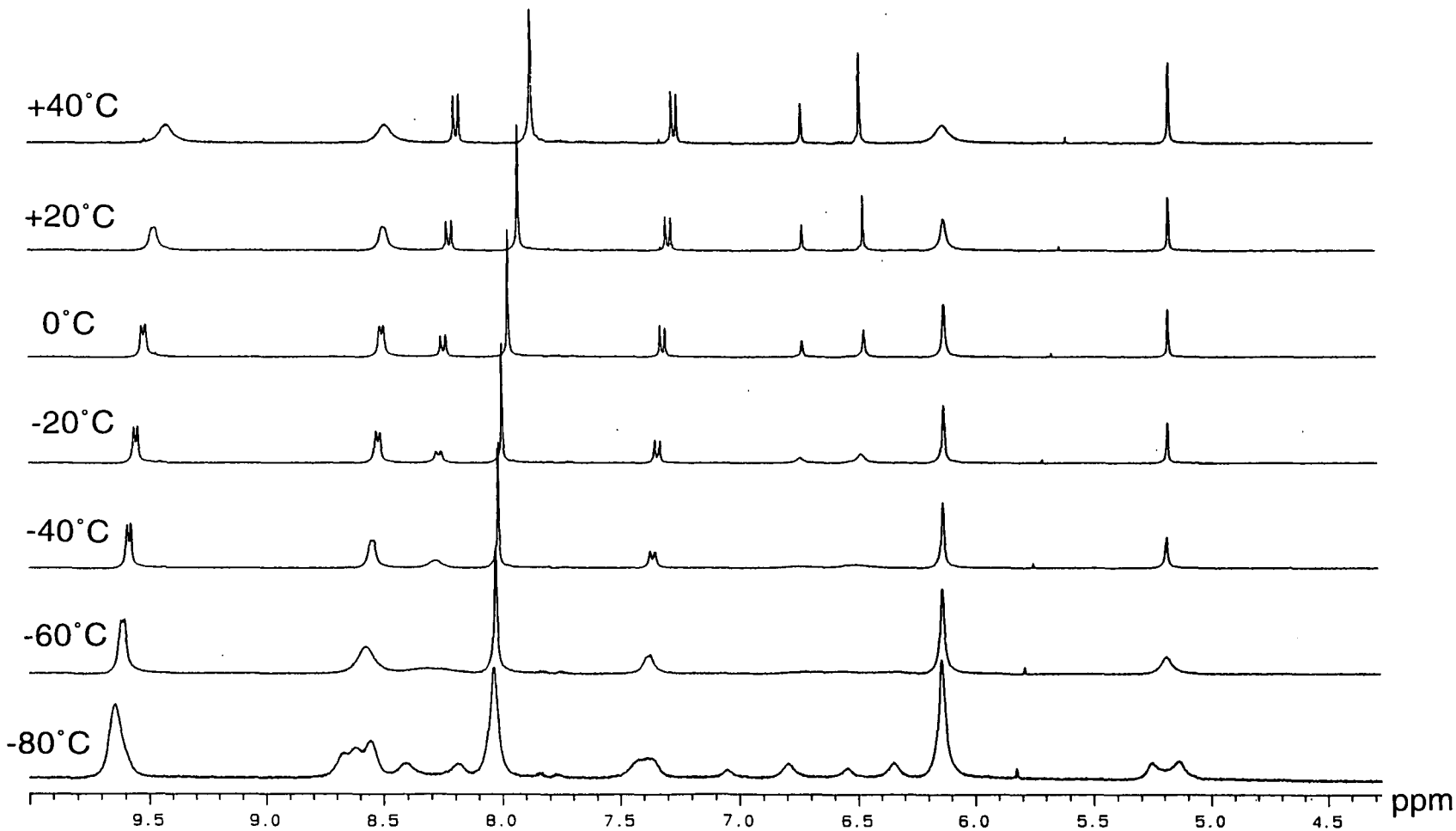


Figure 4.2.1 *Variable Temperature ^{1}H NMR Spectra of [2]Pseudorotaxane* ***76*** *from +40°C to -80°C*

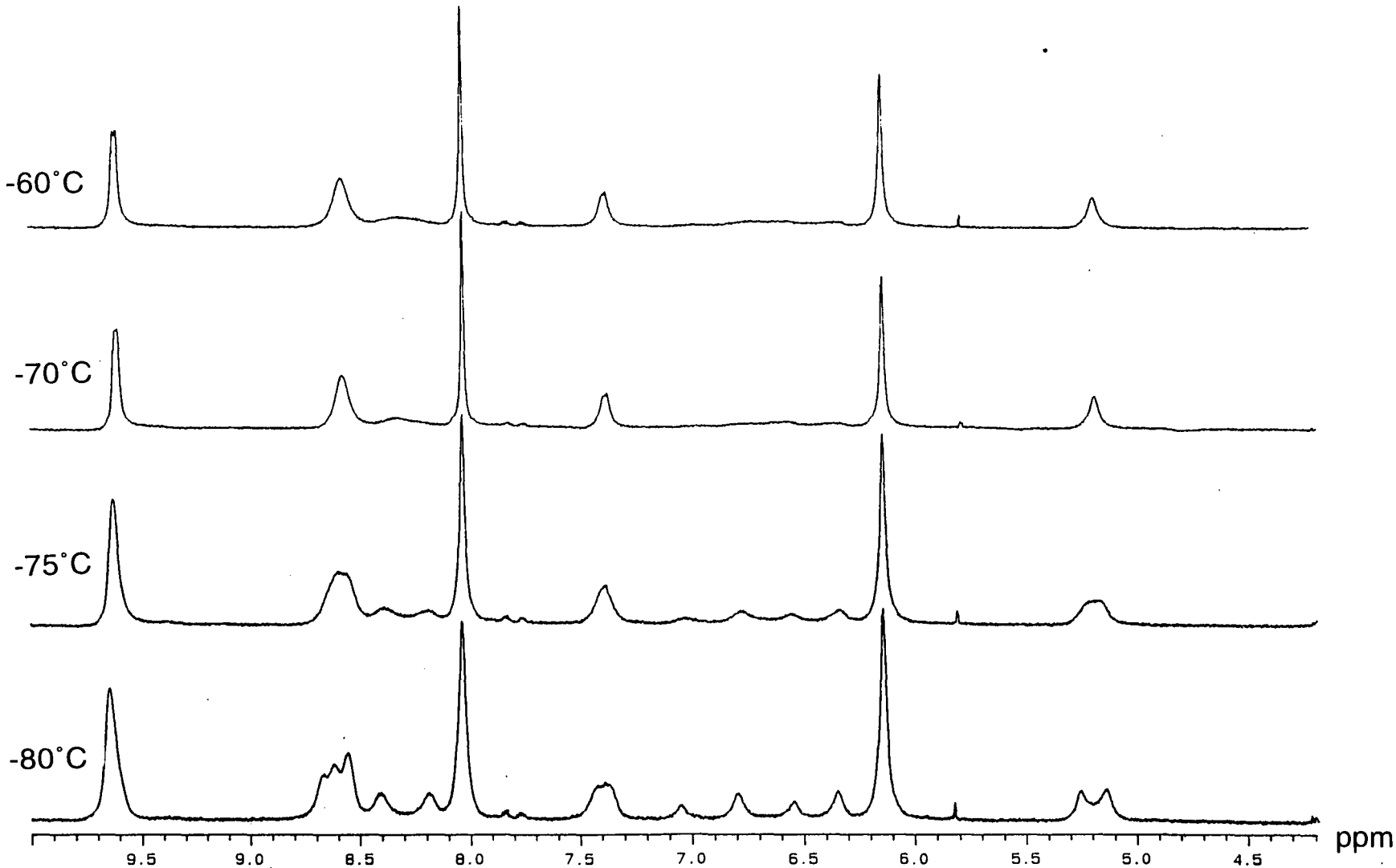


Figure 4.2.2 *Variable Temperature ^{1}H NMR Spectra of [2]Pseudorotaxane* ***76*** *from -60°C to -80°C*

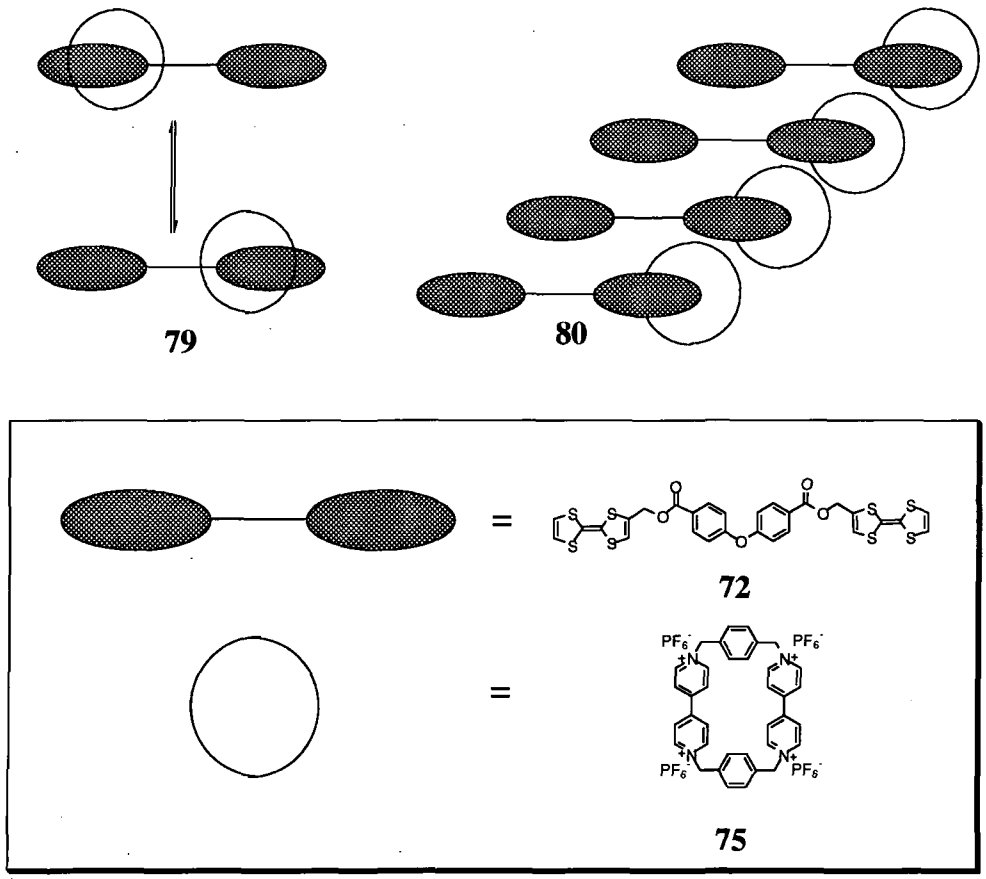
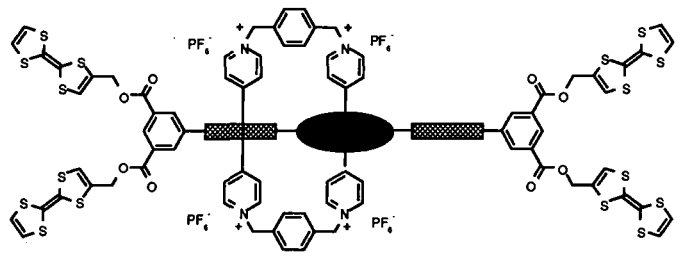


Figure 4.2.3 *Conformations of a Complex of Thread 72 and Cyclophane 75*

4.3 The Pathway to [2]Rotaxanes

The work contained in Chapter 3 and Section 4.2 suggested the synthesis of dendritic analogues of [2]rotaxane **20**. Figure 4.3.1 illustrates our design targets.



	Rotaxane 81	Rotaxane 82	Rotaxane 83
	84	**84**	**85**
	67	**71**	**86**

Figure 4.3.1 *[2]Rotaxane Design Targets*

The products formed by the reaction of the alcohol core of compound **84** with the diacid chloride of cores **67** and **71** were insoluble in all organic solvents. Attempts to assemble the precursors to rotaxane **83** from diol **85** and bis(tosylate) of core **86** were unsuccessful, giving unidentified products. These synthetic pathways were, therefore, discontinued.

4.4 Conclusions

A new [2]pseudorotaxane incorporating tetrathiafulvalene was assembled and characterised; variable temperature ^{1}H NMR spectroscopy provided conformational data, UV-visible spectroscopic studies provided stability data and electrochemical properties were documented. In the course of this work, anomalies were discovered between the binding constant data we obtained for complex **19** and that published by Stoddart *et al.*[71]

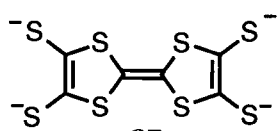
Preliminary attempts to assemble multi-TTF rotaxanes, were unsuccessful, due to the poor solubility of the reaction products, or problems encountered with synthesis.

CHAPTER FIVE

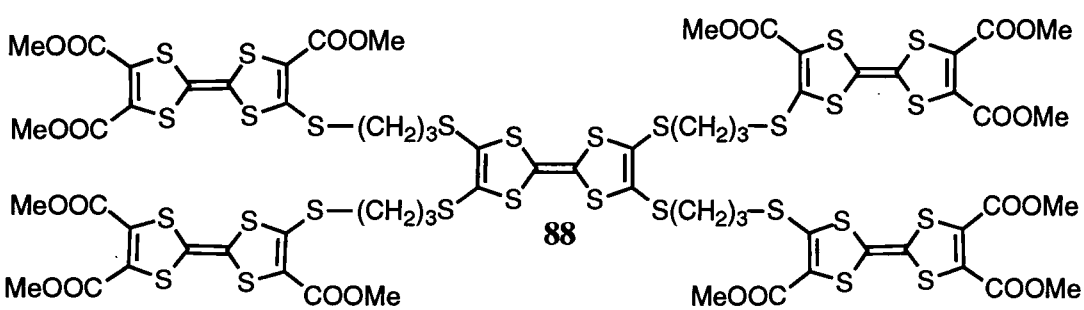
TOWARDS TETRATHIAFULVALENE AT THE CORE OF A MULTI-TTF MACROMOLECULE

5.1 Introduction

It is a logical step to evolve our multi-redox systems into macromolecules where the core itself is a tetrathiafulvalene derivative. Our work on rotaxanes (Section 4.3) aimed at placing a bifunctionalised TTF derivative at the heart of a multi-redox assembly, with disappointing results. The synthesis of the intermediate TTF-tetrathiolate **87** by Becher *et al.*[94] allows a wide variety of multi-TTF systems, such as the pentakis(TTF) **88** to be assembled.[95] The precursor to tetrathiolate **87**, *viz.* the tetra(cyanoethylthio) derivative, is readily available in multi-gram quantities from inexpensive starting materials. Our intention was to surround core **87** with further multi-TTF units, producing macromolecules consisting of two different types of TTF donor fragment, hopefully with new electrochemical characteristics.



