

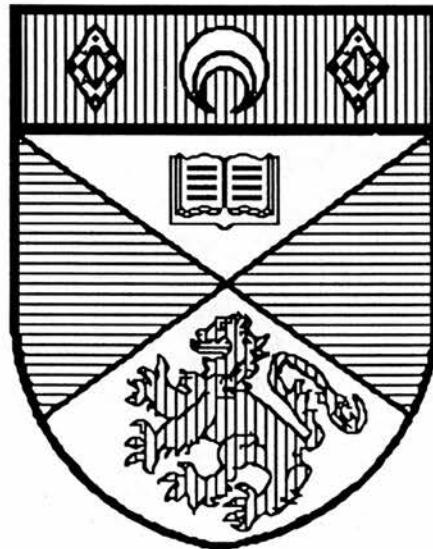
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Electroluminescent Metallo Polymers

A thesis presented by John James Morrison, B.Sc., M.Phil., to the
University of St. Andrews in application for the degree of Doctor of
Philosophy.



August 1997

c 364

Declarations

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

Signed

Date 19/8/97

I was admitted to the Faculty of Science of the University of St. Andrews under Ordinance General No. 12 on 1st of October 1993 and as a candidate for the degree of Ph.D. on the 1st of October 1994.

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Date 19/8/97

I hereby certify that the candidate has fulfilled the conditions of the Resolution and Regulations appropriate to the degree of Ph.D.

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Courses Attended

The School of Chemistry requires that a number of courses be attended. These courses were: "Pharmaceutical Chemistry" (Dr. R. A. Aitken and Dr. A. R. Butler), "Advanced Spectroscopy" (Dr. J. A. Crayston), "Organic Synthesis" (Prof. D. Gani), "Macrocyclic Chemistry" (Prof. R. W. Hay), "Advanced NMR" (Dr. R. K. Mackie) and "Bioinorganic Chemistry" (Dr. D. T. Richens)

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Symbols and Abbreviations

δ	chemical shift
bpy	2,2'-Bipyridine
bp	boiling point
br, s, d, t, q, m	broad, singlet, doublet, triplet, quartet, multiplet
CV	Cyclic voltammetry
dec	decomposed
DMF	Dimethylformamide
DMSO	Dimethylsulphoxide
ECL	Electrochemiluminescence
EL	Electroluminescence
ether	Diethyl ether
GC/MS	Gas chromatography-mass spectrometry
h,min	hours, minutes
IR	Infra-red
ν_{max}	Infra-red absorption frequency
LED	Light emitting diode
LDA	Lithium diisopropylamine
M	mol dm^{-3}
M^+	Mass of molecular ion
MS	Mass spectrometry
m/z	Mass to charge ratio
mp	melting point
mmol	millimoles
NBS	N-Bromo succinimide
NMR	Nuclear magnetic resonance
PPV	Poly(p-phenylenevinylene)
4ry	quaternary

RT	Room temperature
<i>J</i>	Spin-spin coupling constant in Hertz
TBAT	Tetrabutylammonium tetrafluoroborate
THF	Tetrahydrofuran
TLC	Thin layer chromatography
λ_{max}	Ultraviolet / visible absorbtion frequency
UV	Ultra-violet visible spectroscopy

Abstract

The ligand 4-[6-(3-thienyl)hexan-2-oyl],4'-methylbis-2,2'-bipyridine (L) was synthesised and its complexes (L) ruthenium bis(2,2'-bipyridine) dihexafluorophosphate and (L) rhenium tricarbonyl chloride were prepared.

Electrochemical polymerisation of the ruthenium complex led to film growth on both platinum and indium tin oxide electrodes. Once polymerised and transferred to a solution of the same electrolyte in the absence of the monomer the electroactivity of the Ru(II/III) couple was maintained showing the capability of redox reactions within the polymer. Photoluminescence spectroscopy of the polymer coated ITO electrode showed peaks at 540 and 580 nm corresponding to the polythiophene backbone and ruthenium complex respectively. Electropolymerisation of the rhenium complex did not lead to polymer growth. Instead, an exchange reaction between the co-ordinated chloride and acetonitrile solvent was observed.

5,5'-dibromomethyl-2,2'-bipyridine was conveniently prepared by coupling 3-picoline with W-7 Raney nickel followed by bromination with NBS. Attempts at a Gilsch type polymerisation with this monomer failed. It is suggested that this may be due to solubility problems in suitable solvents.

The corresponding Wessling type monomer was prepared by the reaction of 5,5'-dibromomethyl-2,2'-bipyridyl with tetrahydrothiophene. The dibromide salt of the monomer was found to be non-crystalline and thus difficult to purify. Exchange of the counter ion to hexafluorophosphate produced a pure crystalline salt; however, this was insoluble in most solvents. The use of DMF solvent and potassium t-butoxide base has provided a small quantity of a polymer with a ^1H NMR resembling the expected alkyl linked precursor polymer. The small quantity obtained and sparingly soluble nature of this polymer hindered further characterisation. Evidence for

substitution of the tetrahydrothienyl groups by methoxy groups was found; this is a precedented process for the analogous PPV type precursor.

5,5'-Bis(ethoxycarbonylthiomethyl)-2,2'-bipyridyl was prepared by the reaction of potassium ethyl xanthate with the bromomethyl bipyridyl. The use of the xanthate leaving group aided solubility of the monomer however attempted polymerisation led to unexpected products formed presumably by hydrolysis of the xanthate group with base. The presence of disulphide linkages between bipyridyls in these products is suggested and supported by precedented processes and NMR of model compounds. It is also suggested that the Son route to PPV may give rise to contamination by disulphides in both the precursor step and perhaps on the thermal elimination step. This would give rise to the possibility of cross linkages of the polymer chain through disulphides.

5,5'-Bis(triphenylphosphoniomethyl) 2,2-bipyridine dibromide and 1,4-dihexyloxy-2,5-benzenedicarboxaldehyde were prepared and Wittig olefination of these compounds was attempted. This failed to give a polymer presumably because of the insolubility of the bipyridine salt. 2,2'-Bipyridine-5,5'-dicarboxaldehyde and 1,4-dihexyloxy-2,5'-bis (triphenylphosphoniomethyl)benzene were prepared and Wittig olefination of these gave a red solid sparingly soluble in polar organic solvents. UV-VIS, photoluminescence and excitation spectroscopy studies indicate that the product is a co-polymer of bipyridinevinylene.

Dedication

To Flossie.

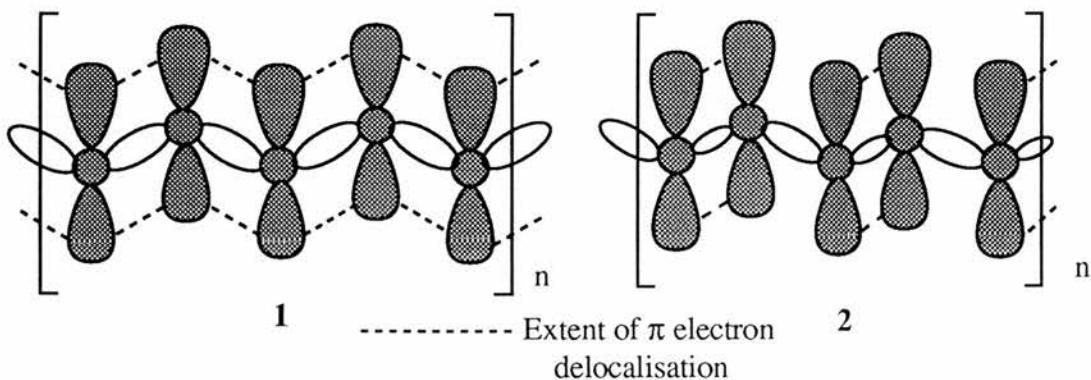
Chapter 1

Introduction

1.1 Conducting Polymers

For most of the century polymers have generally been regarded as electrical insulators; indeed one of the biggest uses of polythene is in the electrical wiring industry. Then in 1977 it was discovered that polyacetylene, a fully conjugated polymer, could undergo a dramatic increase in conductivity via charge transfer oxidation or "doping".^{1,2}

The current understanding of this conductivity change is based on the theory that the charge carriers are radical cations delocalised over several carbon atoms. Let us consider the undoped neutral polymer first of all. In conjugated polymers such as *trans*-polyacetylene the polymer chain exists as a planar sequence of alternating single and double bonds. The result of this is that each carbon has a p_z orbital orientated perpendicular to the polymer backbone which is capable of overlapping with its neighbours. This continuous π system with delocalised electrons would act as a one dimensional metal with a half-filled conduction band if the bonds were all of the same length 1. Unfortunately for such one dimensional systems the energy savings associated with the resonance stabilisation afforded by complete delocalisation is outweighed by the decrease in electronic energy available via bond alternation 2.