87

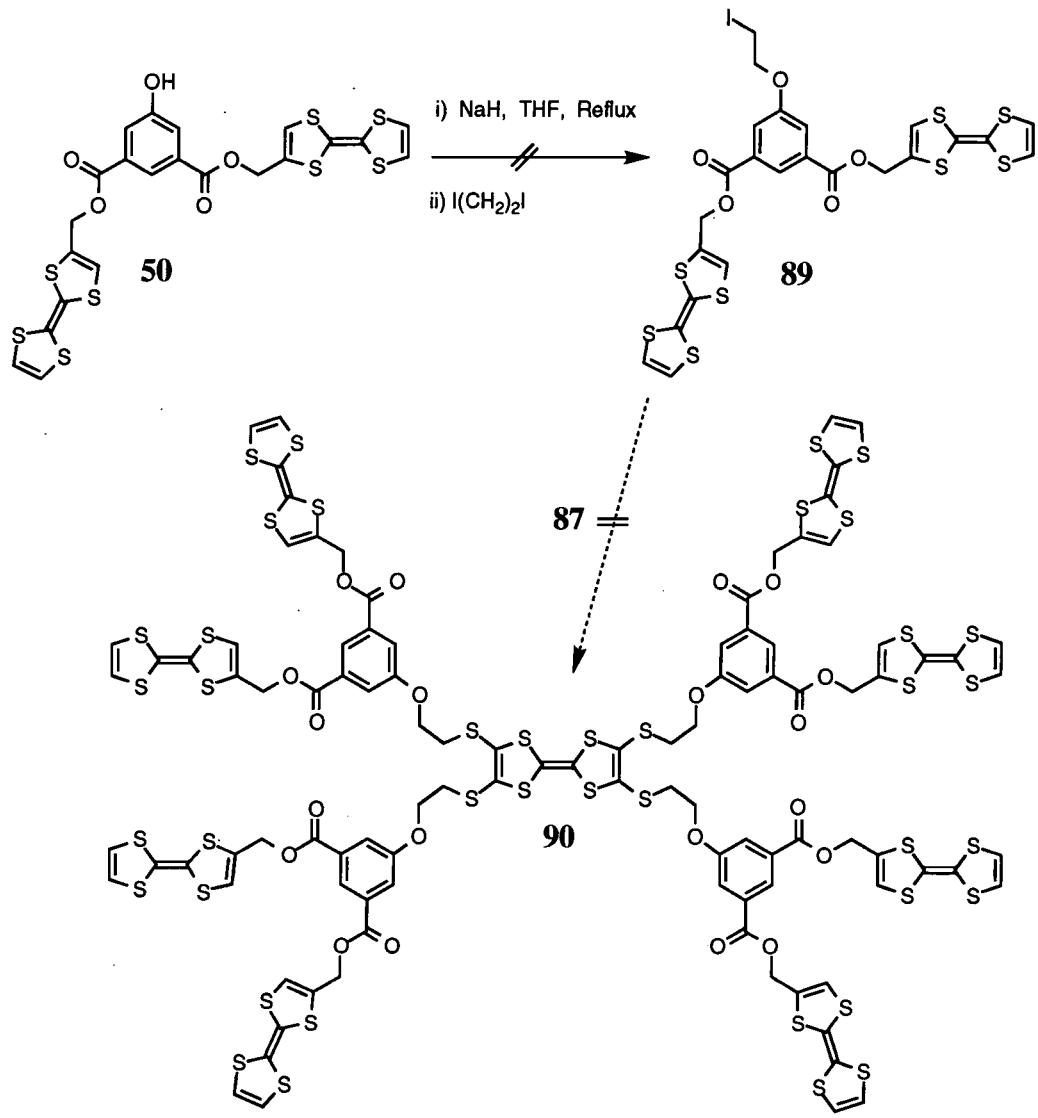


88

5.2 Ester-Thioether Multi-TTF Assemblies

Alcohol **50** has proved to be an excellent building block for the assembly of multi-TTF systems; we intended to generate bis(TTF) ester **89**, with an ethylene spacer group, and then couple it to tetrathiolate core **87** to produce a nona(TTF) macromolecule **90**. Sodium hydride was used to deprotonate alcohol **50**, and the derived alkoxide was then syringed dropwise onto a concentrated solution of 1,2-diiodoethane and refluxed for 2 hours. At the end of this period, it was discovered that the reaction mixture contained only iodine and a dark-coloured material which remained

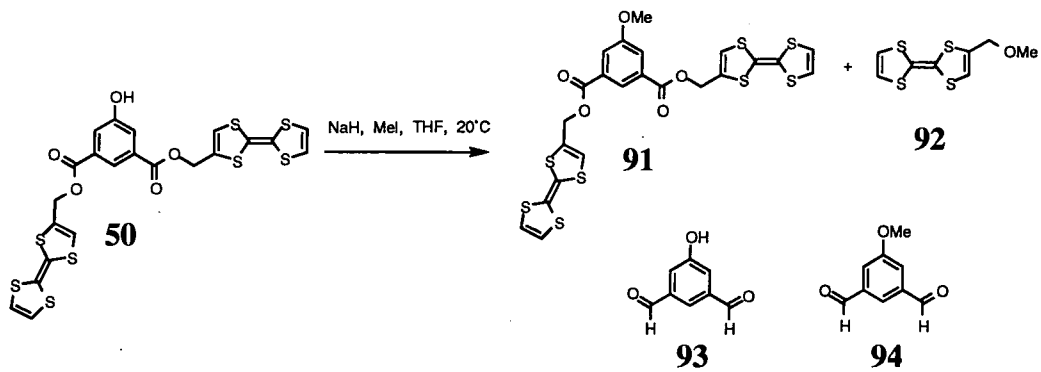
on the baseline of tlc. We concluded that the 1,2-diiodoethane had decomposed at elevated temperature, liberating iodine, which then chemically oxidised the TTF units to the radical cation. To counteract this, the alkoxide was formed at 95°C, cooled and added dropwise to a concentrated solution of 1,2-diiodoethane at 0°C. No reaction occurred under these conditions, but on warming to room temperature, the same dark coloured material was formed as before.



Scheme 5.2.1 *Attempted Synthesis of Nona(TTF) 90*

Attempts were made to produce methyl ether **91**, to prove that the alkoxide of alcohol **50** was forming (Scheme 5.2.2). Alcohol **50** was reacted with methyl iodide, in the presence of sodium hydride for two hours, affording a mixture of methyl ether

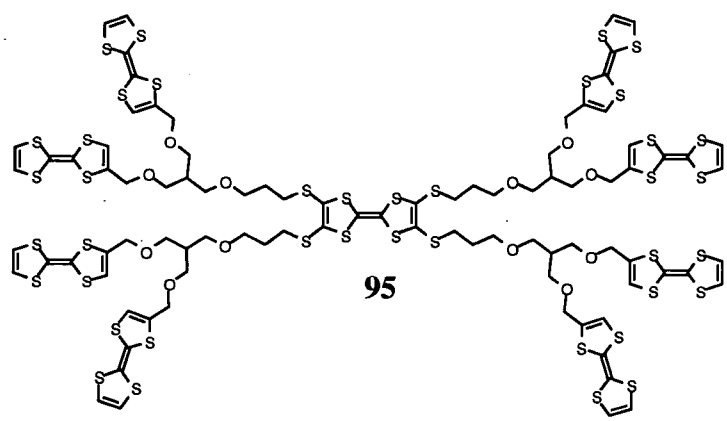
91 and methyl ether **92** (^{1}H NMR evidence), which were inseparable by chromatography. Aldehydes **93** and **94** presumably were also produced, although they were not isolated. Even one equivalent of sodium hydride resulted in the fragmentation of **50** with the formation of by-product **92**; this resulted in the abandonment of this approach using ester linkages.



Scheme 5.2.2 *Synthesis of Methyl Ether 91*

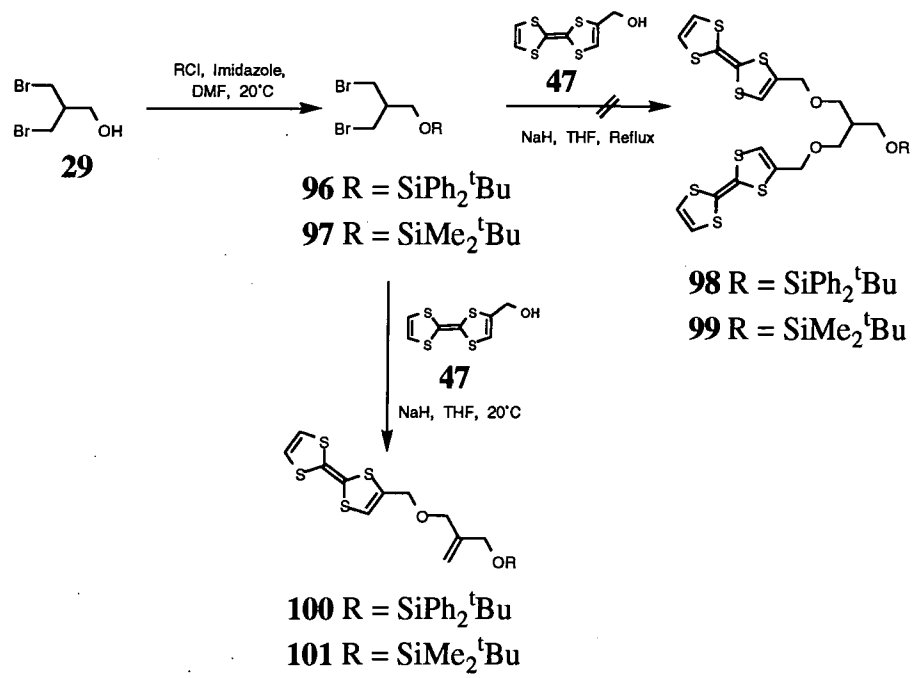
5.3 Alkyl Multi-TTF Assemblies

Ether linkages were used in the design of a new class of multi-TTF macromolecule, which should be more resilient than the polyester species described in Chapters 2 and 3. Alcohol **29** was employed as a building block in attempts to assemble nona(TTF) **95**.



Alcohol **29** was reacted with *tert*-butyldiphenylsilyl chloride in the presence of imidazole, to afford compound **96** in 95% yield (Scheme 5.3.1). Attempts to assemble

bis(TTF) ether **98** by reaction of alcohol **47** with compound **96** in the presence of sodium hydride were unsuccessful; ^{13}C NMR spectroscopy indicated that an olefinic bond had been formed by the elimination of HBr, preventing the formation of the second ether linkage, affording the product that was identified as compound **100** in 49% yield. Variation of temperature and base stoichiometry failed to produce compound **98**. Isolation of the alkoxide of alcohol **47** and subsequent reaction with alcohol **29** also failed to afford bis(TTF) ether **98**, indicating that even the alkoxide of alcohol **47** was able to eliminate HBr from alcohol **96** (or possibly the mono-substituted derivative).

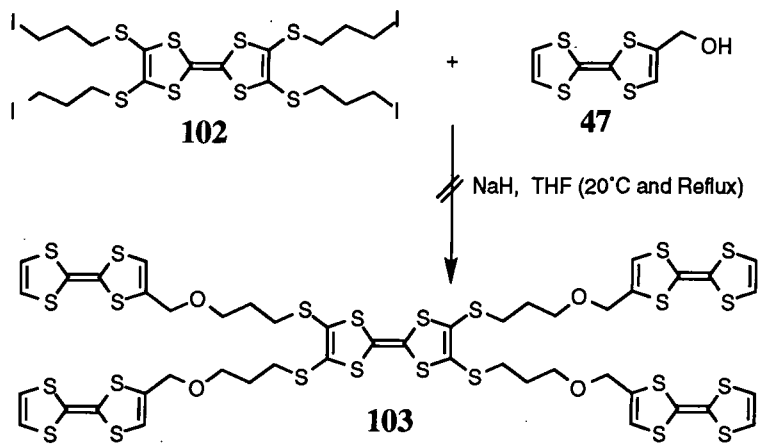


Scheme 5.3.1 *Attempted Synthesis of Bis(TTF) Ether Derivatives*

Attempts were made to facilitate the formation of bis(TTF) ether **98**, by replacing the *tert*-butyldiphenylsilyl protecting group with the *tert*-butyldimethylsilyl group. Reaction of alcohol **29** with *tert*-butyldimethylsilyl chloride in the presence of imidazole afforded dibromo compound **97** in 83% yield. Attempts to assemble bis(TTF) ether **99** proved unsuccessful, affording mono-ether **101** in 32% yield, even when the alkoxide of **47** was added to alcohol **29**. We concluded that the alkoxide of **47** was able to eliminate HBr from compound **97** (or possibly the mono-substituted

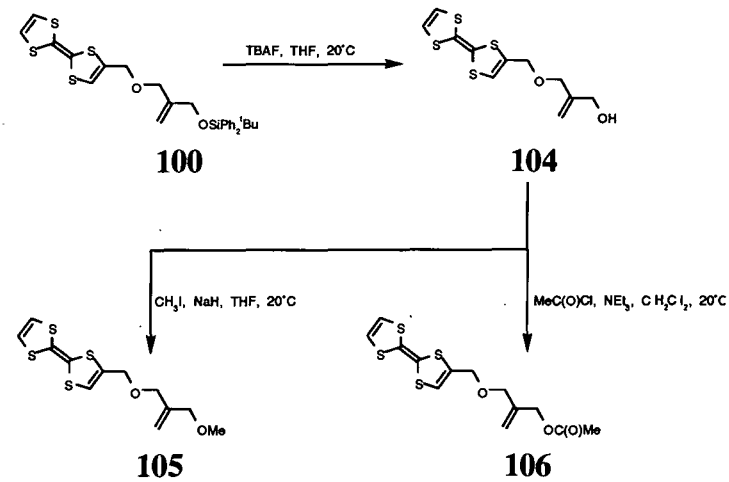
derivative) to afford olefin **101**. During these syntheses it was noted that alcohol **47** decomposed to TTF **1** when in the presence of sodium hydride for longer than 7h. Compound **101** also showed significant decomposition after 12h when stored in the dark, under argon at 4°C. These disappointing results led to the conclusion that we would be unable to assemble bis(TTF) compounds **98** and **99**.

An attempt was made to assemble pentakis(TTF) **103**, by reaction of tetra-iodide **102**[95] with alcohol **47** in the presence of sodium hydride. Variation of base stoichiometry and temperature failed to afford compound **103**, resulting only in the decomposition of alcohol **47** (Scheme 5.3.2).



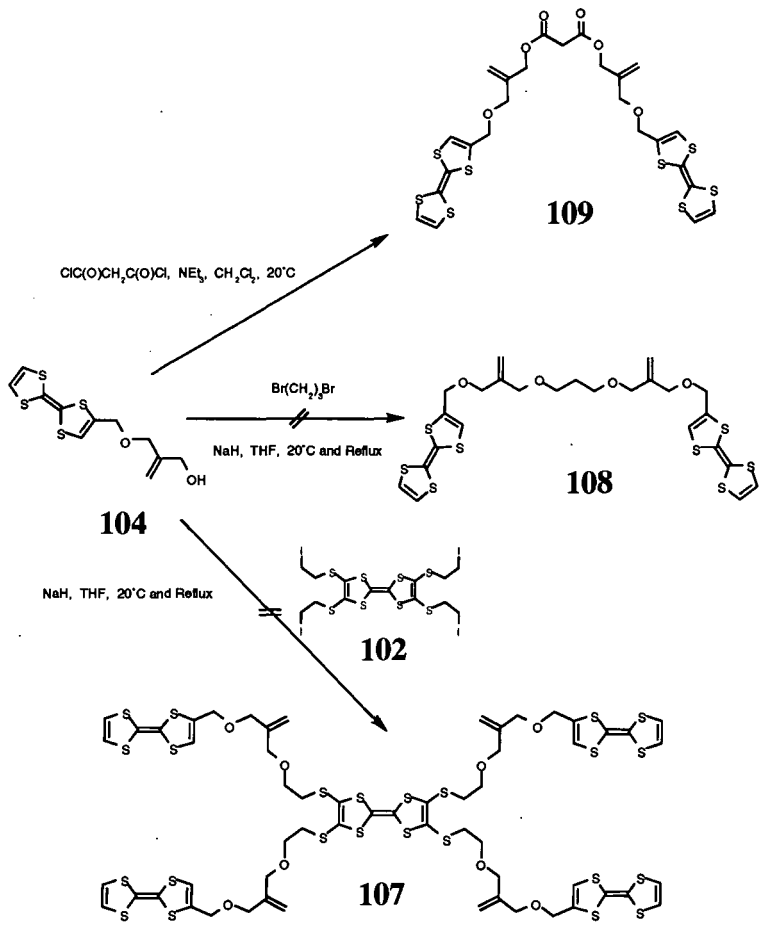
Scheme 5.3.2 *Attempted Synthesis of Pentakis(TTF) 103*

After the failure to obtain compounds **98** and **99**, the decision was made to deprotect mono-ether **100** and continue this synthetic pathway with alcohol **104** (Scheme 5.3.3). Mono-ether **100** reacted with TBAF in THF, affording alcohol **104** in 93% yield. The reactivity of alcohol **104** was explored by reaction with methyl iodide in the presence of sodium hydride, affording compound **105** in 73% yield. The reaction of alcohol **104** with acetyl chloride in the presence of triethylamine afforded ester **106** in 82% yield.



Scheme 5.3.3 *Functionalisation of Alcohol 104*

Attempts were then made to link alcohol **104** to core units **102**, malonyl dichloride and 1,3-dibromopropane (Scheme 5.3.4). Reaction of alcohol **104** with core **102** in the presence of sodium hydride failed to produce ether **107** at room temperature. Heating the reaction mixture to reflux resulted in the decomposition of alcohol **104**, this also occurred when alcohol **104** was reacted under the same conditions with 1,3-dibromopropane, failing to produce ether **108**. Finally, alcohol **104** was reacted with malonyl dichloride in the presence to triethylamine, affording ester **109** in 77% yield.



Scheme 5.3.4 *Alkyl Multi-TTF Assemblies*

5.3.1 Solution Electrochemistry of Alkyl TTF Assemblies

The solution electrochemistry of compounds **104**, **105**, **106** and **109** has been studied by cyclic voltammetry and the data are collated in Table 5.3.1. All the TTF derivatives display two, reversible, single, or two-electron oxidation waves (for mono- or bis(TTF) species, respectively), typical of the parent TTF system. There is no apparent broadening of either of the two oxidation waves, suggesting that there are no significant intra- or inter-molecular Coulombic interactions between charged TTF units and that the TTF moieties are electronically independent. The TTF species described in Table 5.3.1 each show redox waves with a first oxidation similar to TTF **1**, *i.e.* at lower potentials than the multi-TTF esters of alcohol **47** (Table 2.4.1) .

Compound	$E_1^{1/2}$ /V	$E_2^{1/2}$ /V
TTF 1	0.34	0.71
104	0.36	0.75
105	0.36	0.82
106	0.38	0.80
109	0.35	0.78

Data were obtained at 20°C versus Ag/AgCl, in dry MeCN/CH_2Cl_2 (1:1 $^v/_v$) under argon using a platinum wire counter electrode, ca. 5 x 10^{-4} M compound, 0.1 M tetrabutylammonium hexafluorophosphate, scan rate 100 mV s^{-1}.

Table 5.3.1 *Electrochemical Data for TTF Derivatives*

5.4 Conclusions

Preliminary attempts to construct redox-active macromolecules containing a TTF derivative at the core were unsuccessful, failing due to the instability of alcohol **104**, or unexpected reactions of the TTF building blocks. Olefinic mono-TTF compound **104** was demontrated to undergo basic ester and ether formation reactions. Derivatives **104, 105, 106, 109** exhibited lower oxidations than other multi-TTF assemblies described in this Thesis and are very similar to those of TTF **1**. It appears that the results obtained from this investigation restrict alkyl building blocks *e.g.* alcohol **29** from being used in the assembly of multi-TTF macromolecules.

CHAPTER SIX

EXPERIMENTAL

6.1 General Methods

Melting points were recorded on a Reichert-Kofler hot-stage microscope apparatus and are uncorrected.

Infra-red spectra were recorded on a Perkin Elmer 1720X FT-IR spectrophotometer; samples were either embedded in KBr discs, nujol mulls, or analysed neat between KBr plates, as indicated. Solution state electronic spectra were obtained on a Unicam UV2 instrument with dichloromethane as the solvent, unless stated otherwise.

Proton NMR spectra were recorded on Varian Gemini-200, XL-200, Varian VXR-200 and Varian 400 instruments. ^{13}C NMR spectra were recorded on a Varian-400 instrument. Chemical shifts are quoted in ppm, relative to tetramethylsilane (TMS) as an internal reference (0 ppm). Mass spectra were obtained on a VG 7070E instrument, with ionisation modes as indicated; ammonia was used as the impingent gas for chemical ionisation mode. Plasma desorption mass spectrometry was carried out on a BioIon 10 K time of flight instrument (Biosystems, Uppsala, Sweden) over 5 x 10^5 fissions (^{252}Cf) at the Department of Molecular Biology, University of Odense, Denmark. Elemental analyses were obtained on a Carlo-Erba Strumentazione instrument.

Column chromatography was carried out using Merck silica gel (70-230 mesh) or Merck alumina (activity II to III, 70-230 mesh), the latter was neutralised by pre-soaking basic alumina in ethyl acetate for 24h. Solvents were distilled prior to use in column chromatography.

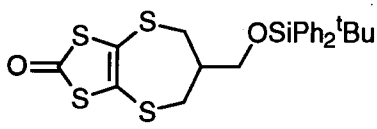
Nitrogen gas was dried by passing it through a column of phosphorus pentoxide. Solvents were dried over, and distilled from, the following reagents, under a dry nitrogen atmosphere; diethyl ether and tetrahydrofuran (THF) (sodium metal), acetonitrile, *N,N*-dimethylformamide (DMF), dichloromethane (calcium hydride), chloroform (phosphorus pentoxide), toluene (lithium aluminium hydride), acetone

(potassium carbonate), and ethanol (magnesium ethoxide). All other reagents were reagent grade and used as supplied, unless otherwise stated.

Cyclic voltammetry experiments were performed in a one-compartment cell with platinum working and counter electrodes. The reference electrode was a silver/silver chloride electrode. Electrochemical measurements at the University of Durham were carried out with a BAS 100 electrochemical analyser and were internal resistance compensated. Electrochemical measurements carried out at the Université d'Angers were carried out on an EG & G Princeton Applied Research Center potentiostat/galvanometer, model no. 273 and were internal resistance compensated. The cell contained a solution of donor compound (*ca.* 1 x 10^{-5}M) with dry tetrabutylammonium hexafluorophosphate (70mg) as supporting electrolyte in acetonitrile/dichloromethane 1:1 $^{v}/_{v}$ (*ca.* 10mL); all solutions were purged with argon and retained under the inert atmosphere whilst measurements were carried out.

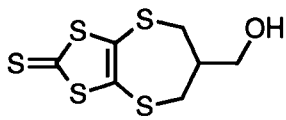
6.2 Experimental to Chapter Two

4,5-[2-(*tert*-Butyldiphenylsiloxymethyl)propylene-1,3-dithio]-1,3-dithole-2-one 25



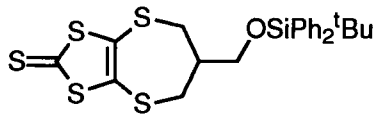
To a solution of thione **31** (Page 101) (1.43g, 2.8mmol) in chloroform/glacial acetic acid (100 mL, 3:1 $^{v}/_{v}$), mercuric acetate (1.0g, 3.1mmol) was added and the reaction stirred under nitrogen at 20°C for 18h. Water was added and the reaction mixture left stirring for a further 1h, after which the resulting white precipitate was removed by filtration. The organic phase was washed with saturated aqueous sodium hydrogen carbonate, dried ($MgSO_4$) and the solvent removed *in vacuo* to afford compound **25** (1.22g, 88%) as a viscous colourless oil. m/z (CI) 508 ($M+NH_3^+$); δ_H ($CDCl_3$) 7.64 (4H, m), 7.39 (6H, m), 3.73 (2H, d, J = 5.9Hz), 2.93 (2H, m), 2.62 (2H, m), 2.46 (1H, m) and 1.06 (9H, s); ν_{max} (nujol) 3070, 1670, 1620, 1430, 1100, 820, 735 and 700cm^{-1}.

4,5-[2-(Hydroxymethyl)propylene-1,3-dithio]-1,3-dithiole-2-thione 30



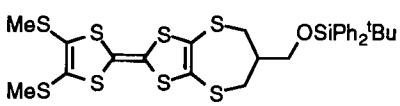
To a solution of alcohol **29**[78] (4.51g, 19.44mmol) in acetonitrile (100mL), zincate salt **27**[79] (6.97g, 9.73mmol) was added. The mixture was refluxed with stirring for 4.5h to yield an orange coloured solution. The solvent was removed *in vacuo* and column chromatography of the residue on silica gel, eluent dichloromethane/acetone (5:1 $^{v}/_{v}$) afforded compound **30** (4.41g, 85%) as an orange solid, mp 128-130°C. Analysis found: C, 31.6; H, 3.0%; Required for $C_7H_8OS_5$: C, 31.3; H, 3.0%; m/z (CI) 269 (M^++1); δ_H [$(CD_3)_2CO$] 4.07 (1H, t, J = 5.2Hz), 3.71 (2H, m), 3.16 (2H, m), 2.81 (2H, m) and 2.47 (1H, m); ν_{max} (nujol) 3300, 1265, 1230, 1060, 1025, 1005, 895 and 815cm^{-1}.

4,5-[2-(*tert*-Butyldiphenylsilyloxymethyl)propylene-1,3-dithio]-1,3-dithiole-2-thione 31

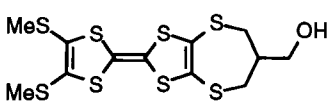


To a solution of thione **30** (Page 101) (0.4g, 1.5mmol) in DMF (80mL), *tert*-butyldiphenylsilyl chloride (0.83g, 3.0mmol) and imidazole (1.1g, 16 mmol) were added and the mixture stirred under nitrogen at 20°C for 18h. The DMF was removed *in vacuo*, and the residue was dissolved in dichloromethane, washed with water, dried ($MgSO_4$) and the solvent removed. Column chromatography of the residue on silica gel, eluent dichloromethane/hexane (1:1 $^{v}/_{v}$) afforded compound **31** (0.63g, 84%) as a viscous orange oil. m/z (CI) 507 (M^{+}+1); δ_H ($CDCl_3$) 7.63 (4H, m), 7.38 (6H, m), 3.73 (2H, d, J = 6.1Hz), 2.96 (2H, m), 2.66 (2H, m), 2.52 (1H, m) and 1.06 (9H, s); ν_{max} (nujol) 3070, 1430, 1110, 1090, 1065, 830, 820 and 700cm^{-1}.

4,5-Di(methylthio)-4',5'-[2-(*tert*-butyldiphenylsiloxymethyl)propylene-1,3-dithio]tetrathiafulvalene 32 and **4,5-Di(methylthio)-4',5'-[2-(hydroxymethyl)propylene-1,3-dithio]tetrathiafulvalene 24**



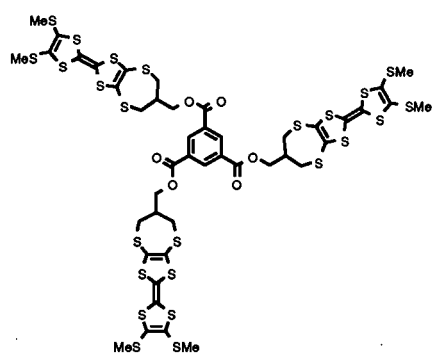
and



A suspension of ketone **25** (Page 100) (430mg, 2.0mmol) and ketone **26**[79] (1.0g, 2.0mmol) in triethylphosphite (5mL) was heated under nitrogen to 130°C, upon which dissolution was complete. The temperature was maintained at 130°C with stirring for 2h, after which the solution had turned dark red. Column chromatography of the crude reaction mixture on silica gel, eluent hexane removed triethylphosphite, then dichloromethane/hexane (3:1 $^{v}/_{v}$) afforded an orange oil consisting of a mixture of the desired cross-coupled product **32** along with self-coupled products, which could not be separated by column chromatography. To the mixture of products dissolved in THF (100ml), tetrabutylammonium fluoride (2.0mL, 1M in

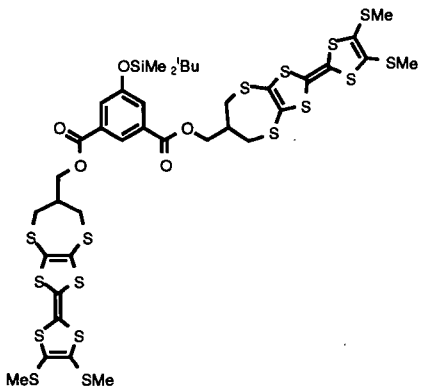
THF, 2.2mmol) was added and the reaction mixture stirred under nitrogen at 20°C for 18h. The solvent was removed *in vacuo* and column chromatography of the residue on silica gel, eluent dichloromethane/acetone (1:1 $^{v}/_{v}$) afforded an orange oil which was then crystallised from dichlomethane/hexane to yield compound **24** (300mg, overall yield 31% from ketone **25**) as a yellow solid, m.p. 128-130°C. Analysis found: C, 33.0; H, 3.2%; Required for $C_{12}H_{14}OS_8$: C, 33.5; H, 3.3%; m/z (CI) 431 (M^++1); δ_H ($CDCl_3$) 3.78 (2H, d, J = 6.0Hz), 2.89 (2H, m), 2.58 (2H, m), 2.45 (1H, m) and 2.41 (6H, s), OH not observed; ν_{max} (nujol) 3300, 1310, 1280, 1060, 1030, 960, 890 and 770cm^{-1}

1,3,5-Tris{4,5-di(methylthio)-4',5'-[2-(methylene)propylene-1,3-dithio]tetrathiafulvalenyl}benzenetricarboxylate 36



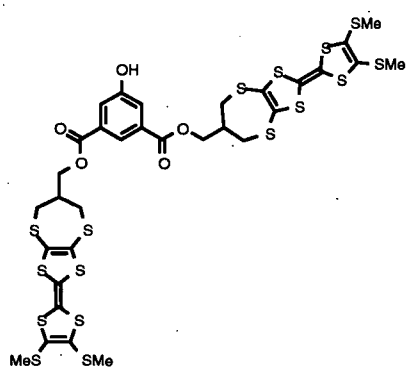
To a solution of alcohol **24** (Page 101) (100mg, 0.23mmol) in dichloromethane (50mL), 1,3,5-benzenetricarbonyl chloride (18.5mg, 0.07mmol) and DMAP (59mg, 0.48mmol) were added and the reaction mixture stirred under nitrogen at 20°C for 18h. The solvent was removed *in vacuo* and column chromatography of the residue on silica gel, eluent dichloromethane/hexane (5:1 $^{v}/_{v}$), afforded compound **36** (66mg, 57%) as an orange solid, m.p. 133-135°C. Analysis found: C, 37.3; H, 3.0%; Required for $C_{45}H_{42}O_6S_{24}$: C, 37.3; H, 2.9%; m/z (PDMS) 1448.4 (M^+); δ_H ($CDCl_3$) 8.78 (3H, s), 4.57 (6H, br.s), 2.96 (6H, m), 2.78-2.66 (9H, m) and 2.40 (18H, s); ν_{max} (KBr) 2915, 1728, 1416, 1235, 998, 893, 771 and 737cm^{-1}; λ_{max} (CH_2Cl_2) 227, 263, 332 and 443nm (after addition of an excess of I_2: 233, 290, 359 and 815nm).

1,3-Bis{4,5-di(methylthio)-4',5'-[2-(methylene)propylene-1,3-diothio] tetrathiafulvalenyl]-5-*tert*-butyldimethylsiloxybenzenedicarboxylate 41



To a solution of alcohol **24** (Page 101) (110mg, 0.26mmol) in dichloromethane (50mL), compound **40**[8] (39mg, 0.12mmol) and DMAP (59mg, 0.48mmol) were added and the reaction mixture stirred under nitrogen at 20°C for 18h. The solvent was removed *in vacuo* and column chromatography of the residue on silica gel, eluent dichloromethane, afforded compound **41** (126mg, 96%) as a orange solid, m.p. 66-67°C. Analysis found: C, 41.3; H, 4.2%; Required for $C_{38}H_{44}O_5S_{16}Si$: C, 40.7; H, 4.0%; m/z (PDMS) 1120.9 (M^+); δ_H ($CDCl_3$) 8.15 (1H, t, J = 1.5Hz), 7.65 (2H, d, J = 1.5Hz), 4.50 (4H, br.s), 2.90 (2H, m), 2.75 (8H, m) 2.40 (12H, s) 1.03 (9H, s) and 0.25 (6H, s); λ_{max} (CH_2Cl_2) 230, 278 and 335nm (after addition of an excess of I_2: 230, 278, 332 and 797nm).