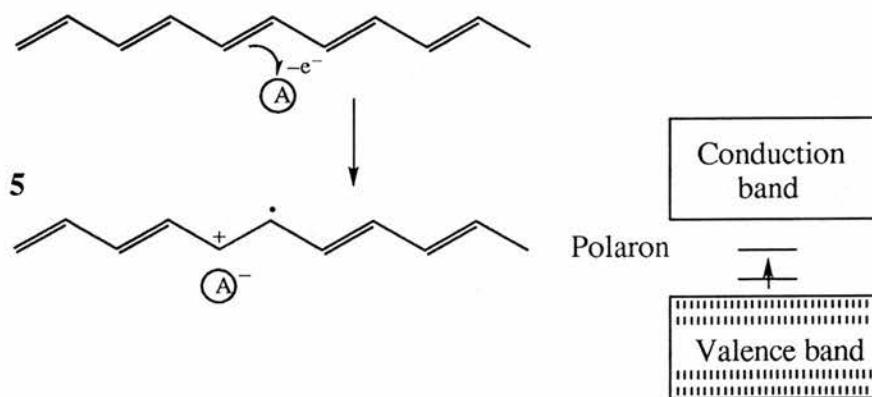


This phenomenon was originally postulated by Peierls³ and is responsible for the localised electronic structure of conjugated polymers or one dimensional conductors. The mathematical treatment is identical to the Jahn-Teller theorem which explains, for example,

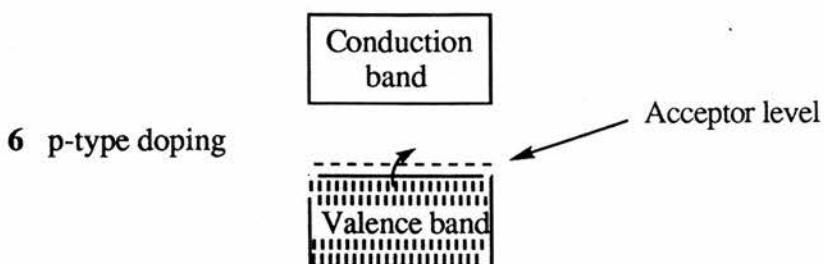
why cyclobutadiene has unequal bond lengths. Rather than providing a continuous π system with delocalised electrons which would allow conduction through a half filled band **3** the bond alternation limits the extent of delocalisation to provide a large band gap semiconductor **4**.



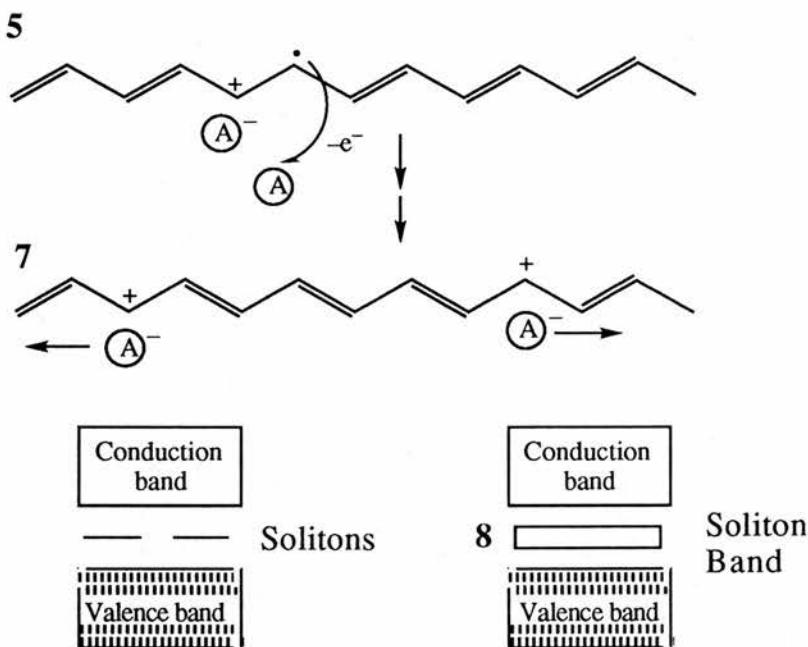
The process of charge transfer oxidative (or reductive) doping greatly changes the electronic properties of polyacetylene. The first step in oxidation involves the formation of a radical cation via the one electron transfer from the polymer chain to an oxidising agent forming a species known as a polaron **5**. The polaron exhibits an electronic structure



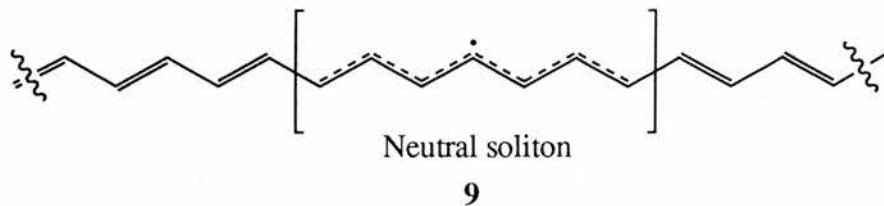
somewhat analogous to that of a p-type semiconductor **6**, normally manufactured by the doping of an inorganic crystal such as silicon. With the p-type semiconductor, conductivity is facilitated by the band-like conduction of free unpaired electrons in an acceptor level near the valence band.



With doped polyacetylene, however, two important points lead away from this model. Firstly, extremely low levels of dopant (typically in the parts per million range) are used in the inorganic p-type conductors while much larger amounts in the range of a few molar percent are often used to achieve significant conductivity in polyacetylene. Secondly, the concentration of free spins as determined by electron spin resonance (E.S.R) spectroscopy has been found to be too low to account for the conductivity of polyacetylene, and it has been found that as the amount of dopant is increased the conductivity also increases past a point where any spins are observed.⁴ This increase in conductivity, termed spinless conductivity, is accounted for by the further oxidation of the polyacetylene chain to form two charged solitons. This oxidation occurs at the original polaron site utilising the radical electron produced from the first oxidation. Since the ground state structure of polyacetylene is two-fold degenerate the charged cations can then freely separate along the chain **7**. Some detailed calculations by Heeger *et al*^{5,6} have concluded that solitons are delocalised over some 12-14 CH units and have the effect of lowering the degree of bond alternation thus reducing the extent of the Peierls instability. As the degree of doping is increased a soliton band **8** is formed which can eventually merge with the band edges of the valence and conduction bands to provide metallic conductivity.

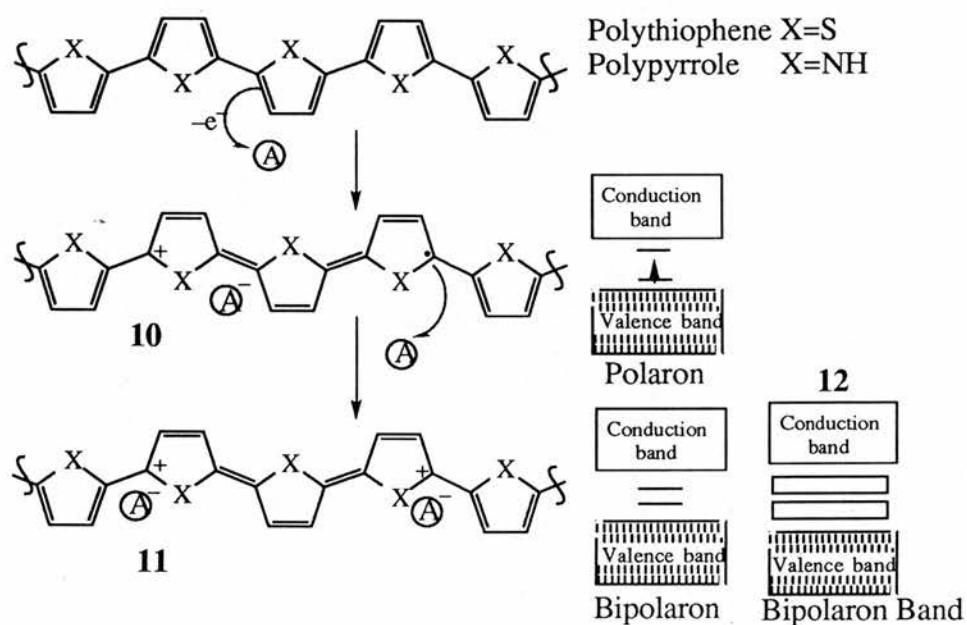


The solitons may be either charged or neutral and in the case of a neutral soliton the defect in the polyacetylene chain consists of a free radical. The radical has a similar effect to that of the cations reducing the degree of bond alternation to give a more delocalised π electron structure illustrated below **9**.