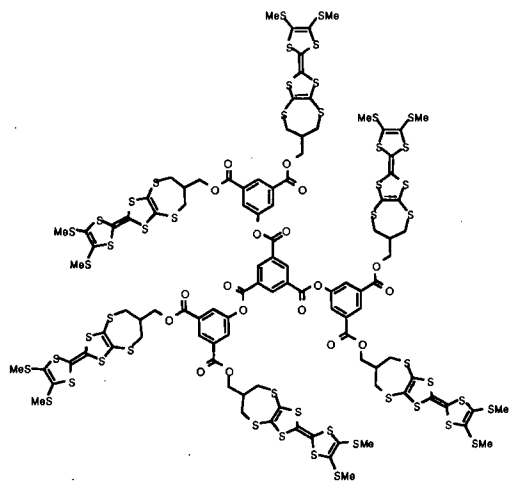
1,3-Bis{4,5-di(methylthio)-4',5'-[2-(methylene)propylene-1,3-diothio] tetrathiafulvalenyl}-5-hydroxybenzenedicarboxylate 42



To a solution of compound **41** (100mg, 0.09mmol) in THF (50mL), tetrabutylammonium fluoride (0.2mL, 1.1M in THF, 0.22mmol) was added and the reaction mixture stirred under nitrogen at 20°C for 18h. The solvent was removed *in vacuo* and column chromatography of the residue on silica gel, eluent dichloromethane/acetone (1:1 $^v/_v$), afforded compound **42** as an orange solid (59mg, 66%), m.p. 238-239°C. Analysis found: C, 38.8; H, 3.3%; Required for $C_{32}H_{30}O_5S_{16}$: C, 38.1; H, 3.0%; m/z (PDMS) 1007.6 (M^+); δ_H [$(CD_3)_2SO$] 10.18 (1H, s), 7.90 (1H, s), 7.61 (2H, s), 4.45 (4H, m), 3.11 (2H, m),

2.72 (8H, m) and 2.42 (12H, s); λ_{max} (CH_2Cl_2) 233, 263, 335 and 395nm (after addition of an excess of I_2: 233, 290, 338 and 812nm).

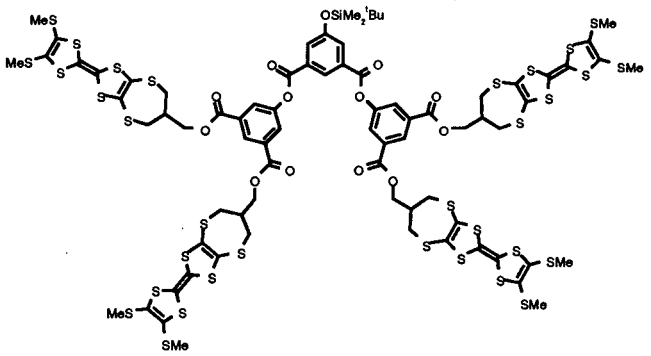
1,3,5-Tris{5-(2-oxo-1-oxaethyl)-1,3-bis{3-{4,5-di(methylthio)-4',5'-[2-propylene-1,3-dithio]tetrathiafulvalenyl}-1-oxo-2-oxapropyl}phenylene}benzene 43



To a solution of alcohol **42** (50mg, 0.05mmol) in THF (50mL), 1,3,5-benzenetricarbonyl chloride (4mg, 0.015mmol) and sodium hydride (30mg, 1.25mmol) were added and the reaction mixture stirred under nitrogen at 20°C for 18h. The solvent was removed *in vacuo* and column chromatography of the residue on silica gel, eluent dichloromethane/hexane (5:1 $^{v}/_{v}$), afforded compound **43** (28mg, 58%) as an orange oil. m/z (PDMS) 1579.0 ($M^{2+}/2$); δ_H ($CDCl_3$) 8.73 (3H, s), 8.25 (3H, s), 7.95 (6H, s), 4.57 (12H, br.s), 2.96 (6H, m), 2.78-2.66 (24H, m) and 2.40 (36H, s); λ_{max} (CH_2Cl_2) 233, 263, 311, 335 and 440nm (after addition of an excess of I_2: 230, 296, 335 and 827nm).

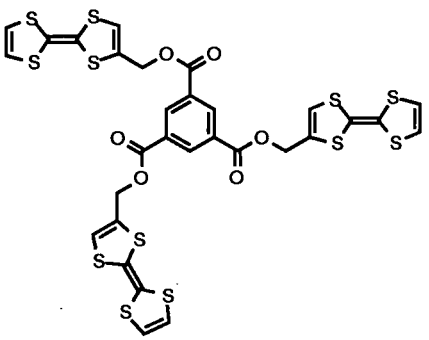
1,3-Bis{5-(2-oxo-1-oxaethyl)-1,3-bis{3-{4,5-dimethylthio-4',5'-[2-propylene-1,3-diothio]tetrathiafulvalenyl}-1-oxo-2-oxapropyl}-phenylene}-5-*tert*-butyldimethylsiloxybenzene 44

To a solution of alcohol **42** (50mg, 0.05mmol) in THF (50mL), compound **40**[8] (16mg, 0.05mmol), sodium hydride (10mg, 0.42mmol) were added and the solution stirred under nitrogen at 20°C for 18h. The solvent was removed *in vacuo* and column chromatography of the residue on silica gel, eluent dichloromethane/hexane (5:1 $^{v}/_{v}$), afforded compound **44** as an orange oil (55mg, 50%). m/z (PDMS) 1137.6 ($M^{2+}/2$);



δ_H ($CDCl_3$) 8.16 (2H, d, J = 1.5Hz), 7.77 (1H, t, J = 1.5Hz), 7.66 (4H, d, J = 1.5Hz), 7.41 (2H, d, J = 1.5Hz), 4.55 (8H, br.s), 2.9 (4H, m), 2.77-2.66 (16H, m), 2.42 (24H, s), 1.0 (9H, s) and 0.24 (6H, s); λ_{max} (CH_2Cl_2) 230, 272, 335 and 392nm (after addition of an excess of I_2: 230, 287, 335 and 812nm).

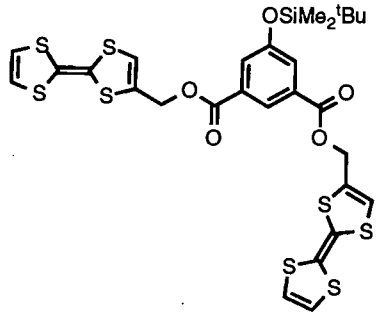
1,3,5-Tris(4-tetrathiafulvalenylmethyl)benzenetricarboxylate 48



To a solution of alcohol **47**[80] (100mg, 0.43mmol) in dichloromethane (100mL), 1,3,5-benzenetricarbonyl chloride (34mg, 0.13mmol) and DMAP (127mg, 1.0mmol) were added and the solution stirred under nitrogen at 20°C for 18h. The solvent was removed *in vacuo* and column chromatography of the residue on silica gel, eluent dichloromethane, afforded compound **48** (94mg, 85%) as an orange solid, m.p. 53-54°C. Analysis found: C, 40.7; H, 2.3%; Required for $C_{30}H_{18}O_6S_{12}$: C, 41.9; H, 2.1%; m/z (PDMS) 859.3 (M^+); δ_H ($CDCl_3$) 8.85 (3H, s), 6.45 (3H, s), 6.29 (6H, s) and 5.10 (6H, s); λ_{max} (CH_2Cl_2) (ε x 10^3 L mol^{-1} cm^{-1}) 220 (4.0), 307 (4.5) and 365 (0.8) nm (after addition of an excess of I_2: 225, 363, 439 and 590nm).

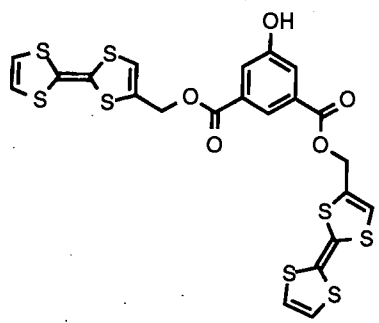
1,3-Bis(4-tetrathiafulvalenylmethyl)-5-*tert*-butyldimethylsiloxybenzenedicarboxylate 49

To a solution of alcohol **47**[80] (100mg, 0.43mmol) in dichloromethane (50mL), compound **40**[8] (64mg, 0.19mmol) and triethylamine (0.2mL, 1.43mmol) were added and the solution stirred under nitrogen at 20°C for 18h. The solvent was removed *in*



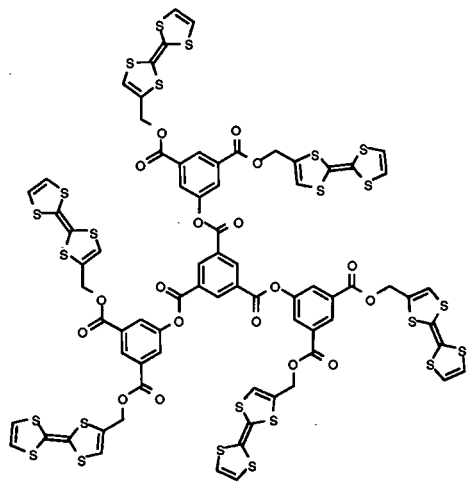
vacuo and column chromatography of the residue on silica gel, eluent dichloromethane, afforded compound **49** (116mg, 83%) as a yellow solid, m.p. 45-46°C. Analysis found: C, 45.9; H, 3.9%; Required for $C_{28}H_{28}O_5S_8Si$: C, 46.1; H, 3.9%; m/z (PDMS) 729.1 (M^+); δ_H [$(CD_3)_2CO$] 8.26 (1H, t, J = 1.5Hz), 7.74 (2H, d, J = 1.5Hz), 6.84 (2H, s), 6.62 (4H, s), 5.21 (4H, s), 1.03, (9H, s) and 0.30 (6H, s); λ_{max} (CH_2Cl_2) (ε x 10^3 L mol^{-1} cm^{-1}) 222 (5.5), 306 (6.3) and 363 (1.1) nm (after addition of an excess of I_2: 224, 309 and 581nm).

1,3-Bis(4-tetrathiafulvalenylmethyl)-5-hydroxybenzenedicarboxylate 50



To a solution of compound **49** (5.67g, 7.78mmol) in THF (75mL), tetrabutylammonium fluoride (7.5mL, 1.1M in THF, 8.25mmol) was added and the solution stirred under nitrogen at 20°C for 18h. The solvent was removed *in vacuo* and column chromatography of the residue on silica gel, eluent dichloromethane, afforded compound **50** (4.1g, 85%) as a yellow solid, m.p. 76-77°C. Analysis found: C, 43.4; H, 2.7%; Required for $C_{22}H_{14}O_5S_8$: C, 43.0; H, 2.3%; m/z (PDMS) 614.7 (M^+); δ_H [$(CD_3)_2CO$] 9.24 (1H, s), 8.16 (1H, t, J = 1.5Hz), 7.73 (2H, d, J = 1.5Hz), 6.85 (2H, s), 6.85 (4H, s) and 5.19 (4H, s); λ_{max} (CH_2Cl_2) (ε x 10^3 L mol^{-1} cm^{-1}) 222 (7.8) and 306 (0.5) nm (after addition of an excess of I_2: 222, 306 and 591nm).

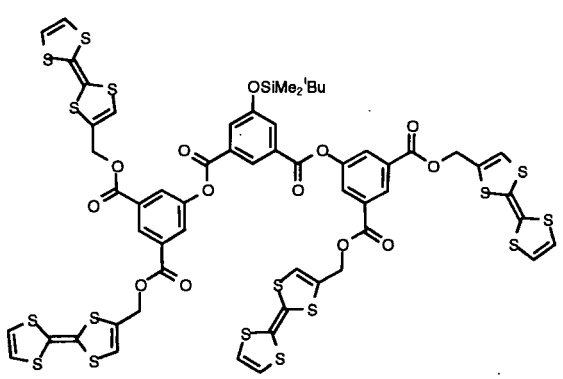
1,3,5-Tris{5-(2-oxo-1-oxaethyl)-1,3-bis[3-(4-tetrathiafulvalenyl)-1-oxo-2-oxapropyl]phenylene}benzene 51



To a solution of alcohol **50** (155mg, 0.25mmol) in dichloromethane (60mL), 1,3,5-benzenetricarbonyl chloride (20mg, 0.075mmol) and DMAP (75mg, 0.61mmol) were added and the solution stirred under nitrogen at 20°C for 18h. The solvent was removed *in vacuo* and column chromatography of the residue on silica gel, eluent dichloromethane/acetone (5:1 $^{v}/_{v}$), afforded compound **51** (113mg, 75%) as a yellow solid, m.p. 80-81°C. m/z (PDMS) 2000.6 (M^+); δ_H [$(CD_3)_2SO$] 9.10 (3H, s), 8.44 (3H, t, J = 1.5Hz), 8.32 (6H, d, J = 1.5Hz), 7.00 (6H, s), 6.70 (12H, s) and 5.20 (12H, s); λ_{max} (CH_2Cl_2) (ε x 10^3 L mol^{-1} cm^{-1}) 220 (5.7), 263 (2.9), 305 (3.9) and 360 (0.6) nm (after addition of an excess of I_2: 222, 294, 363 and 590nm).

1,3-Bis{5-(2-oxo-1-oxaethyl)-1,3-bis[3-(4-tetrathiafulvalenyl)-1-oxo-2-oxapropyl]phenylene}-5-*tert*-butyldimethylsiloxybenzene 52

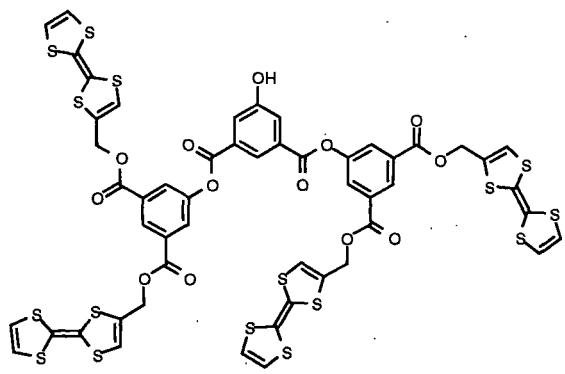
To a solution of alcohol **50** (100mg, 0.16mmol) in dichloromethane (50mL), compound **40**[8] (24mg, 0.072mmol) and DMAP (70mg, 0.58mmol) were added and the solution stirred under nitrogen at 20°C for 18h. The solvent was removed *in vacuo*



and column chromatography of the residue on silica gel, eluent dichloromethane, afforded compound **52** (91mg, 85%) as a yellow solid, m.p. 85-86°C. Analysis found: C, 46.5; H, 2.9%; Required for $C_{58}H_{44}O_{13}S_{16}Si$: C, 46.7; H, 3.2%;

m/z (PDMS) 1490.0 (M^+); δ_H [$(CD_3)_2CO$] 8.61 (1H, t, J = 1.5Hz), 8.55 (2H, t, J = 1.5Hz), 8.25 (4H, d, J = 1.5Hz), 7.95 (2H, d, J = 1.5Hz), 6.84 (4H, s), 6.58 (8H, s), 5.22 (8H, s), 1.04 (9H, s) and 0.32 (6H, s); λ_{max} (CH_2Cl_2) (ε x 10^3 L mol^{-1} cm^{-1}) 222 (7.8), 307 (2.6), and 364 (1.1) nm (after addition of an excess of I_2: 222, 308, 367 and 602nm).

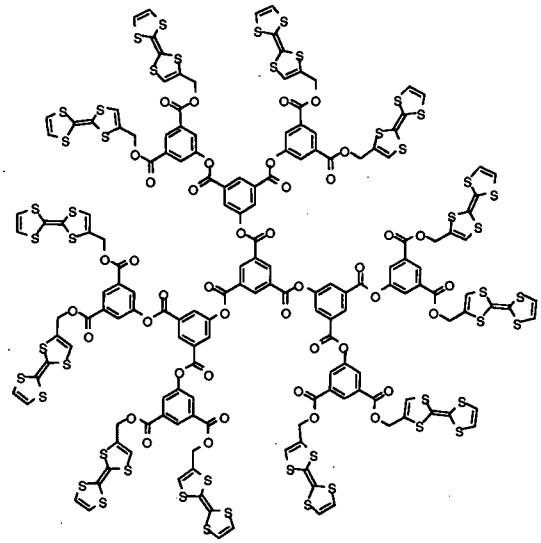
1,3-Bis{5-(2-oxo-1-oxaethyl)-1,3-bis[3-(4-tetrathiafulvalenyl)-1-oxo-2-oxapropyl]phenylene}-5-hydroxybenzene 53



To a solution of compound **52** (5.76g, 3.9mmol) in THF (60mL), tetrabutyl ammonium fluoride (7mL, 1.1M in THF, 7.7mmol) was added and the solution stirred under nitrogen at 20°C for 18h. The solvent was removed *in vacuo* and column chromatography of the residue on silica gel, eluent dichloromethane, afforded compound **53** as a yellow oil (5.1g, 95%). m/z (PDMS) 1375.8 (M^+); δ_H [$(CD_3)_2CO$] 9.30 (1H, br.s), 8.15 (3H, t, J = 1.5Hz), 7.73 (6H, d, J = 1.5Hz), 6.68 (4H, s), 6.63 (8H, s) and 5.20 (8H, s); λ_{max} (CH_2Cl_2) (ε x 10^3 L mol^{-1} cm^{-1}) 223 (4.0), 299 (4.0), 364 (1.0) and 433 (0.7) nm (after addition of an excess of I_2: 222, 299, 364, 433 and 590nm).