Moving from polyacetylene to more complex conjugated polymers the effect of dopants follows the same trend providing increasing conductivity with increasing amounts of the oxidising or reducing agents added. Polythiophene^{7,8,9} and polypyrrole^{10,11} are two commonly used polymer backbones which exhibit conducting behaviour on doping. However, they do not have twofold degenerate ground states which is a requirement in the construction of a soliton band. The conductivity is seen to be due to a different mechanism which relies on localised alteration of bonding on oxidation or reduction. The mechanism

again involves the formation of polarons **10** but here (in the case of oxidation) the radical and cation are coupled to each other via a local bond rearrangement which takes the form of a series of quinoid like rings. Further oxidation is believed to take advantage of the ease of removal of the free radical of the polaron;¹² however, the reaction may also result in the formation of further polarons. Then, once saturation is approached bipolarons **11** are formed.



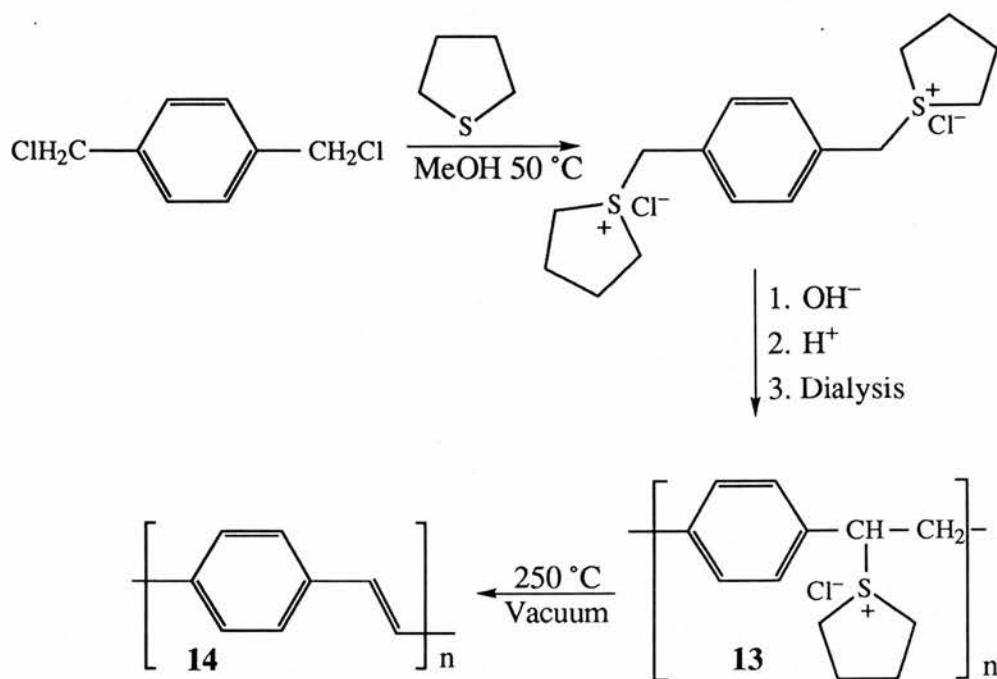
The bipolarons, like the solitons, are spinless defects and as their numbers increase bipolaron bands **12** are formed which, like solitons, may overlap to theoretically provide metal-like conductivity.

1.2 Electroluminescence from Semiconducting Polymers

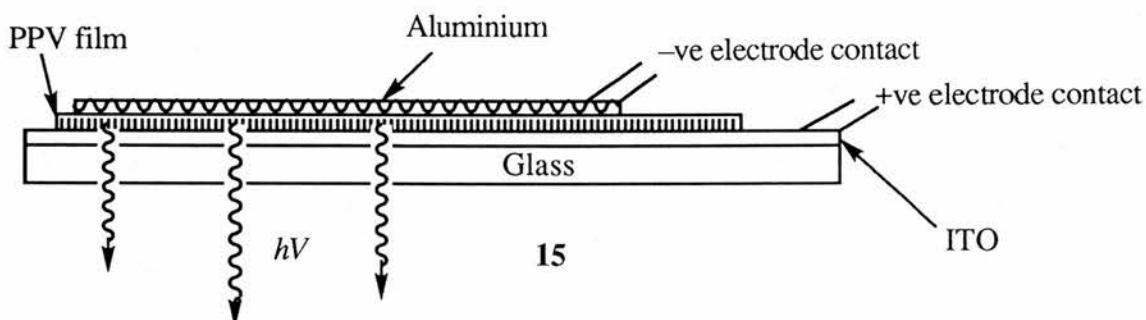
The phenomenon of electroluminescence (EL) from semiconducting polymers was discovered by Bradley, Friend and Holmes¹³ on passing a current through a film of poly(p-phenylenevinylene) (PPV) sandwiched between two electrodes. Their original report in 1990 has since seen tremendous interest develop in the area as displayed by over 200 citations to date.

Prior to the discovery of EL, conjugated polymers had seen great interest as new conducting materials as discussed earlier. This field relied greatly on the action of charge transfer coupling or "doping" of the polymers. It is now known that this leads to degradation of the polymers' luminescence characteristics, and may help to explain why the discovery of EL arrived much later. "Doped" conjugated polymers such as polyacetylene that have undergone oxidation with iodine display only a weak photoluminescence. The weakness of the spectrum is due to a "quenching" effect of the dopants; this will be discussed in detail later. In order to observe strong photoluminescence it is advantageous to have a large bandgap semiconductor of high purity and PPV is one such material that can be manufactured to provide these properties.

PPV was prepared via the precursor polymer **13** which was easily synthesised and was soluble in methanol and easily processable. The precursor maintained these properties due to the lack of conjugation between the rings which in the PPV product **14** is responsible for the "stiffness" of the structure and also subsequent difficulties in solubility and processing.



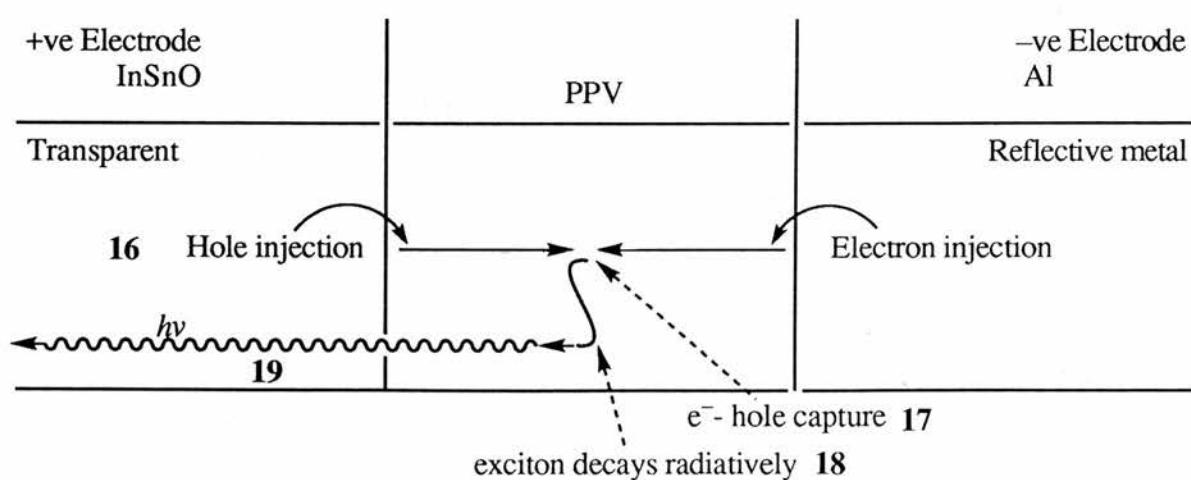
The precursor polymer was spin coated onto indium tin oxide (ITO) covered glass which was used as the hole-injecting (positive) electrode. The electrode was then heat treated in vacuo to convert the precursor to PPV. The electron-injecting (negative) electrode was prepared by covering the PPV film with a high work function metal such as aluminium or calcium. A diagram of the device is shown below **15**.