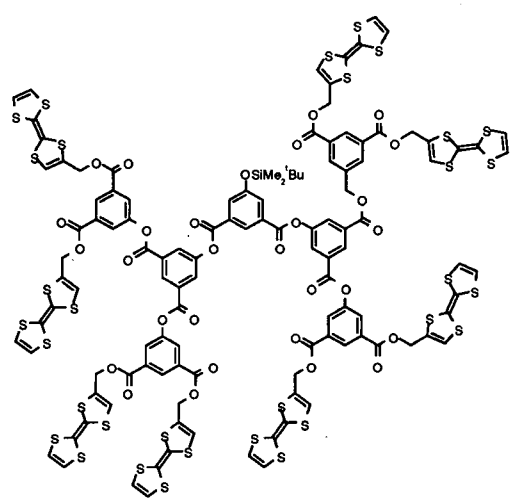
1,3,5-Tris{5-(2-oxo-1-oxaethyl)-1,3-bis{5-(2-oxo-1-oxaethyl)-1,3-bis[3-(4-tetrathiafulvalenyl)-1-oxo-2-oxapropyl]phenylene}phenylene} benzene 54

To a solution of alcohol **53** (50mg, 0.036mmol) in dichloromethane (60mL), 1,3,5-benzenetricarbonyl chloride (2.0mg, 0.0075mmol), DMAP (30mg, 0.25mmol) and *N,N*-dimethylaniline (0.05mL, 0.39mmol) were added and the solution stirred under nitrogen at 20°C for 54h. The solvent was removed *in vacuo* and column



chromatography of the residue on silica gel, eluent dichloromethane/acetone (5:1 $^{v}/_{v}$), afforded compound **54** (15mg, 48%) as an orange oil. m/z (PDMS) 2141.7 ($M^{2+}/2$); δ_H [$(CD_3)_2CO$] 8.54 (3H, s), 8.17 (9H, t, J = 1.5Hz), 7.73 (18H, d, J = 1.5Hz), 6.84 (12H, s), 6.61 (24H, s) and 5.19 (24H, s); λ_{max} (CH_2Cl_2) (ε x 10^3 L mol^{-1} cm^{-1}) 220 (0.2), 296 (1.5), and 363 (0.2) nm (after addition of an excess of I_2: 223, 262, 291, 363 and 590nm).

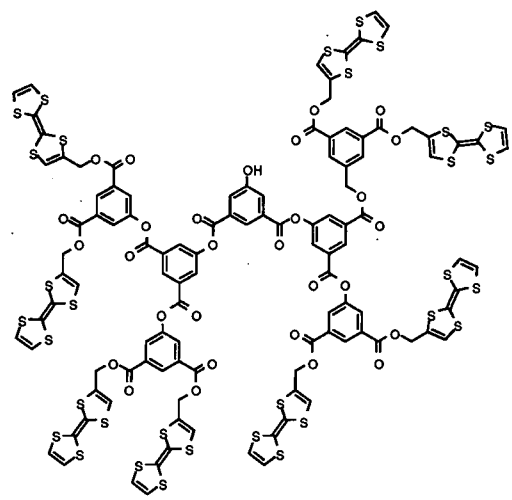
1,3-Bis{5-(2-oxo-1-oxaethyl)-1,3-bis{5-(2-oxo-1-oxaethyl)-1,3-bis[3-(4-tetrathiafulvalenyl)-1-oxo-2-oxapropyl]phenylene}phenylene}-5-*tert*-butyldimethylsiloxybenzene 55



To a solution of alcohol **53** (110mg, 0.08mmol) in dichloromethane (60mL), compound **40**[8] (13mg, 0.039mmol), DMAP (40mg, 0.33mmol) and *N,N*-dimethylaniline (0.05mL, 0.39mmol) were added and the solution stirred under nitrogen at 20°C for 54h. The solvent was removed *in vacuo* and column chromatography of the residue on silica gel, eluent dichloromethane, afforded compound **55** (90mg, 76%) as an orange oil. m/z (PDMS) 1505.0 ($M^{2+}/2$); δ_H [$(CD_3)_2CO$] 8.62 (1H, t, J = 1.5Hz), 8.56 (2H, t, J = 1.5Hz), 8.25 (12H, d, J = 1.5Hz), 7.94 (6H, d, J = 1.5Hz), 6.81 (8H, s), 6.58 (16H, s) 5.18 (16H, s), 1.03 (9H, s) and 0.30 (6H, s); λ_{max} (CH_2Cl_2) (ε x 10^3 L mol^{-1} cm^{-1})

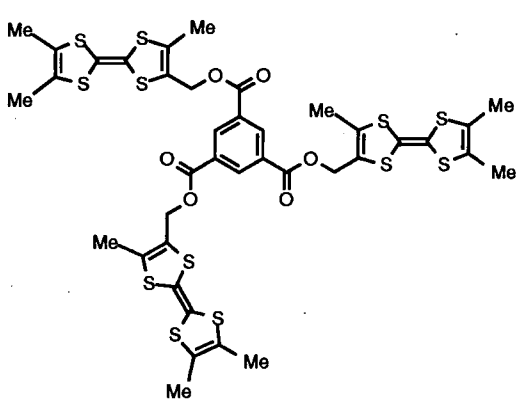
222 (6.5), 303 (3.6) and 434 (0.6) nm (after addition of an excess of I_2: 222, 259, 302, 435 and 590nm).

1,3-Bis{5-(2-oxo-1-oxaethyl)-1,3-bis{5-(2-oxo-1-oxaethyl)-1,3-bis[3-(4-tetrathiafulvalenyl)-1-oxo-2-oxapropyl]phenylene}phenylene}-5-hydroxybenzene 56



To a solution of compound **55** (90mg, 0.029mmol) in THF (60mL), tetrabutyl ammonium fluoride (0.2mL, 1.1M, 0.22mmol) was added and the solution stirred under nitrogen at 20°C for 18h. The solvent was removed *in vacuo* and column chromatography of the residue on silica gel, eluent dichloromethane/acetone (5:1 $^{v}/_{v}$), afforded compound **56** (42mg, 50%) as an orange oil. m/z (PDMS) 2897.6 (M^+); δ_H [$(CD_3)_2CO$] 9.30 (1H, br.s), 8.14 (7H, t, J = 1.5Hz), 7.78 (14H, d, J = 1.5Hz), 6.83 (8H, s), 6.58 (16H, s) and 5.15 (16H, s); λ_{max} (CH_2Cl_2) (ε x 10^3 L mol^{-1} cm^{-1}) 223 (10.9), 307 (3.4) and 360 (0.7) nm (after addition of an excess of I_2: 223, 294, 367 and 821nm).

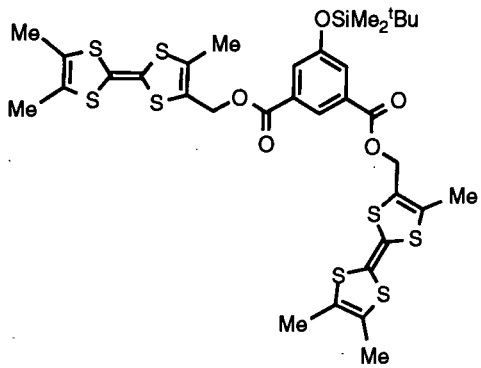
1,3,5-Tris[4-(4',5,5'-trimethyltetrathiafulvalenylmethyl)] benzenetricarboxylate 58



To a solution of alcohol **57**[81] (100mg, 0.36mmol) in toluene (100mL), 1,3,5-benzenetricarbonyl chloride (30mg, 0.11mmol) and triethylamine (0.3mL, 2.2mmol) were added and the solution stirred under nitrogen at 20°C for 18h.

The solvent was removed *in vacuo* and column chromatography of the residue on alumina, eluent toluene, afforded compound **58** (53mg, 48%) as an orange solid, m.p. 170°C ≥ (dec.). Analysis found: C, 47.7; H, 3.8%; Required for $C_{39}H_{36}O_6S_{12}$: C, 47.5; H, 3.7%; m/z (PDMS) 985.0 (M^+); δ_H [$(CD_3)_2CO$] 8.63 (3H, s), 5.11 (6H, d, J = 6.36Hz), 2.12 (9H, s) and 1.90 (18H, s); λ_{max} (PhMe) 231, 326 and 470nm (after addition of an excess of I_2: 230, 296, 363, 457 and 633nm).

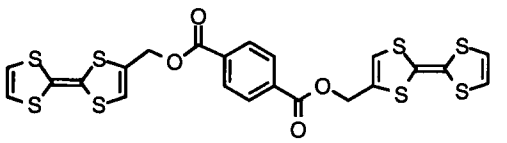
1,3-Bis[4-(4',5,5'-trimethyltetrathiafulvalenylmethyl)]-5-*tert*-butyldimethylsiloxybenzenedicarboxylate 59



To a solution of alcohol **57**[81] (250mg, 0.9mmol) in toluene (50mL), compound **40**[8] (110mg, 0.4mmol) and triethylamine (0.2mL, 1.43mmol) were added and the solution stirred under nitrogen at 20°C for 18h. The solvent was removed *in vacuo* and column chromatography of the residue on alumina, eluent toluene, afforded compound **59** (240mg, 90%) as a orange solid, m.p. 44-45°C. Analysis found: C, 51.1; H, 5.2%; Required for $C_{34}H_{40}O_5S_8Si$: C, 50.2; H, 5.0%; m/z (PDMS) 812.8 (M^+); δ_H [$(CD_3)_2CO$] 8.25 (1H, t, J = 1.5Hz), 7.73 (2H, d, J = 1.5Hz), 5.12 (4H, s), 2.17 (6H, s), 1.93 (12H, s), 1.03, (9H, s) and 0.30 (6H, s); λ_{max} (PhMe) 229, 312 and 466nm (after addition of an excess of I_2: 233, 296, 368, 470 and 626nm).

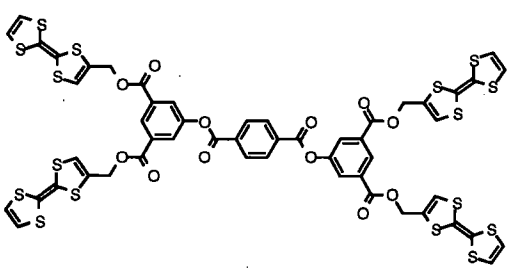
6.3 Experimental to Chapter Three

1,4-Bis(4-tetrathiafulvalenylmethyl)benzenedicarboxylate 64



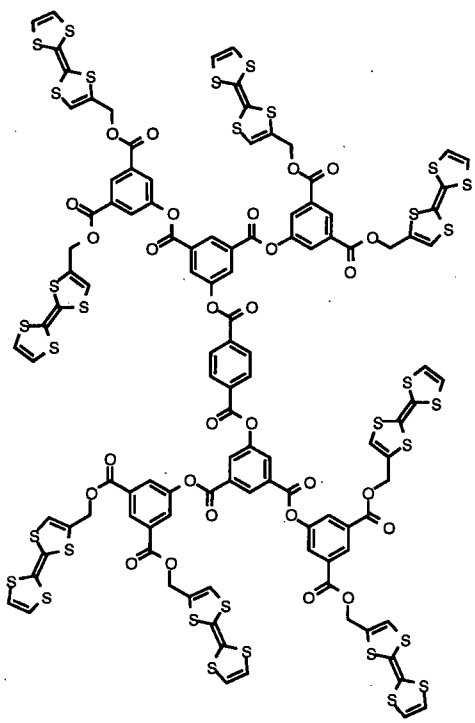
To a solution of compound **47**[80] (156mg, 0.67mmol) in dichloromethane (60mL), terephthaloyl chloride (67mg, 0.33mmol) and triethylamine (0.3mL, 2.2mmol) were added and the solution stirred under nitrogen at 20°C for 18h. The solvent was removed *in vacuo* and column chromatography of the residue on silica gel, eluent dichloromethane/acetone (5:1 $^{v}/_{v}$), afforded compound **64** (117mg, 59%) as a salmon coloured solid, m.p. 188-189°C. Analysis found: C, 44.0; H, 2.2%; Required for $C_{22}H_{14}O_4S_8$: C, 44.1; H, 2.4%; m/z (EI) 599 (M^+); δ_H [$(CD_3)_2SO$] 8.14 (4H, s), 7.01 (2H, s), 6.75 (4H, s) and 5.19 (4H, s); λ_{max} [$(CH_3)_2SO$] 222, 242, 302 and 370nm (after addition of an excess of I_2: 222, 295, 362, 433 and 516nm).

1,4-Bis{5-(2-oxo-1-oxaethyl)-1,3-bis[3-(4-tetrathiafulvalenyl)-1-oxo-2-oxapropyl]phenylene}benzene 65



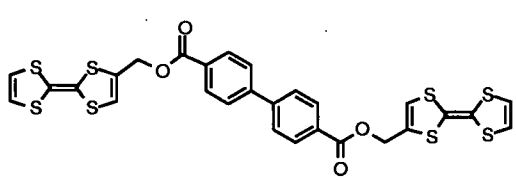
To a solution of compound **50** (Page 106) (100mg, 0.16mmol) in dichloromethane (60mL), terephthaloyl choride (16mg, 0.08mmol) and DMAP (40mg, 0.32mol) were added and the solution stirred under nitrogen at 20°C for 18h. The solvent was removed *in vacuo* and column chromatography of the residue on silica gel, eluent dichloromethane/acetone (5:1 $^{v}/_{v}$), afforded compound **65** (117mg, 59%) as a salmon coloured solid, m.p 113-114°C. Analysis found: C, 46.1; H, 2.3%; Required for $C_{52}H_{30}O_{12}S_{16}$: C, 45.9; H, 2.2%; m/z (PDMS) 1359.7 (M^+); δ_H [$(CD_3)_2SO$] 8.59 (2H, t, J = 1.5Hz), 8.28 (4H, d, J = 1.5Hz), 8.12 (4H, s), 6.89 (4H, s), 6.65 (8H, s) and 5.24 (8H, s); λ_{max} [$(CH_3)_2SO$] 222, 250, 300 and 362nm (after addition of an excess of I_2: 221, 294, 365, 433 and 516nm).

1,4-Bis{5-(2-oxo-1-oxaethyl)-1,3-bis{5-(2-oxo-1-oxaethyl)-1,3-bis[3-(4-tetrathiafulvalenyl)-1-oxo-2-oxapropyl]phenylene}phenylene} benzene 66



To a solution of compound **53** (Page 108) (132mg, 0.096mmol) in dichloromethane (60mL), terephthaloyl chloride (8.5mg, 0.042 mmol), DMAP (190mg, 1.56mmol) and *N,N*-dimethylaniline (0.2mL, 1.56mmol) were added and the solution stirred under nitrogen at 20°C for 72h. The solution was washed with cold acetic acid (1M) and saturated aqueous sodium carbonate to precipitate compound **66** (21mg, 15%) as a salmon coloured solid, m.p. > 250°C. Analysis found: C, 46.1; H, 2.3%; Required for $C_{112}H_{62}O_{28}S_{32}$: C, 46.7; H, 2.2%; m/z (PDMS) 1440.8 ($M^{2+}/2$); δ_H [$(CD_3)_2CO$] 8.59 (6H, t, J = 1.5Hz), 8.27 (12H, d, J = 1.5 Hz), 8.23 (4H, s), 6.88 (8H, s), 6.62 (16H, s) and 5.24 (16H, s); λ_{max} [$(CH_3)_2SO$] 222, 250, 300 and 362nm (after addition of an excess of I_2: 221, 294, 365, 433 and 516nm).