The first devices constructed using PPV required a potential of just below 14 V for substantial charge injection and the integrated light output was found to be nearly linear with current. The quantum efficiencies of the first devices (the ratio of photons emitted per electron injected) were around 0.05% and the electroluminescence spectrum was very

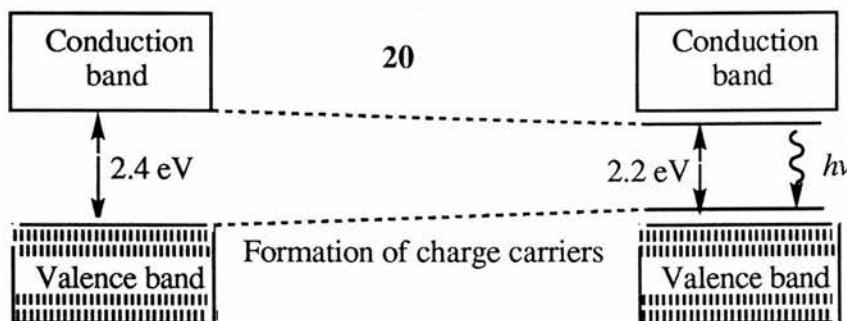
similar to that of the photoluminescence spectrum with the peak maximum at around 2.2 eV (ca. 560 nm) corresponding to the green-yellow part of the spectrum.

The efficiency of PPV in light emission is affected by the structure and purity of the polymer. The formation of defect sites in the polymer along with impurities such as any dopants present, have the effect of lowering the efficiency by acting as non-radiative recombination centres. In order to understand why this is the case, the mechanisms behind the EL in this system must be probed. Rather than acting as a conducting polymer the PPV is used as a thin film of tens to a few hundred nm of pure undoped polymer through which an electric field is applied. As with the case of undoped polyacetylene, this polymer acts as a large bandgap semiconductor. The electric field drives a current through the polymer by injecting holes at the anode and electrons at the cathode **16**. The holes and electrons then migrate through the polymer until electron-hole capture occurs **17** and an annihilation takes place. The annihilation may result in the formation of either a singlet or a triplet exciton. The singlet excitons **18** are the higher energy species and, where confined from defect sites, will decay radiatively **19** to give photons of a characteristic energy dictated by the band gap of the polymer. The triplet excitons also decay non-radiatively and in this case produce lower energy phonons (lattice vibrations).



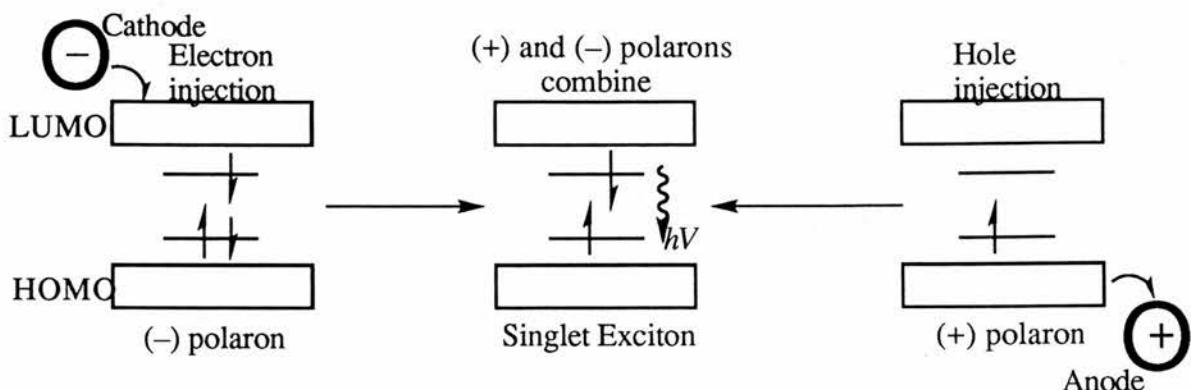
The energy of the photons released from the singlet exciton's decay (ie emission) is the same as the energy of photons obtained from photoluminescence (about 2.2 eV) and so

the two spectra are very similar. The bandgap of PPV is about 2.4 eV which is somewhat larger than the energy of the photons and this discrepancy may be accounted for by the distortion of the polymer's band gap under the influence of charge carriers **20**. As with the conducting polymers discussed earlier the formation of charge carriers such as polarons and bipolarons insert either occupied or non occupied levels within the band gap. Since the polymer is not under the influence of dopants these levels are not subject to such broadening and so have the effect of only narrowly lowering the band gap.



The nature of the charge carriers has been the subject of some debate which has been nicely outlined by Jenekhe.¹⁴ However, it can be argued that the major cause of singlet exciton formation seems to be in the annihilation of positively and negatively charged polarons.^{15,16} These have in turn been generated by the injection of holes and electrons and not by charge transfer oxidation or reduction. Taking this into account the mechanism of electroluminescence may be elegantly described by the scheme below **21**.¹⁷

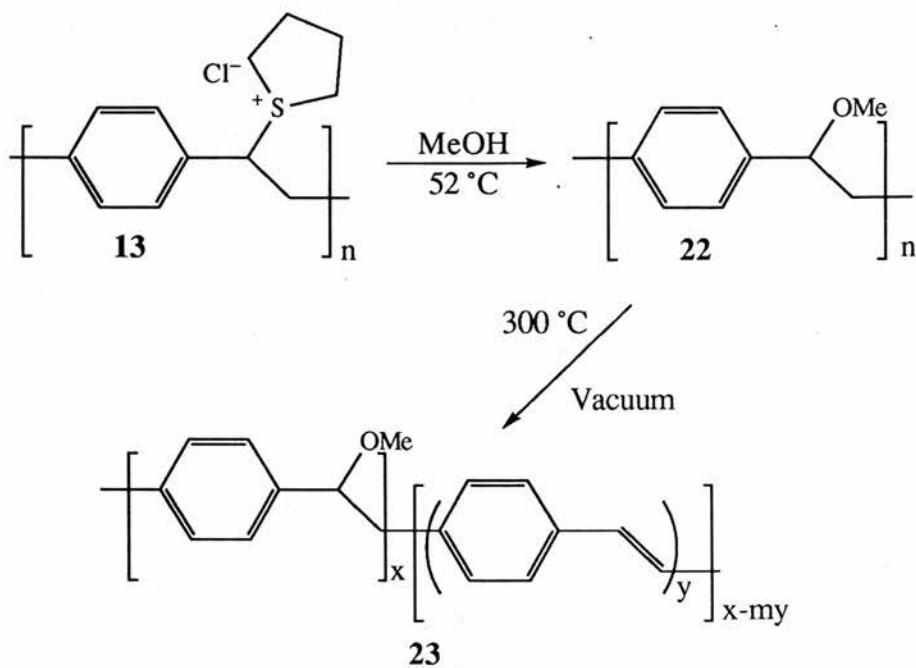
Scheme for radiative decay



21

Here, electrons are injected via a cathode to the LUMO of the polymer to form negative polarons, whilst holes are formed at the anode to give positive polarons. These migrate under the influence of an applied electric field and combine on a segment of the polymer chain to form the singlet exciton.

Now that the mechanism for photon emission and the energy of this emission have been demonstrated to be dependent on the band gap of the polymer, this factor may be exploited to produce light of different colours. One relatively simple method of altering the band gap of PPV lies in restricting the degree of conjugation in the molecule. This may be achieved by alternating the vinyl groups on the polymer to having a fraction retained as conjugated vinyl groups and some as unconjugated single bonded species. This is conveniently achieved by simple alteration of the precursor polymer **13**. Direct reaction of this precursor with methanol at 52 °C leads¹⁸ to the methoxy substituted precursor **22**. Heating the methoxy substituted precursor to 300 °C under vacuo leads to a “tent frame precursor”,¹⁹ so named due to the likeness to such assemblies which contain rigid rod segments linked by spacer springs. The degree of conjugation (the rods) versus unsaturated sites (flexible springs) has a direct effect on both the energy of the band gap and the solubility of the resultant polymer **23**. In fact it increases both of these properties and at the lesser extent of saturation the segmented conjugated polymer has been found to produce blue shifted electroluminescence^{18,20} with an emission maximum at 508 nm.



The same concepts mentioned above may also be exploited to effectively isolate excitons from defect sites. This “isolation” is believed to be partly responsible for the blue-shifted PPV’s two-fold improvement in light emitting efficiency over that of the fully conjugated material.¹⁸ The saturated sites in the PPV chain act as effective blocks to the motion of the charge carriers set up by the incoming holes and electrons. These “blocks” tend to trap the charge carriers and avoid them travelling along the chain to defect sites, so the degree of quenching of the charge carriers is decreased with a corresponding increase in efficiency. In a more recent attempt at the controlled engineering of such blocks, Hadzioannou et al²¹ synthesized a series of alternating copolymers of alkylsilanylene units as one block and oligothiophenes as the other block. As with PPV the polythiophene chains are wide band gap semiconductors and as such are capable of displaying EL on application of an electric field through the polymer. Here the effect of polymer chain length and number of unsaturated σ bond interruptions on the photoelectron spectroscopy and EL generated from the polymers was studied. The results **24** showed that a startling variety of colour is available. On descending the table, as the number of thiophene rings in the conjugated segment increases the λ_{max} for both PL and EL increases. The first of the

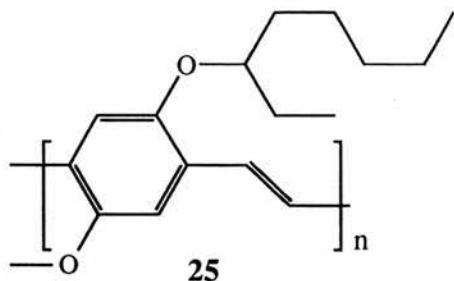
devices produced is reported to be so stable as to have operated for 7 months without any apparent degradation.

	λ_{\max} Photo-Luminescence (nm)	λ_{\max} Electro-Luminescence (nm)
	428	np
	429 470 520	415 474 508
	524	np
	470 525	np
	605	607
	620	612

24

(np= not published)

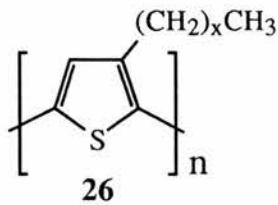
Heeger *et al*^{22,23} have approached the band gap alteration and processability problems of PPV by an alternative route involving substitution on the phenyl ring. By this method a polymer of 2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylenevinylene **25** was found to give a red shifted EL with an emission maximum of 591 nm.



A further advantage of this approach lies in the solubility of the 2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylenevinylene polymer. The polymer is readily soluble in the fully conjugated form in THF or xylenes and can thus be spin-coated, dried and used with no further processing of the polymer itself. This is a second example where the use of a flexible side chain aids the solubility of the conjugated polymer. In general, conjugated polymers in which less than half of the carbon atoms per unit are saturated are difficult to process due to low solubility.

The use of long alkyl side chains involves further considerations over those of solubility and the alteration of the band gap. The main concern is one of how the overall 3-dimensional structure of the polymer is altered by the inclusion of such chains. The alkyl side chains have the effect of "insulating" the conjugated polymer backbone chains against one another. This factor of spacing between chains is important when the overall mechanism of EL is looked into from the point of where the electron / hole collisions take place. Since increasing alkyl chain length spaces out the semiconducting conjugated chains then the alkyl chain length will have a direct effect on the probability of interchain charge transfer.

In a study of alkyl chain length versus emission intensity in devices constructed from poly(3-alkylthiophenes)²⁴ **26** with chain lengths of 12, 18 and 22 units a remarkable trend was found showing marked increase in emission intensity with increasing alkyl chain length.



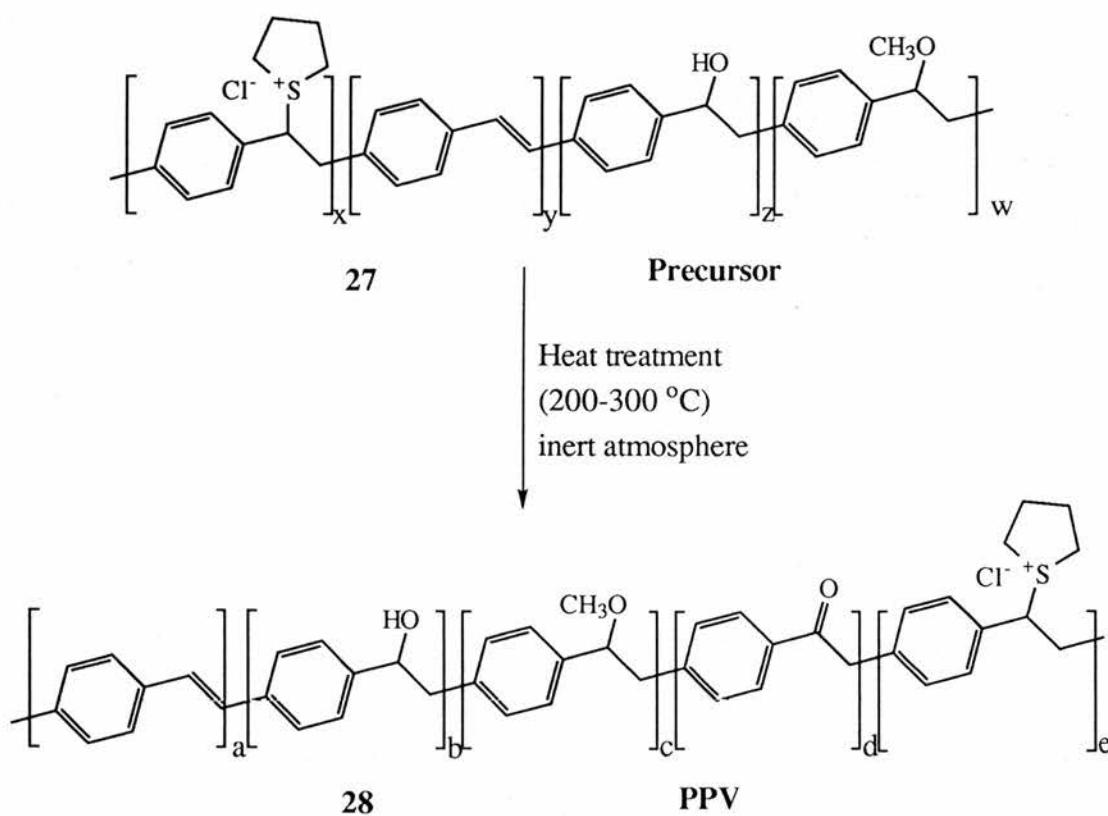
The change in the chain length had no marked effect on the wavelength of maximum emission at 610 nm (in the orange-red region). These two factors strongly suggest that EL from semiconducting polymers takes place solely via intrachain charge carrier annihilations. It also indicates that corresponding interchain processes may not result in EL but perhaps in non-radiative relaxations. This presents a challenge to a recently proposed interchain model which describes the photoexcitations of PPV as partly due to negatively and positively charged polarons on adjacent chains.^{25,26}

1.3 Polymer LED Devices: synthetic and electronic considerations

If a polymer is to be used in a LED device a foremost consideration is to provide a film of uniform thickness free from defects. Since EL polymers are largely, if not fully, conjugated the rigid structure of the backbone presents processing problems due to insolubility. As mentioned earlier this may be overcome by the use of solubilising groups or non-conjugated precursor polymers.

The first PPV's used in LED's were synthesised using Wessling's route²⁷ which provides a non-conjugated and hence flexible precursor polymer with the added advantage of maintaining a solublising sulphonium group on each repeat unit. A solution of the precursor in a volatile solvent is then spin coated onto an electrode and thermally converted via removal of the sulphonium groups to give a high quality film of the fully conjugated PPV.

Due to the surge of interest in the field of polymer LED's the Wessling route has been investigated and adapted by many different groups. To give but some examples, studies by Hsieh *et al*,²⁸ Murase *et al*²⁹ and Galvin *et al*³⁰ have accumulated evidence that the PPV precursor polymer prepared by the conventional Wessling synthesis can give rise to a polymer in various states of conversion **27**. Moreover, the synthesis can also lead to the incorporation of some chemical defects such as hydroxyl groups. Most significantly, on conversion to the fully conjugated PPV traces of carbonyl moieties **28** were found to be present. Although found as a very minor component the carbonyl moieties may play an important role in limiting the efficiencies of PPV LEDs since intersystem crossing of the singlet to the nonluminescent triplet state is a common phenomenon in carbonyl compounds.³¹



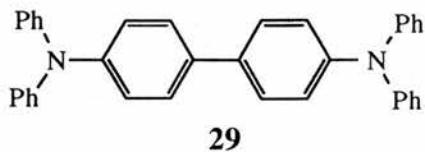
On moving to more convenient conversion conditions, ie. under an inert gas rather than a vacuum, Schwoerer *et al*³² discovered that carbonyl moieties were not formed. Additionally the conversion temperature could be lowered to 160 °C. This milder

conversion technique allowed the PPV precursor to be converted on flexible substrates such as poly(ethylene terephthalate) that would not have survived the original Wessling conditions, and so enables the manufacture of flexible PPV LED's similar to those of Heeger et al.³³

Perhaps the major electronic concern involved in polymer LED device construction is that of balancing the rates of electron and hole injection into the polymer. PPV and many other candidates such as polythiophene may be regarded chemically as π -excessive polymers. This in turn implies that they will lose electrons more readily than accept electrons. PPV may therefore be regarded as a p-type semiconductor. The consequence of this factor leads to problems in injecting electrons into the polymer at the cathode of a polymer LED device. Since the polymer is a p-type semiconductor there is little barrier to the flow of holes through the HOMO of the polymer, but conversely it is difficult to inject electrons into the LUMO.