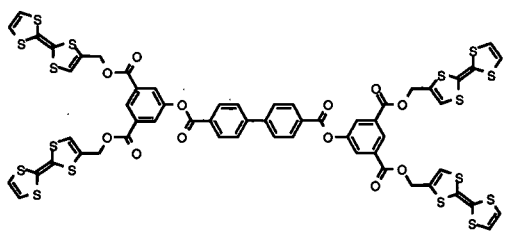
4,4'-Bis(4-tetrathiafulvalenylmethyl)biphenyldicarboxylate 68



To a solution of compound **47**[80] (105mg, 0.45mmol) in dichloromethane (60mL), 4,4'-biphenyldicarbonyl chloride (61mg, 0.22mmol) and DMAP (220mg, 1.80mmol) were added and the solution stirred under nitrogen at 20°C for 48h. The solvent was removed *in vacuo* and column chromatography of the residue on silica gel, eluent dichloromethane, afforded compound **68** (81mg, 55%) as an orange solid, m.p. 219-222°C. Analysis found: C,

48.1; H, 2.7%; Required for $C_{28}H_{18}O_4S_8$: C, 47.8; H, 2.7%; m/z (CI) 675 (M^+); δ_H [$(CD_3)_2SO$] 8.06 (4H, d, J = 7.9Hz), 7.91 (4H, d, J = 8.7Hz), 6.97 (2H, s), 6.7173 (4H, s) and 5.16 (4H, s); λ_{max} [$(CH_3)_2SO$] 223, 291 and 363nm (after addition of an excess of I_2: 221, 291, 365 and 840nm).

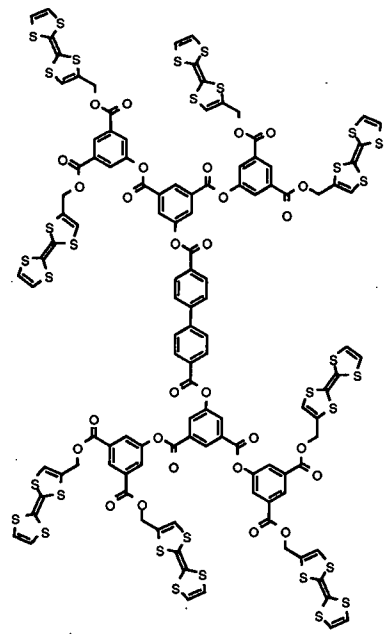
1,4-Bis{5-(2-oxo-1-oxaethyl)-1,3-bis[3-(4-tetrathiafulvalenyl)-1-oxo-2-oxapropyl]phenylene}biphenyl 69



To a solution of compound **50** (Page 106) (100mg, 0.16mmol) in dichloromethane (60mL), 4,4'-biphenyldicarbonyl chloride (22mg, 0.08mmol) and DMAP (156mg, 1.28mmol) were added and the solution stirred under nitrogen at 20°C for 18h. The solution was filtered and the residue washed sequentially with water, dichloromethane, isopropanol and diethyl ether to afford compound **69** (94mg, 83%) as an orange solid, m.p. > 250°C. Analysis found: C, 48.7; H, 2.5%; Required for $C_{58}H_{34}O_{12}S_{16}$; C, 48.5; H, 2.4%; m/z (PDMS) 1435.8 (M^+); δ_H [$(CD_3)_2SO$] 8.57 (2H, t, J = 1.5Hz), 8.29 (4H, d, J = 8.8Hz), 8.24 (4H, d, J = 1.5Hz), 8.03 (4H, d, J = 8.7Hz), 7.01 (4H, s), 6.72 (8H, s) and 5.21 (8H, s); λ_{max} [$(CH_3)_2SO$] 293, 365 and 398nm (after addition of an excess of I_2: 262, 318, 363, 438 and 831nm).

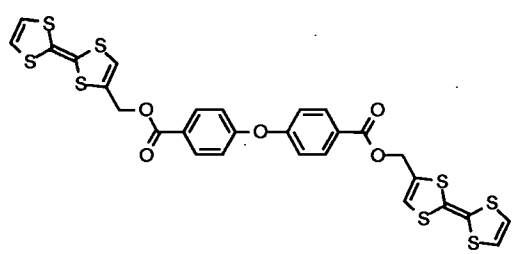
4,4'-Bis{5-(2-oxo-1-oxaethyl)-1,3-bis{5-(2-oxo-1-oxaethyl)-1,3-bis[3-(4-tetrathiafulvalenyl)-1-oxo-2-oxapropyl]phenylene}phenylene} biphenyl 70

To a solution of compound **53** (Page 108) (85mg, 0.062mmol) in dichloromethane (60mL), 4,4'-biphenyldicarbonyl chloride (7.5mg, 0.027mmol), DMAP (190mg, 1.56mmol), and *N,N*-dimethylaniline (0.2mL, 1.56mmol) were added and the solution stirred under nitrogen at 20°C for 54h. The solution was washed sequentially with cold



acetic acid(1M), saturated aqueous sodium carbonate, brine and the organic layer dried ($MgSO_4$). The solvent was removed *in vacuo* and column chromatography of the residue on silica gel, eluent dichloromethane/hexane (5:1 $^{v}/_{v}$), afforded compound **70** (28mg, 35%) as an orange oil. m/z (PDMS) 2954.7 (M^+); δ_H [$(CD_3)_2CO$] 8.33 (2H, t, J = 1.5Hz), 8.29 (4H, d, J = 1.5Hz), 8.14 (4H, t, J = 1.5Hz), 8.02 (8H, d, J = 1.5Hz), 7.80 (4H, d, J = 6.7Hz), 7.77 (4H, d, J = 7.22Hz), 6.85 (8H, s), 6.62 (16H, s) and 5.22 (16H, s); λ_{max} [$(CH_3)_2SO$] 229, 306 and 370nm (after addition of an excess of I_2: 233, 296, 368 and 836nm).

4,4'-Oxybis(4-tetrathiafulvalenylmethyl)benzenecarboxylate 72

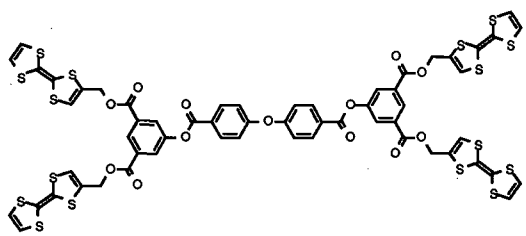


To a solution of alcohol **47**[80] (105mg, 0.45mmol) in dichloromethane (60mL), 4,4'-oxybis(benzenecarbonyl chloride) (66mg, 0.22mmol) and DMAP (110mg, 0.9mmol) were added and the solution stirred under nitrogen at 20°C for 18h. The solvent was removed *in vacuo* and column chromatography of the residue on silica gel, eluent dichloromethane/acetone (5:1 $^{v}/_{v}$), afforded compound **72** (113mg, 73%) as a yellow solid, m.p. 154-156°C. Analysis found: C 48.9; H, 2.6%; Required for $C_{28}H_{18}O_5S_8$: C, 48.7; H, 2.6%; m/z (DCI) 691 (M^+); δ_H [$(CD_3)_2CO$] 8.04 (4H, d, J = 9.0Hz), 7.17 (4H, d, J = 9.0Hz), 6.80 (2H, s), 6.59 (4H, s) and 5.13 (4H, s); λ_{max} (CH_2Cl_2) (ε x 10^3 L mol^{-1} cm^{-1}) 222 (10.9), 270 (10.1), 308 (7.1) and 363 (1.4) nm (after addition of an excess of I_2: 222, 280, 363, 437 and 578nm).

TCNQ Complex of 4,4'-oxybis(4-tetrathiafulvalenylmethyl) benzenecarboxylate 72

To a hot solution of compound **72** (6.2mg, 9.0μmol) in acetonitrile (10mL), a hot solution of TCNQ (3.9mg, 18.0μmol) in acetonitrile (10mL) was added and allowed to cool. The solution was filtered and a black precipitate obtained. The precipitate was washed with cold acetonitrile until the washings were colourless. Analysis found: C 49.9; H, 2.2; N, 4.0%; Required for $C_{68}H_{40}O_{10}N_4S_{16}$ (2:1 Complex): C, 50.0; H, 2.6; N, 3.6%; ν_{max} (KBr) 3420, 2177, 1714, 1594, 1499, 1340, 1245, 1162, 1090, 766 and 704 cm^{-1}; σ_{rt} (Compressed Pellet) 3 x 10^{-3} S cm^{-1}.

4,4'-Oxybis{5-(2-oxo-1-oxaethyl)-1,3-bis[3-(4-tetrathiafulvalenyl)-1-oxo-2-oxapropyl]phenylene}benzene 73

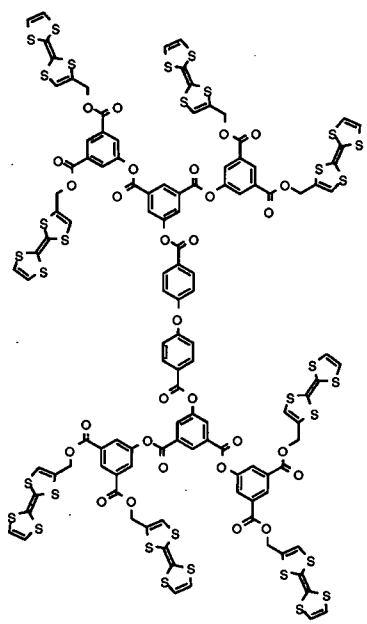


To a solution of compound **50** (Page 106) (75mg, 0.12mmol) in dichloromethane (60mL), 4,4'-oxybis(benzenecarbonyl chloride) (17mg, 0.06mmol) and DMAP (117mg, 0.96mmol) were added and the solution stirred under nitrogen at 20°C for 18h. The solvent was removed *in vacuo* and column chromatography of the residue on silica gel, eluent dichloromethane, afforded compound **73** (43mg, 52%) as an orange solid, m.p. 110-112°C. Analysis found: C, 47.9; H, 2.4%; Required for $C_{58}H_{34}O_{13}S_{16}$: C, 48.0; H, 2.4%; m/z (PDMS) 1451.7 (M^+); δ_H [$(CD_3)_2CO$] 8.57 (2H, t, J = 1.5Hz), 8.30 (4H, d, J = 8.12Hz), 8.24 (4H, d, J = 1.5Hz), 7.32 (4H, d, J = 8.2Hz), 6.88 (4H, s), 6.62 (8H, s) and 5.25 (8H, s); λ_{max} (CH_2Cl_2) (ε x 10^3 L mol^{-1} cm^{-1}) 223 (8.2), 307 (8.4) and 364 (1.2) nm (after addition of an excess of I_2: 233, 281, 314 and 830nm).

TCNQ Complex of 4,4'-oxybis{5-(2-oxo-1-oxaethyl)-1,3-bis[3-(4-tetrathiafulvalenyl)-1-oxo-2-oxapropyl]phenylene}benzene 73

To a hot solution of compound **73** (8.8mg, 6.1μmol) in acetonitrile (10mL), a hot solution of TCNQ (5.0mg, 24.4μmol) in acetonitrile (10mL) was added and allowed to cool. The solution was filtered and a black precipitate obtained. The precipitate was washed with cold acetonitrile until the washings were colourless. Analysis found: C 49.9; H, 2.2; N, 4.0%; Required for $C_{70}H_{38}O_{13}N_4S_{16}$ (1:1 Complex): C, 49.9; H, 2.4; N, 3.6%; ν_{max} (KBr) 3428, 2176, 1734, 1636, 1560, 1310, 1238, 1163, 1065, 796 and 668cm^{-1}; σ_{rt} (Compressed Pellet) 3 x 10^{-3} S cm^{-1}.

4,4'-Oxybis{5-(2-oxo-1-oxaethyl)-1,3-bis{5-(2-oxo-1-oxaethyl)-1,3-bis[3-(4-tetrathiafulvalenyl)-1-oxo-2-oxapropyl]phenylene}phenylene} benzene 74



To a solution of compound **53** (Page 108) (108mg, 0.078mmol) in dichloromethane (60mL), 4,4'-oxybis(benzenecarbonyl chloride) (10.9mg, 0.037mmol), DMAP (190mg, 1.56mmol) and *N,N*-dimethylaniline (0.2mL, 1.56mmol) were added and the solution stirred under nitrogen at 20°C for 72h. The solution was washed sequentially with cold acetic acid (1M), saturated aqueous sodium carbonate, and the organic layer dried ($MgSO_4$). The solvent was removed *in vacuo* and column chromatography of the residue on silica gel, eluent dichloromethane/acetone (5:1 $^{v}/_{v}$), afforded compound **74** (18mg, 16%) as an orange oil. m/z (PDMS) 2971.1 (M^+); δ_H [$(CD_3)_2CO$] 8.57 (4H, t, *J* = 1.5Hz), 8.29 (4H, d, *J* = 9.0Hz), 8.24 (8H, d, *J* = 1.5Hz), 8.14 (2H, t, *J* = 1.5Hz), 7.72 (4H, d, *J* = 1.5Hz), 7.30 (4H, d, *J* = 9.0Hz), 6.88 (8H, s), 6.62 (16H, s) and 5.24 (16H, s);

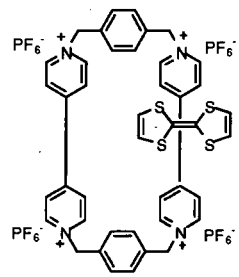
λ_{max} (CH_2Cl_2) (ε x 10^3 L mol^{-1} cm^{-1}) 233 (6.5), 281 (8.1) and 362 (1.2) nm (after addition of an excess of I_2: 233, 281, 362 and 830nm).

TCNQ Complex of 4,4'-oxybis{5-(2-oxo-1-oxaethyl)-1,3-bis{5-(2-oxo-1-oxaethyl)-1,3-bis[3-(4-tetrathiafulvalenyl)-1-oxo-2-oxapropyl] phenylene}phenylene}benzene 74

To a hot solution of compound **74** (21mg, 7.0μmol) in acetonitrile (10mL), a hot solution of TCNQ (11.5mg, 56.3μmol) in acetonitrile (10mL) was added and allowed to cool. The solution was filtered and a black precipitate obtained. The precipitate was washed with cold acetonitrile until the washings were colourless. Analysis found: C 48.5; H, 2.8; N, 4.2%; Required for $C_{154}H_{78}O_{29}N_{12}S_{32}$ (≈ 1:3 Complex): C, 51.6; H, 2.2; N, 4.7%; ν_{max} (KBr) 3423, 2180, 1734, 1653, 1560, 1314, 1239, 1162, 1065, 798 and 668cm^{-1}; σ_{rt} (Compressed Pellet) 1.5 x 10^{-3} S cm^{-1}.

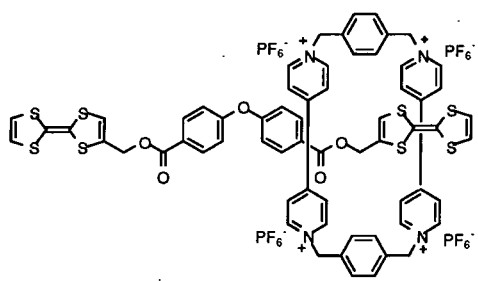
6.4 Experimental to Chapter Four

Tetrathiafulvalene:cyclobis(paraquat-*p*-phenylene)[2]pseudorotaxane 19



[2]Pseudorotaxane **19** was prepared following the literature method.[71]

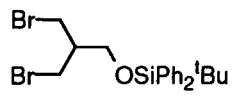
4,4'-Oxybis(4-tetrathiafulvalenylmethyl)benzenecarboxylate :cyclobis(paraquat-*p*-phenylene)[2]pseudorotaxane 76



To a solution of compound **72** (Page 115) (5.9mg, 8.5μmol) in acetone (2mL), a solution of compound **75** (9.4mg, 8.5μmol) in acetone (2mL) was added and shaken vigourously for 2min, affording an emerald green solution, which upon evaporation afforded an emerald green solid. m/z (FAB) 1645 $(M\text{-}PF_6)^+$; δ_H [$(CD_3)_2CO$] 9.50 (8H, s), 8.50 (8H, s), 8.24 (4H, d, *J* = 8.4Hz), 7.92 (8H, s), 7.23 (4H, d, *J* = 8.8Hz), 6.72 (2H, s), 6.46 (4H, s), 6.11 (8H, s) and 5.17 (4H, s); λ_{max} [$(CH_3)_2CO$] (ε x 10^3 L mol^{-1} cm^{-1}) 327 (3.7), 360 (1.1), 447 (0.2), 828 (0.2) nm.

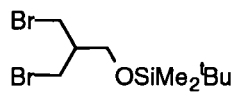
6.5 Experimental to Chapter Five

2-Bromomethyl-3-bromo-*tert*-butyldiphenylsilyloxypropane 96



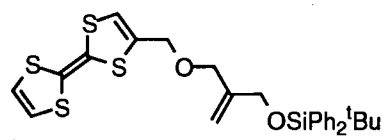
To a solution of compound **29**[78] (4.8g, 22.2mmol) in DMF (50mL), *tert*-butyldiphenylsilyl chloride (6.5g, 23.6mmol) and imidazole (2.2g, 32.3mmol) were added and the solution stirred under nitrogen at 20°C for 18h. The solution was added to water (1L), extracted with dichloromethane and washed with brine. The solvent was removed *in vacuo* and column chromatography of the residue on silica gel, eluent dichloromethane, afforded compound **96** (9.93g, 95%) as a colourless oil. m/z (CI) 471 (M^++1); δ_H ($CDCl_3$) 7.68 (4H, m), 7.43 (6H, m), 3.76 (2H, d, J = 5.76Hz), 3.59 (4H, d, J = 5.88Hz), 2.27 (1H, m) and 1.10 (9H, s); ν_{max} (neat) 3070, 2958, 2930, 2857, 1589, 1471, 1427, 1112, 823 and 702cm^{-1}.

2-Bromomethyl-3-bromo-*tert*-butyldimethylsilyloxypropane 97



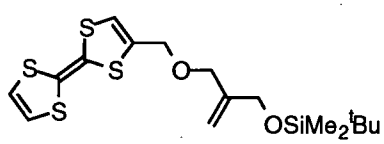
To a solution of compound **29**[78] (3.2g, 14.8mmol) in DMF (50mL), *tert*-butyldimethylsilyl chloride (2.4g, 15.9mmol) and imidazole (2.2g, 32.3mmol) were added and the solution stirred under nitrogen at 20°C for 18h. The solution was added to water (1L), extracted with dichloromethane, washed with brine and dried ($MgSO_4$). The solvent was removed *in vacuo* to afford compound **97** (4.1g, 60%) as a colourless oil. m/z (CI) 347 (M^++1); δ_H ($CDCl_3$) 3.73 (2H, d, J = 5.82Hz), 3.59 (2H, d, J = 1.84Hz), 3.56 (2H, d, J = 2.0Hz), 2.23 (1H, m), 0.94 (9H, s), 0.12 (6H, s); ν_{max} (neat) 2955, 2930, 2857 1471, 1433, 1257, 1104, 836 and 778cm^{-1}.

5-(4-Tetrathiafulvalenyl)-2-methylene-4-oxa-*tert*-butyl diphenylsilyloxypentane 100



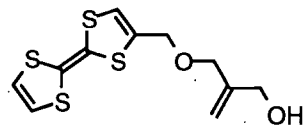
To a solution of compound **96** (390mg, 0.85mmol) in THF (60mL), compound **47**[80] (390mg, 1.66mmol) and sodium hydride (23mg, 0.94mmol) were added and the solution stirred at 20°C under nitrogen for 56h. Water was added and the solution extracted with dichloromethane, washed with brine, and dried ($MgSO_4$). The solvent was removed *in vacuo* and column chromatography of the residue on silica gel, eluent dichloromethane/hexane (1:1: $^{v}/_{v}$), afforded compound **100** (220mg, 49%) as a yellow oil. m/z (CI) 544 (M^{+}+1); δ_H ($CDCl_3$) 7.71 (4H, m), 7.38 (6H, m), 6.30 (2H, s), 6.10 (1H, s), 5.37 (1H, s), 5.17 (1H, s), 4.23 (2H, s), 4.13 (2H, s), 4.01 (2H, s), and 1.10 (9H, s); ν_{max} (neat) 3423, 3069, 2926, 2852, 1427, 1112 and 702cm^{-1}.

5-(4-Tetrathiafulvalenyl)-2-methylene-4-oxa-*tert*-butyl dimethylsilyloxypentane 101



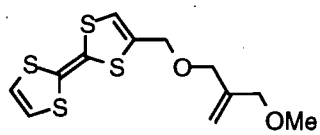
To a solution of compound **97** (218mg, 0.35mmol) in THF (60mL), compound **47**[80] (73mg, 0.31mmol) and sodium hydride (24mg, 1.02mmol) were added and the solution refluxed under nitrogen for 72h. Water was added and solution extracted into dichloromethane, washed with brine, and dried ($MgSO_4$). The solvent was removed *in vacuo* and column chromatography of the residue on silica gel, eluent dichloromethane/hexane (1:1: $^{v}/_{v}$), afforded compound **101** (81mg, 32%) as a yellow oil. m/z (CI) 404 (M^{+}+1); δ_H ($CDCl_3$) 6.30 (2H, s), 6.20 (1H, s), 5.24 (1H, s), 5.11 (1H, s), 4.21 (2H, s), 4.17 (2H, s), 4.00 (2H, s), 0.91 (9H, s) and 0.08 (6H, s); ν_{max} (neat) 3070, 2953, 2927, 2854, 1462, 1256, 1112, 1075, 836 and 777cm^{-1}.

5-(4-Tetrathiafulvalenyl)-2-methylene-4-oxapentan-1-ol 104



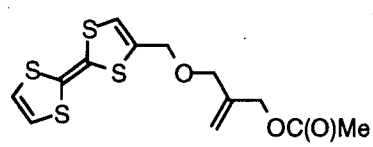
To a solution of compound **100** (1.2g, 2.2mmol) in THF (60mL), tetrabutylammonium fluoride (3.2mL, 1.1M in THF, 3.5mmol) was added and the solution stirred under nitrogen at 20°C for 18h. The solvent was removed *in vacuo* and column chromatography of the residue on silica gel, eluent dichloromethane, afforded compound **104** (0.73g, 93%) as a yellow oil. HRMS found: 303.9758 (M^+); Required for $C_{11}H_{12}O_2S_4$; 303.9720; δ_H ($CDCl_3$) 6.30 (2H, s), 6.20 (1H, s), 5.22 (1H, s), 5.15 (1H, s), 4.24 (2H, s), 4.17 (2H, s), 4.01 (2H, s), and 1.86 (1H, s); λ_{max} (CH_2Cl_2) 226, 276 and 306; ν_{max} (neat) 3070, 3384, 3065, 2918, 2852, 1448, 1065 and 918cm^{-1}.

5-(4-Tetrathiafulvalenyl)-4-methylene-2,6-dioxaheptane 105



To a solution of compound **104** (70mg, 2.3mmol) in THF (60mL), methyl iodide (0.5mL, 8.0mmol) and sodium hydride (60mg, 2.5mmol) were added and the solution stirred under nitrogen at 20°C for 18h. The solvent was removed *in vacuo* and column chromatography of the residue on silica gel, eluent dichloromethane, afforded compound **105** (53mg, 73%) as a yellow oil. HRMS found: 317.9888; Required for $C_{12}H_{14}O_2S_4$: 317.9876; δ_H ($CDCl_3$) 6.30 (2H, s), 6.19 (1H, s), 5.21 (2H, s), 4.23 (2H, s), 4.00 (2H, s), 3.93 (2H, s) and 3.34 (3H, s); λ_{max} (CH_2Cl_2) 230, 276 and 306; ν_{max} (neat) 3065, 2923, 2852, 1448, 1080 and 914cm^{-1}.

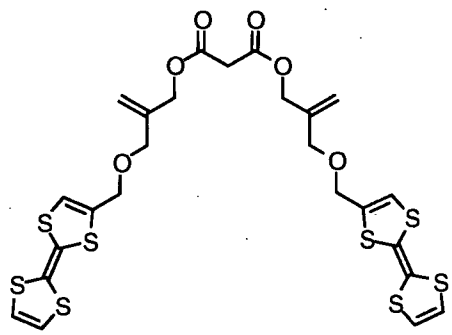
5-(4-Tetrathiafulvalenyl)-2-methylene-4-oxapentyl acetate 106



To a solution of compound **104** (70mg, 2.3mmol) in dichloromethane (60mL), acetyl choride (0.5mL, 7.0mmol) and sodium hydride (60mg, 2.5mmol)

were added and the solution stirred under nitrogen at 20°C for 18h. The solvent was removed *in vacuo* and column chromatography of the residue on silica gel, eluent dichloromethane, afforded compound **106** (65mg, 82%) as a yellow oil. HRMS found; 345.9801; Required for $C_{13}H_{14}O_3S_4$: 345.9801; δ_H ($CDCl_3$) 6.30 (2H, s), 6.19 (1H, s), 5.24 (2H, s), 4.59 (2H, s), 4.23 (2H, s), 4.01 (2H, s) and 2.09 (3H, s); δ_C ($CDCl_3$) 170.6 (C=O), 139.9 (Quaternary C), 134.2 (Quaternary C), 119.1 (CH), 118.9 (CH), 116.4 (CH), 116.1 (CH_2), 111.1 (Quaternary C), 109.5 (Quaternary C), 70.4 (CH_2), 66.9 (CH_2), 64.5 (CH_2) and 20.9 (CH_3); λ_{max} (CH_2Cl_2) 226, 284, 318, 306 and 358; ν_{max} (neat) 3067, 2927, 2853, 1732, 1440, 1229, 1072 and 922cm^{-1}.

1,3-Bis[5-(4-tetrathiafulvalenyl)-2-methylene-4-oxapentyl] malonate 109



To a solution of compound **104** (140mg, 4.6mmol) in dichloromethane (60mL), malonyl dichoride (0.5mL, 5.1mmol) and triethylamine (1.0mL, 7.3mmol) were added and the solution stirred under nitrogen at 20°C for 18h. The solvent was removed *in vacuo* and column chromatography of the residue on silica gel, eluent dichloromethane/hexane (1:1 $^{v}/_{v}$), afforded compound **109** (156mg, 77%) as a yellow oil. HRMS found: 675.9350; Required for $C_{25}H_{24}O_6S_8$: 675.9339; δ_H ($CDCl_3$) 6.29 (2H, s), 6.20 (1H, s), 5.26 (2H, s), 4.67 (2H, s), 4.21 (2H, s), 4.00 (2H, s) and 3.45 (2H, s); λ_{max} (CH_2Cl_2) 226, 284, 318 and 362; ν_{max} (neat) 3067, 2927, 2853, 1733, 1427, 1261, 1073 and 927cm^{-1}.

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APPENDIX ONE

ELECTROCHEMICAL CALCULATIONS

A.1.1 Electrochemical Determinations

The number of electrons involved in the cyclic voltammetric oxidation reactions can be determined using two methods[96]: i) classical cyclic voltammetry, ii) UME cyclic voltammetry, in conjuction with chronoamperometry.

In both cases a known amount of compound is combined with a known amount of a reference compound (*viz.* 2,3-dichloronaphthoquinone), dissolved in dry solvent (*ca.* 3mL) and degassed with argon. Cyclic voltammetry is then performed using conventional platinum electrodes, or with ultra micro electrodes at conditions approaching steady-state.[96] For UME determinations, chronoamperometry is then used on the same sample to determine the limiting current from a plot of current against $t^{-1/2}$.

A1.1.2 Theory for Electron Determinations Using Classical CV

The number of electrons involved in a reversible electrochemical oxidation can be determined using the *Sevcik-Randles* equation[97]

$$i_p = 2.687 \times 10^5 n^{3/2} A D^{1/2} C v^{1/2}$$

where i_p is the peak limiting current (A), n is the number of electrons removed, A is the electrode area (7.85×10^{-3} cm^2), D is the diffusion coefficient (cm^2 s^{-1}, assumed to be equal for both species in solution), C is concentration (mol L^{-1}), and v is the sweep rate (Vs^{-1}, usually 100 mV s^{-1}). The concentrations of the reference and the study compound were known. The reference compound is known to undergo a one electron reduction at 430mV. Hence, for a known concentration it will provide a measurable limiting current that can be equated to a detector response of h_r; this can then be compared to the response h_c, obtained from a known amount of the compound being

studied. Assuming that each species obeys the *Sevcik-Randles* equation we obtain expressions for each species in solution:

$$h_r = 2.687 \times 10^5 n_r^{3/2} A D_r^{1/2} C_r \nu^{1/2}$$

$$h_c = 2.687 \times 10^5 n_c^{3/2} A D_c^{1/2} C_c \nu^{1/2}$$

where the subscript r denotes the reference compound and the subscript c denotes the compound being studied. A ratio of these equations affords the expression

$$\frac{h_r}{h_c} = \frac{2.687 \times 10^5 n_r^{3/2} A D_r^{1/2} C_r \nu^{1/2}}{2.687 \times 10^5 n_c^{3/2} A D_c^{1/2} C_c \nu^{1/2}}$$

Applying the assumptions stated earlier we obtain

$$\frac{h_r}{h_c} = \frac{n_r^{3/2} C_r}{n_c^{3/2} C_c}$$

By linearising this equation an expression for n_c is obtained

$$n_c^{3/2} = \frac{h_c n_r^{3/2} C_r}{h_r C_c}$$

Substitute the value of one for n_r

$$n_c^{3/2} = \frac{h_c C_r}{h_r C_c}$$

This expression allows the number of electrons involved in the oxidation of the compound to be obtained directly from the concentration and the detector response.

A1.1.3 Theory for Electron Determinations Using UME CV

At slow scan rates UME CV eliminates diffusion and Faradaic currents, producing steady state voltammogram (Figure 2.4.2), which deals with an electrode surface where concentration is effectively unchanging with time *i.e.* obeys Fick's Second law.[96] At steady state the limiting current (equating to the maximum detector response) is equal to:

$$i_{\infty} = 4rn\mathrm{FCD}$$

where r is the electrode radius, n is the number of electrons involved in the reversible oxidation, F is the *Faraday constant* (96500 C), C is the concentration of the species being studied (mol L^{-1}) and D is the *diffusion coefficient.* The concentrations of the reference and the study compound were known. The reference compound is known to undergo a one electron reduction at 430mV. Hence, for a known concentration it will provide a measurable limiting current that can be equated to a detector response of h_r; this can then be compared to the response h_c. Hence,

$$i_{\infty r} = i_r = h_r = 4rn\mathrm{FC_rD_r}$$

and

$$i_{\infty c} = i_c = h_c = 4rn\mathrm{FC_cD_c}$$

A ratio of these equations provides

$$\frac{i_c}{i_r} = \frac{h_c}{h_r} = \frac{n_c\mathrm{D_cC_c}}{n_r\mathrm{D_rC_r}}$$

Equation 1

Chronoamperometry can now be used in conjunction with UME CV to determine the ratio of diffusion coefficients from *Cottrell* equation.[96]

$$i = \frac{nFAD^{1/2}C}{\pi^{1/2}t^{1/2}}$$

This equation applies to both the reference and the compound being studied, hence,

$$i_r = \frac{n_rFAD_r^{1/2}C_r}{\pi^{1/2}t^{1/2}} \quad \text{and} \quad i_c = \frac{n_cFAD_c^{1/2}C_c}{\pi^{1/2}t^{1/2}}$$

where the subscripts *r* and *c* denote the reference and study compounds, respectively. A ratio of these equations affords

$$\frac{i_c}{i_r} = \frac{n_cD_c^{1/2}C_c}{n_rD_r^{1/2}C_r}$$

Equation 2

An estimate of the ratio of D_c/D_r can be obtained from a plot of *i* against $t^{1/2}$; the slope of which is equal to

$$S = \frac{nFAD^{1/2}C}{\pi^{1/2}}$$

The slope of this plot can be obtained for the reference compound (2,4-dichloronaphthoquinone $\approx 4.5 \times 10^6$ cm s^{-1})[96] and the compound being studied, then a ratio of the two formulas reveals

$$\frac{S_c}{S_r} = \frac{n_cFAD_c^{1/2}C_c}{n_rFAD_r^{1/2}C_r} = \frac{n_cD_c^{1/2}C_c}{n_rD_r^{1/2}C_r}$$

Equation 3

Substitution of D_c/D_r from equation 3 into Equation 1 yields

$$\frac{n_c}{n_r} = \frac{S_c^2 i_r C_r}{S_r^2 i_c C_c}$$

This equation allows the calculation of the number of electrons involved in the reversible oxidation of the compound under study to be compared to the number of electrons reversibly reduced in the reference compound.

Substituting for C_c/C_r from Equation 3 into Equation 1 reveals the diffusion coefficient of the compound being studied. When this calculation was performed for our dendritic macromolecules, the values obtained failed to exhibit a correlation between molecular weight and diffusion speed, so these results were regarded as flawed and disregarded.