For maximum device efficiency the holes and electrons must meet within the polymer matrix to form the maximum number of radiative excitons. This problem may be addressed by the use of low work function metals as the cathode. Low work function metals such as calcium are able to supply electrons to the LUMO of PPV. However, calcium is very reactive towards air and moisture leading to problems in manufacture and device reliability. Aluminium would be a much better and more stable cathode material, but, its higher work function leads to lower luminescence efficiencies in comparable devices.²²

Yoshino *et al*³³ reported that the use of a carrier-confinement layer sandwiched between the ITO anode and the polymer results in a dramatic (around 3-fold) increase in the emission intensity from the polymers. The carrier confinement was supplied by a layer of tetraphenylbenzidine (TPB) **29** about 50 nm thick that had been applied to the ITO anode

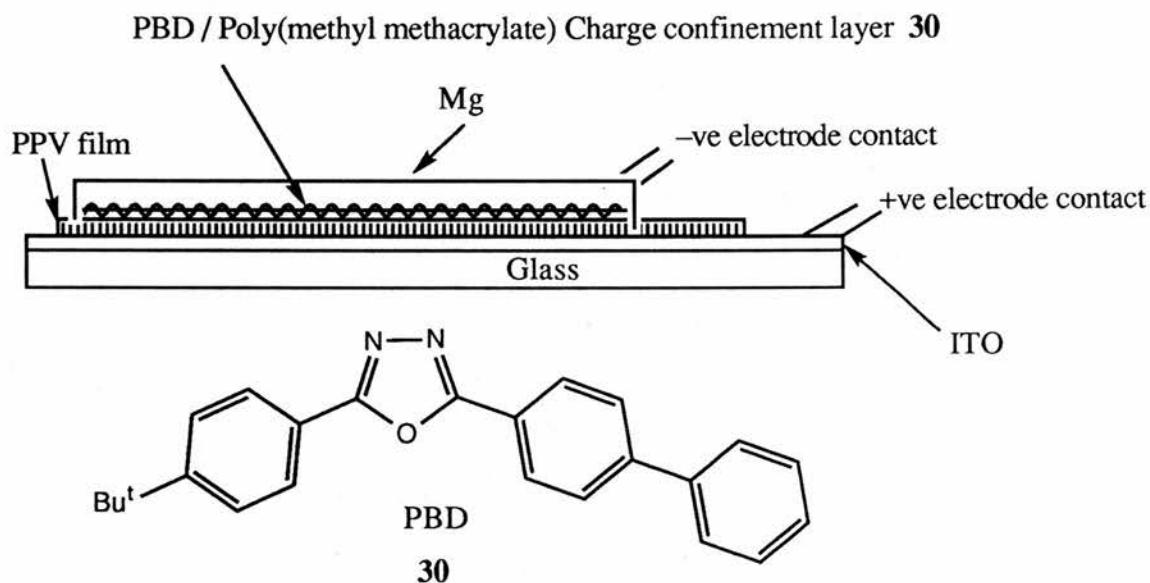


by vacuum sublimation prior to spin-coating the electrode with the polymer. The TPB layer apparently works by increasing the number of electrons at the interface of this layer and the polymer layer and also more directly by isolating the polymer from non-emissive charge transfers available on the polymer / ITO interface. This form of carrier-confinement effectively regulates the transport of the mobile holes which may otherwise be lost without radiative decay on the polymer / metal interface.

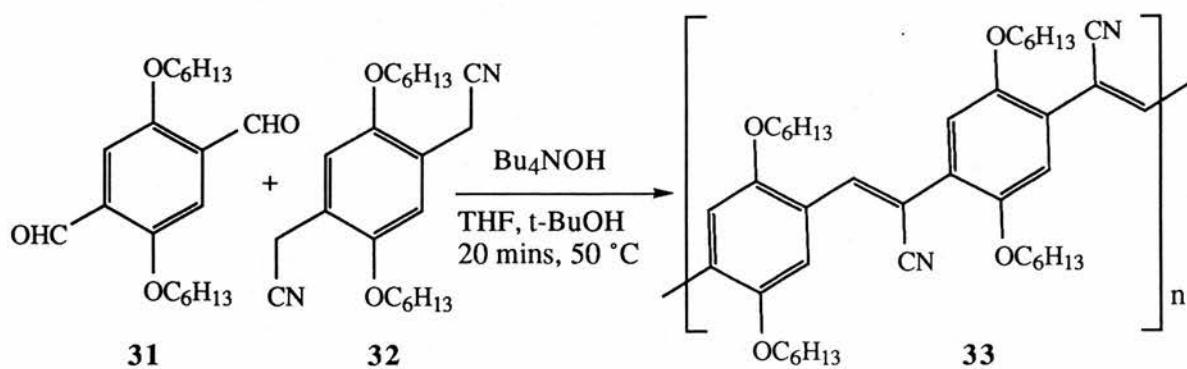
A more common practice has been in the use of charge confinement layers separating the polymer and metal cathode. In an exhaustive study of the interface between aluminium and conjugated polymers by Bredas *et al*³⁴ it was concluded that covalent Al-C bonds are formed along the polymer backbone. This was found to deeply modify the chain geometry resulting in a dramatic reduction of the polymers π electron conjugation. Separating the polymer from this interface should therefore avoid such structural defects and increase luminescence efficiency. This technique has been well established in earlier molecular organic LEDs^{35,36} and consists of applying a layer of organic molecules with a higher electron affinity than that of the emissive polymer layer

The main hurdle facing those working with polymer LEDs rather than with their molecular counterparts is the need to apply a charge confinement layer by vacuum sublimation. This increases the cost, limits the size, and limits the range of emissive polymers that can be used to those that will survive the process. A clever way around this problem has been described by Friend *et al*²⁰ and later developed by Strukelj *et al*³⁷. Here an electron transporting layer consisting of a solid suspension of (2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole) in poly(methyl methacrylate) abbreviated to PBD is prepared and may be spin coated into the emissive polymer prior to depositing the metal

cathode. The devices made incorporating the PBD layer **30** show efficiencies an order of magnitude better than those with monolayer PPV (typically 1% photons / electron compared to a typical monolayer device output of 0.01 - 0.1%).

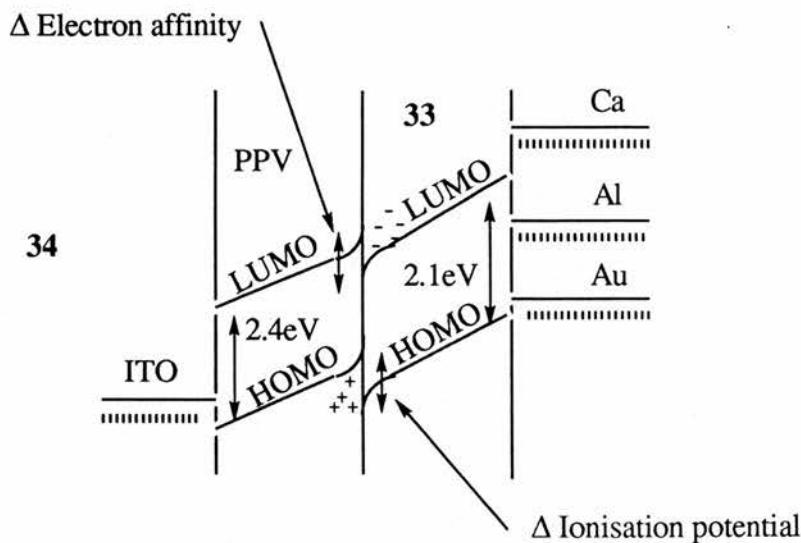


As already discussed, PPV can be described as a p-type semiconductor. An opportunity exists for chemical modification of the polymer to increase its electron affinity and therefore the ease with which electrons can be injected into a polymer LED device. In some such modifications, electron withdrawing cyano groups are introduced to the polymer.^{38, 39} The problem of such modification is that the polarity of the polymer is increased and this gives rise to the expected solubility and processing problems. More recently a processable cyano substituted PPV was described by Holmes *et al*⁴⁰ and here the Wessling route has been replaced by a Knoevenagel condensation reaction. 2,5-Bis(hexyloxy)terephthalaldehyde **31** and 2,5-bis(hexyloxy)benzene-1,4-diacetonitrile **32** undergo condensation to form the soluble and processable cyano substituted polymer **33**.