APPENDIX TWO

MOLECULAR MODELS

A2.1 Computer Molecular Modelling

A Silicon Graphics Indigo^2 workstation, running Biosym Technologies Insight II (version 2.3.5) molecular modelling package was used to determine the minimum energy conformations of the oligomeric and dendritic esters described in this thesis; selected average conformations were then presented as colour pictures.

Molecules were built using the 'Builder' program, then studied using the 'Discover' program. Initially the molecules were contorted for 10,000 iterations at a temperature of 750K, breaking any intra-molecular attractions resulting from the initial conformation, and providing a constant starting point for all studies. Further iterations were used on larger molecules when necessary. The structure was minimised using the VA09A minimisation algorithm for 10,000 iterations and the average minimum energy conformation selected for printing and inclusion in this Thesis. No other data were acquired using this program, as it was felt that this was outside the accuracy of the program.

APPENDIX THREE

PSEUDOROTAXANE STUDIES AND THEORY

A3.1 Determination of Stability Constants

Methods for the determination of stability constants of complexes of π-electron rich and π-electron deficient units have been discussed by Connors.[91] This type of complexation results in the formation of a charge-transfer band in the UV-visible spectrum of the sample. This absorption may be used as a quantitative measure of complex formation. The two methods of calculating stability constants that are used in this Thesis are the *dilution* and the *titration* methods.

A3.1.1 *Dilution* Methodology

The *dilution* method[92] is the simplest experimental technique and is suitable for the calculation of stability constants of complexes with K_a values in excess of 500 M^{-1}. The procedure involved making an equimolar solution of both components of the complex in a standard solvent of known weight.[98] A sample was removed and the UV-visible spectrum obtained in the range of 300 to 900nm. The sample was discarded and the original stock solution regenerated to the original volume with a known weight of standard solvent, and the solution allowed to reach equilibrium. Some of the diluted stock solution (*ca.* 2mL) was then removed and the UV-visible spectrum recorded. The solution was discarded and the whole procedure repeated until a range of concentrations from *ca.* 10^{-3} to 10^{-5} mol L^{-1} was obtained. UV-visible spectra were then obtained for the uncomplexed components at a known concentration (*ca.* 10^{-3} mol L^{-1}), so that any absorption for the complex could be corrected for the contibutions of either component of the complex. The data collected from the variation in the charge-transfer band allowed the stability constant to be calculated as follows:

Assume that components **A** and **B** are in equilibrium with a constant of K_a, associating to give a 1:1 complex of concentration **[A•B]**

$$\mathbf{A} + \mathbf{B} \underset{}{\overset{K_a}{\rightleftharpoons}} \mathbf{[A \bullet B]} \qquad K_a = \frac{\mathbf{[A \bullet B]}}{\mathbf{[A]\ [B]}}$$

If the total concentration of the components in the solution is d, then

$$[\mathbf{A}] + [\mathbf{A{\bullet}B}] = d = [\mathbf{B}] + [\mathbf{A{\bullet}B}]$$

letting x equal the equilibrium concentration of the complex, then

$$K_a = \frac{x}{(d\text{-}x)(d\text{-}x)} = \frac{x}{(d\text{-}x)^2}$$

Assuming that the *Beer-Lambert* law is obeyed for all the species in solution, then

$$A_c = \varepsilon_c x l \qquad \text{so} \qquad x = \frac{A_c}{\varepsilon_c l}$$

where A_c is the *charge-transfer absorbance*, ε_c is the *extinction coefficient* of the complex, x is the concentration of the complex [**A•B**], and l is the path length of the cell (1cm), then

$$K_a = \frac{A_c/\varepsilon_c l}{(d\text{-}\ A_c/\varepsilon_c l)^2}$$

Linearisation of this expression yields the equation

$$\frac{d}{A_c} = \left(\frac{1}{K_a \varepsilon_c l}\right)^{1/2} \bullet \frac{1}{(A_c)^{1/2}} + \frac{1}{\varepsilon_c l}$$

Provided that the complex is 1:1 with respect to both components, then a graph of d/A_c against $1/(A_c)^{1/2}$ yields a linear plot, where the slope = $(1/K_a\varepsilon_c l)^{1/2}$ and the intercept on the y-axis = $1/\varepsilon_c l$. Therefore, $(\text{slope})^2 = 1/K_a\varepsilon_c l$, but $K_a = 1/\varepsilon_c l(\text{slope})^2$, thus,

$$K_a = \frac{\text{y-Intercept}}{(\text{Slope})^2}$$

Hence, this method of determining the stability constants for a complex can simply and accurately be deduced from an easily obtainable graph.

A3.1.2 *Titration* Method

This method is suitable for the determination of stability constants with K_a values below 500 M^{-1}; stability constant and complex stoichiometry are revealed from one experiment. This procedure involves making a solution of one component of the complex of known concentration, in a known mass of standard solution, in a volumetric flask. A sample of the solution was removed and the UV-visible spectrum obtained. The sample was returned to the volumetric flask, along with the washings from the UV cell. A known weight of a standard solution containing the second component of the complex was then added to the stock solution of the first component and the volume reduced to the original level by blowing a stream of dry nitrogen over the solution. The procedure was then repeated until the stock solution of the second component was exhausted and a solution of 1:1 complex was obtained. This method effectively examines a solution containing a fixed concentration of one component, whilst gradually increasing the concentration of the second component to form a complex of the two species.

In a system where n molecules of one component **A** associate with one molecule of a second component **B**, to form a complex, then

$$n\mathbf{A} + \mathbf{B} \underset{}{\overset{K_a}{\rightleftharpoons}} [n\mathbf{A}\bullet\mathbf{B}] \qquad K_a = \frac{[n\mathbf{A}\bullet\mathbf{B}]_{eq}}{[\mathbf{A}]^n_{eq}\,[\mathbf{B}]_{eq}}$$

The subscript *eq* denotes the the state of the system at equilibrium. It follows that

$$[\mathbf{A}]_{eq} = [\mathbf{A}]_{tot} - n[n\mathbf{A}\bullet\mathbf{B}]_{eq}$$

$$[\mathbf{B}]_{eq} = [\mathbf{B}]_{tot} - [n\mathbf{A}\bullet\mathbf{B}]_{eq}$$

Where the subscript *tot* denoted the total concentration of the species in solution. K_a can be expressed as follows

$$K_a = \frac{[n\mathbf{A}\bullet\mathbf{B}]_{eq}}{([\mathbf{A}]_{tot} - n[n\mathbf{A}\bullet\mathbf{B}]_{eq})^n \quad ([\mathbf{B}]_{tot} - [n\mathbf{A}\bullet\mathbf{B}]_{eq})}$$

Assuming that the *Beer-Lambert* law holds for the complex, and that corrections were made for the absorptions arising from **A** and **B** we find that

$$[n\mathbf{A}\bullet\mathbf{B}]_{eq} = A_c/\varepsilon_c l$$

where A_c is the absorbance arising from the charge-transfer band, ε_c is the *extinction coefficient* of the complex, and l is the path length of the sample. Substituting for $[n\mathbf{A}\bullet\mathbf{B}]_{eq}$ we can write K_a as

$$K_a = \frac{A_c/\varepsilon_c l}{([\mathbf{A}]_{tot} - n(A_c/\varepsilon_c l))^n \quad ([\mathbf{B}]_{tot} - A_c/\varepsilon_c l)}$$

This equation can now be simplified using the *Benesi-Hildebrand* approximation for weak complexes,[99] where it is assumed that when $[\mathbf{A}]_{tot} \gg [\mathbf{B}]_{tot}$ and from that we can assume that $[\mathbf{A}]_{eq} \gg [\mathbf{B}]_{eq}$. We can now express K_a as

$$K_a = \frac{[n\mathbf{A}\bullet\mathbf{B}]_{eq}}{[\mathbf{A}]^n_{tot}\,([\mathbf{B}]_{tot} - [n\mathbf{A}\bullet\mathbf{B}]_{eq})}$$

and substituting for $[n\mathbf{A}\bullet\mathbf{B}]_{eq}$ we obtain the expression

$$K_a = \frac{A_c/\varepsilon_c l}{[\mathbf{A}]^n_{tot}\,([\mathbf{B}]_{tot} - A_c/\varepsilon_c l)}$$

which can be linearised to give

$$\boxed{\frac{A_c}{[\mathbf{A}]^n_{tot}} = -K_a A_c - K_a[\mathbf{B}]_{tot}\varepsilon_c l}$$

Hence, a plot of $A_c/[\mathbf{A}]_{tot}$ against A_c is linear when the complex has 1:1 stoichiometry. The gradient of the line is $-K_a$. If a straight line is acheived from a plot of $A_c/[\mathbf{A}]^2_{tot}$ against A_c, then the complex is of 2:1 stoichiometry. The use of the *Benesi-Hildebrande* approximation in the calculations induces errors in the data obtained, for this reason, it is not the most suitable method for the calculation of stability constants.

A3.1.3 Free Energy of Association

The free energy of association ΔG°, is given by the equation

$$-\Delta G^\circ = RT\ln K_a$$

where R is the *molar gas constant* (1.987 cal K^{-1} mol^{-1}), T is the temperature at which the study was carried out and K_a is the stability constant.

APPENDIX FOUR

RESEARCH COLLOQUIA, SEMINARS, LECTURES AND CONFERENCES

A4.1 Colloquia, Lectures and Seminars Attended

1992-1993

November 5 Dr. C.J. Ludman, University of Durham
Explosions, A Demonstration Lecture

November 11 Prof. D. Robins, Glasgow University
Pyrrolizidine Alkaloids : Biological Activity, Biosynthesis and Benefits

November 18 Dr. R. Nix, Queen Mary College, London
Characterisation of Heterogeneous Catalysts

November 25 Prof. Y. Vallee, University of Caen
Reactive Thiocarbonyl Compounds with Uncommon Bonding

December 2 Prof. A.F. Hegarty, University College, Dublin
Highly Reactive Enols Stabilised by Steric Protection

December 2 Dr. R.A. Aitken, University of St. Andrews
The Versatile Cycloaddition Chemistry of $Bu_3P.CS_2$

January 21 Prof. L. Hall, Cambridge
NMR - Window to the Human Body

January 27 Dr. W. Kerr, University of Strathclyde
Development of the Pauson-Khand Annulation Reaction:
Organocobalt Mediated Synthesis of Natural and Unnatural Products

January 28 Prof. J. Mann, University of Reading
Murder, Magic and Medicine

February 3 Prof. S.M. Roberts, University of Exeter
Enzymes in Organic Synthesis

February 11 Prof. S. Knox, Bristol University
The Tilden Lecture Organic Chemistry at Polynuclear Metal Centres

February 24 Prof. C.J.M. Stirling, University of Sheffield
Chemistry on the Flat-Reactivity of Ordered Systems

March 11 Dr. R.A.Y. Jones, University of East Anglia
The Chemistry of Wine Making

March 17 Dr. R.J.K. Taylor, University of East Anglia
Adventures in Natural Product Synthesis

March 24 Prof. I.O. Sutherland, University of Liverpool
Chromogenic Reagents for Cations

May 13 Prof. J.A. Pople, Carnegie-Mellon University, Pittsburgh, USA
The Boys-Rahman Lecture Applications of Molecular Orbital Theory

June 1 Prof. J.P. Konopelski, University of California, Santa Cruz
Synthetic Adventures with Enantiomerically Pure Acetals

June 16 Prof. A.K. Covington, University of Newcastle
Use of Ion Selective Electrodes as Detectors in Ion Chromatography

1993-1994

September 13 Prof. Dr. A.D. Schlüter, Freie Universität Berlin, Germany
Synthesis and Characterisation of Molecular Rods and Ribbons

October 4 Prof. F.J. Feher, University of California, Irvine, USA
Bridging the Gap between Surfaces and Solution with Sessilquioxanes

October 20 Dr. P. Quayle, University of Manchester
Aspects of Aqueous ROMP Chemistry

October 27 Dr. R.A.L. Jones, Cavendish Laboratory, Cambridge
Perambulating Polymers

November 24 Dr. P.G. Bruce, University of St. Andrews
Structure and Properties of Inorganic Solids and Polymers

December 1 Prof. M.A. McKervey, Queen's University, Belfast
Synthesis and Applications of Chemically Modified Calixarenes

December 8 Prof. O. Meth-Cohn, University of Sunderland
Friedel's Folly Revisited - A Super Way to Fused Pyridines

March 10 Prof. S.V. Ley, University of Cambridge
New Methods for Organic Synthesis

1994-1995

November 16 Prof. M. Page, University of Huddersfield
Four Membered Rings and β-Lactamase

November 23 Dr. J. Williams, University of Loughborough
New Approaches to Asymmetric Catalysis

November 30 Prof. P. Parsons, University of Reading
Applications of Tandem Reactons in Organic Synthesis

January 18 Dr. G. Rumbles, Imperial College
Real or Imaginary 3rd Order Non-Linear Optical Materials

February 8 Dr. D. O'Hare, Oxford University
Synthesis and Solid State Properties of Poly- Oligo- and Multidecker Metallocenes

February 15 Prof. W. Motherwell, University College, London
New Reactions for Organic Synthesis

February 22 Prof. E. Schaumann, University of Clausthal
Silicon and Sulfur Mediated Ring Opening Reactions of Epoxides

March 1 Dr. M. Rosseinsky, Oxford University
Fullerene Intercalation Chemistry

March 2 Prof. E.W. Meijer, Eindhoven University of Technology
Dendrimers and Supramolecular Polymer Chemistry

April 26 Dr. M. Schröder, University of Edinburgh
Redox-Active Macrocyclic Complexes:
Rings, Stacks and Liquid Crystals

May 9, Prof. R. Townsend, Unilever's Exploratory Research Council
Polymers for the Year 2000 - The Challenge Ahead

A4.2 Lectures and Posters Presented

Lecture: "Redox-Active Dendritic Macromolecules", March 23, 1994, Université d'Angers, Angers, France.

Lecture: "Redox-Active Dendritic Macromolecules", July 13, 1994, MacroAkron '94. 35th IUPAC International Symposium on Macromolecules, Akron, OH, USA.

Lecture: "Oligomeric and Dendritic Macromolecules Incorporating Tetrathiafulvalene", March 8, 1995, University of Durham, Durham, UK.

Poster: "Redox-Active Dendritic Macromolecules", September 22-23, 1993, IRC in Polymer Science & Technology Industrial Club Meeting, University of Durham, Durham, UK.

Poster: "Redox-Active Dendritic Macromolecules", December 22, 1994, Zeneca Science Poster Competition, University of Durham, Durham, UK.

A4.3 Conferences Attended

September 1993 IRC in Polymer Science & Technology Industrial Club Meeting, University of Durham, Durham, UK.

July 1994 MacroAkron '94. 35th IUPAC International Symposium on Macromolecules, Akron, OH, USA.

March 1995 Graduate Symposium, University of Durham, Durham, UK.

APPENDIX FIVE

PUBLICATIONS

The following publications have arisen from the work of the author during this period of study:

1. M.R. Bryce, **W. Devonport**, A.J. Moore; "Dendritic Macromolecules Incorporating Tetrathiafulvalene Units", *Angew. Chem. Int. Ed. Engl.*, **1994**, *33*, 1761.

2. M.R. Bryce, A.S. Batsanov, **W. Devonport**, J.N. Heaton, J.A.K. Howard, G.J. Marshallsay, A.J. Moore, P.J. Skabara, S. Wegener; "New Materials Based on Highly Functionalised Tetrathiafulvalene Derivatives", J. Becher and K. Schaumburg (*Eds.*), Kluwer, Dordrecht, **1995**.

3. M.R. Bryce, **W.Devonport**; "New Oligomeric Hyper-Branched Esters Incorporating Tetrathiafulvalene: Synthesis, Electrochemistry and Charge-Transfer Complexes", *Synthetic Metals*, **1995**, In Press.

4. M.A. Blower, M.R. Bryce, **W. Devonport**; "The Self-Assembly of a Redox-Active Bis(Tetrathiafulvalene) [2]Pseudorotaxane", In Preparation.

5. M.A. Blower, M.R. Bryce, **W. Devonport**; "Synthesis and Aggregation of Redox-Active Phthalocyanines Incorporating Tetrathiafulvalene Units", *Adv. Mater.*, **1995**, In Press.