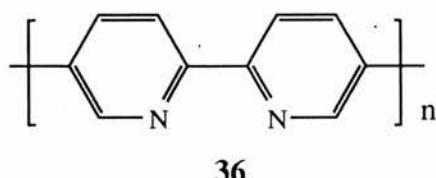
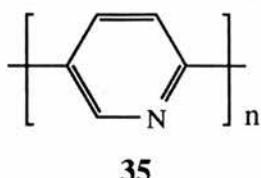
On incorporating a monolayer of **33** into a Polymer LED device red shifted (from PPV) luminescence was achieved and remarkably little difference in efficiency was found on changing the cathode from Ca to Al. The device efficiency was thus more affected by processes occurring at the ITO anode.

Taking polymer **33** one stage further on by incorporation into a bilayer device with PPV proved very successful. Using a device constructed of an ITO anode coated with PPV followed by **33** and an aluminium cathode quantum efficiencies of 4% were achieved with emission in the red region as seen in the **33** monolayer device. The reason for this behaviour is shown schematically in **34**. Since PPV readily accepts holes and **33** is a better electron acceptor than PPV, the charges are confined at their interface. Exciton formation therefore takes place very close to the hetero junction and so emission is seen only from the lower bandgap polymer which is, in this case, **33**.



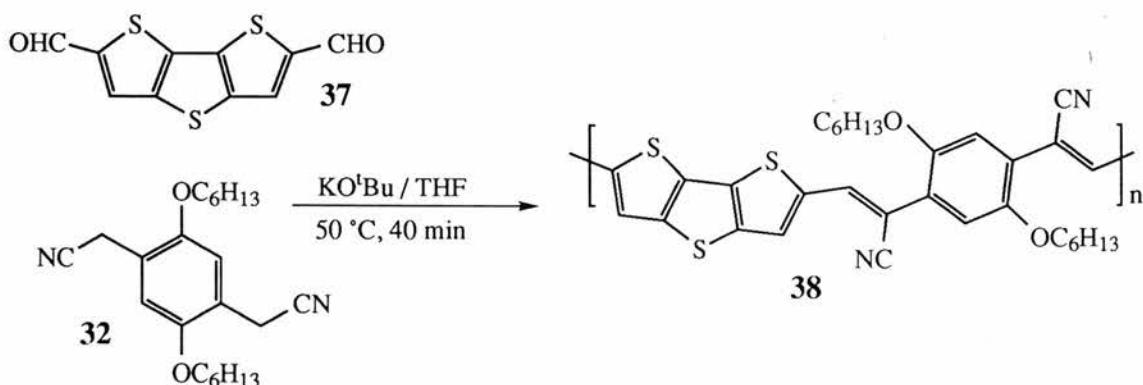
Currently there is a great deal of interest in the synthesis and processing of conjugated polymers with high electron affinities for use both in monolayer or multilayer devices. Perhaps the simplest of these are the polypyridinevinylenes investigated by Onada⁴¹ and Swager et al.⁴² In both cases these materials were synthesised by cross coupling of the desired 2,5-dibromopyridine and 1,2-bis(tributylstannyl)ethylene in the presence of a palladium phosphine complex by the method of Galarini et al.⁴³ This gave rise to polymers that were difficult to solublise in anything other than strong acids but modification to incorporate a solublising alkyl group on the 3-position of the pyridine afforded limited solubility and hence processability in organic solvents.

The advantage afforded in polypyridinevinylenes is that the band gap is larger than that associated with cyano PPVs **33** and blue shifted luminescence is possible. Typically emission is observed in the yellow-orange region. Perhaps the most π electron deficient, and thus most n-type dopable, conjugated polymers synthesised so far have been made by Yamamoto et al.⁴⁴ Poly(pyridine-2,5-diyl) **35** and Poly(2,2'-bipyridine-2,5-diyl) **36** were made by dehalogenation polycondensation of the corresponding dihalo compounds with a Ni⁰ complex.



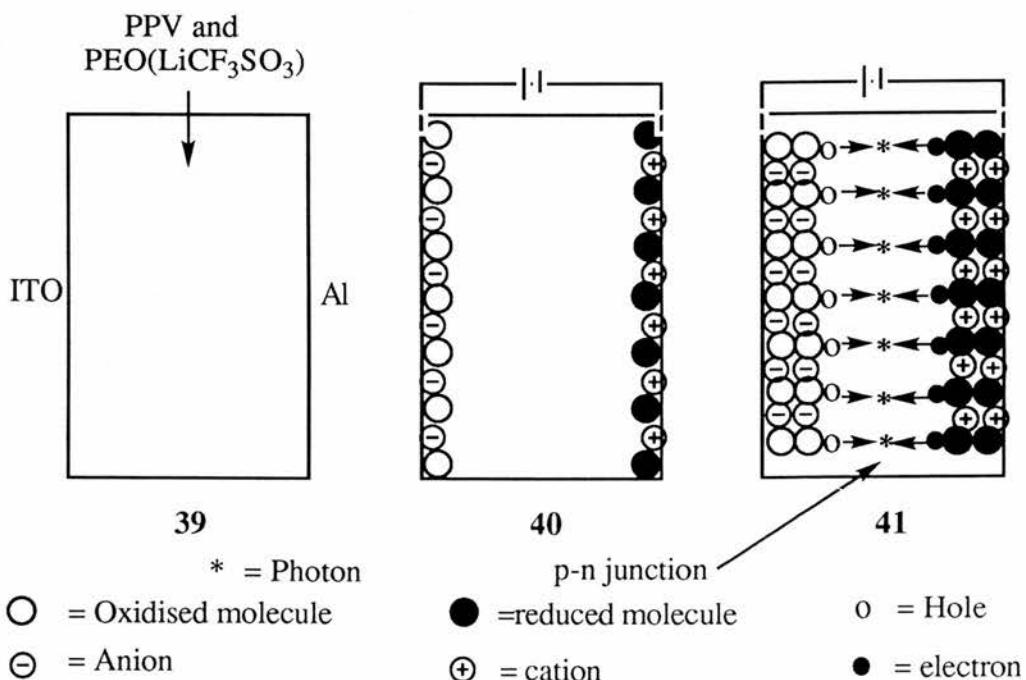
The most striking feature of these polymers **35** and **36** is the inability to accept p-type doping either chemically or electrochemically. This gives rise to questions as to whether a polymer bilayer device may be constructed to operate exactly as an inorganic device with emission from the p-n junction. Doubtless many groups are currently investigating this field.

A further field of interest lies in the synthesis of polymers that are both easily p- and n- dopable. By the Knoevenagel condensation of fused dithienylthiophenes **37**, whose rigid planar structures favour high exciton mobilities, with the solubilising monomer **32** Holmes et al⁴⁵ have produced novel conjugated thiophene copolymers **38**. The redox properties of **37** have shown both p- and n-dopable properties and such materials have exciting potential as new electroluminescent and electronic materials.



In a recent development Pei *et al*⁴⁶ have demonstrated polymer Light Emitting Electrochemical cells. Rather than using a polymer layer structure such as found in the devices previously described, the emissive polymer (PPV) is mixed with a polymer electrolyte poly(ethylene oxide) complexed with lithium trifluoromethanesulphonate) and sandwiched between ITO and Al electrodes **39**.

Although the operation of the device is not yet fully understood, it is suggested that under a sufficiently high voltage applied via the ITO anode and Al cathode, the PPV near the anode is initially oxidised and the PPV near the cathode is similarly reduced. Counterions from the electrolytes move to compensate the charges on the oxidised and reduced polymer chains thus providing symmetrical p- and n- doped PPV layers **40**. These layers are good conductors and so the PPV / Electrode interfaces become low resistance contacts. On increasing the applied voltage oxidation and reduction will continue to occur until the cell reaches electrochemical equilibrium. At this point the ionic contribution to the current passed goes to zero as a p-n junction is formed. The electronic contribution to the current does not go to zero and now the holes in the π -band of the PPV (p-type carriers) propagate from the cathode to the anode and the electrons in the π^* -band (n-type carriers) propagate from the cathode towards the anode. The holes and electrons meet within the electrochemically induced p-n junction **41** and here they recombine to form neutral charge carrier pairs (excitons) which decay radiatively to the ground state.



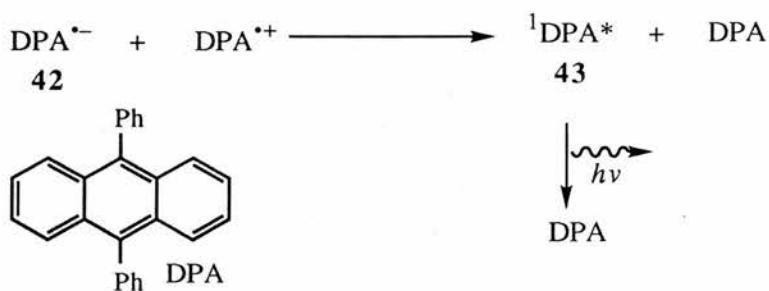
Since the device is effectively an electrochemical cell in which a p-n junction is set up under an applied voltage, it is reasonable to further investigate the reversibility of the

processes occurring within. It was found that by turning off the applied voltage or by shorting out the two electrodes the, p-n junction discharged displaying reversibility. Indeed in short circuit conditions this discharge was observed as a gradual process occurring with an exponential decay over several minutes thus showing the cells possibilities for energy storage.

Such reversibility is also displayed by further operation of the device under a reverse bias. Using the ITO as the cathode and Al as the electrode the device worked as before. This highlights the major difference and advantage of the polymer light emitting electrochemical cell compared to the polymer LED. No doping occurs in the polymer LED and the transport of holes and electrons is governed by processes at the electrode / polymer interface. With the reversible doping processes occurring within the cell the electrode processes become less important and consequently stable electrode materials such as gold may be used which will ease device manufacture and lifetimes. Further work in this field may improve device efficiencies to those comparable to polymer LEDs.

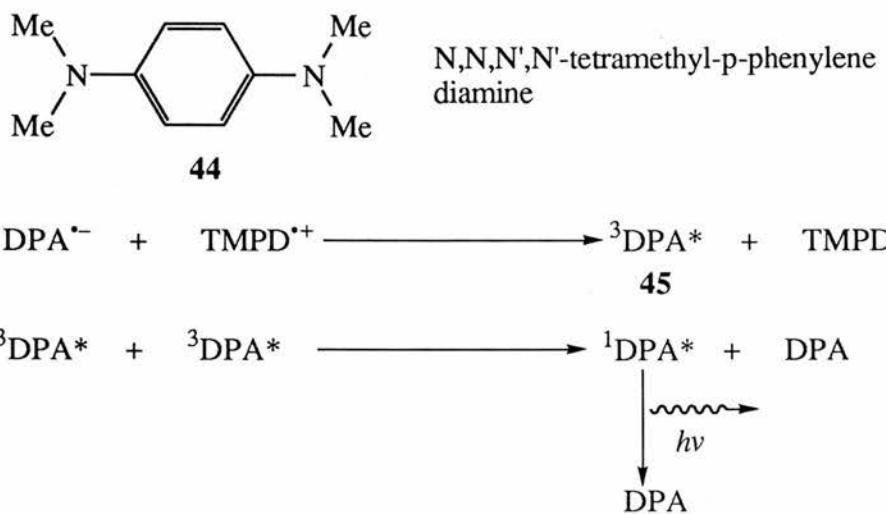
1.4 Electrochemiluminescence

Chemiluminescence results from a chemical reaction leading to a product molecule in its excited state, followed by radiative decay to its ground state. The electrochemical route to the excited state required to produce such emission is via an energetic electron transfer in solution between a radical anion and radical cation produced at the electrode. This is called electrochemiluminescence or ECL. A very good example of this phenomenon is observed in the ion annihilation reaction of the radical cation and anion of 9,10-diphenylanthracene (DPA) **42** in acetonitrile. The products of the annihilation are a ground state molecule and a molecule of DPA in its first singlet excited state **43**. The molecule in the singlet excited state radiatively decays to the ground state with an easily identifiable blue emission.



The EL generated from conjugated polymers seems to rely solely on the decay of singlet excited states (singlet excitons) and this creates a limit to the efficiency of the light emission since for every singlet excited state generated, a triplet excited state will also be formed, which as seen already, decays non-radiatively. This will limit the maximum efficiency of the polymers to 25% photons emitted per electron - hole capture. For the electrochemiluminescence observed from DPA the picture is a little more complicated. The radical cation / radical anion collision and exchange provides enough energy to produce a singlet state on every event. The collision is estimated to provide 3.2 eV which is greater than the 3.0 eV required to give the singlet. However, a different story emerges with lower energy collisions such as those reviewed by Tachikawa and Faulkner.⁴⁷ A quite striking discovery was found when the radical anion of DPA was reacted with the radical cation of

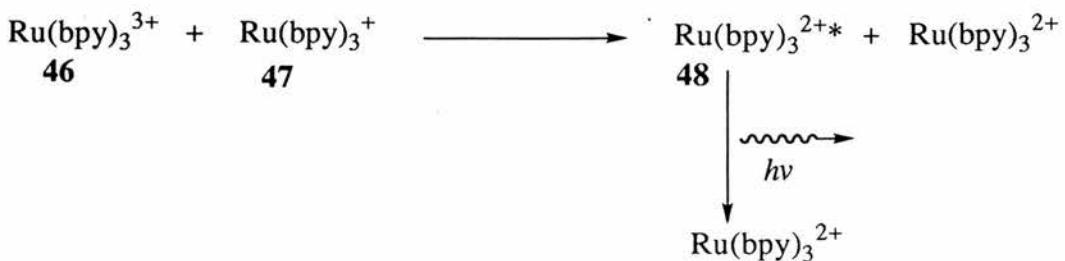
another molecule, in this case TMPD **44**. The energy of the electron transfer here is only 2.0 eV which is clearly insufficient to provide singlet excited DPA but the characteristic blue luminescence was still observed. This is accounted for by the formation of DPA triplet states **45** that collide to form a ground state DPA and a singlet DPA which may then decay radiatively as before. This is known as triplet-triplet annihilation.



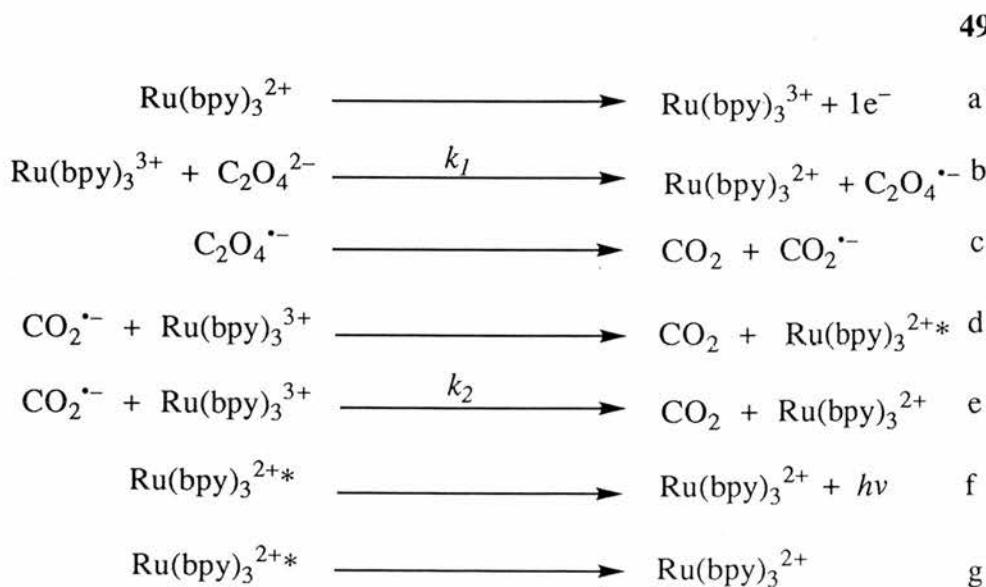
The ion annihilation reactions discussed are not limited to aromatic radical ions and more recently interest has developed in ECL from inorganic systems such as tris(2,2'-bipyridyl) ruthenium(II) (abbreviated to $[Ru(bpy)_3]^{2+}$). Among the first of these reports, Hercules and Lytle⁴⁸ generated ECL from the reduction of $[Ru(bpy)_3]^{3+}$ to $[Ru(bpy)_3]^{2+}$ by hydroxide ion. The reaction produced an orange luminescence (emission maximum at 594 nm) which was clearly visible in a dimly lit room.

Martin et al⁴⁹ studied the action of the hydrated electron with $[Ru(bpy)_3]^{3+}$. This group suggested on the evidence of the photoluminescence and ECL spectra that the light emitting species in the reaction was the $[Ru(bpy)_3]^{2+*}$ triplet. This idea was supported by Bard et al^{50,51} from electrochemical and luminescence studies. Cyclic voltammetry showed that the unstable $[Ru(bpy)_3]^{3+}$ **46** and $[Ru(bpy)_3]^{1+}$ **47** species were generated as a result of the redox reactions. The charge transfer reaction between these two species is

sufficiently energetic (ΔG° -2.7 eV for the reaction) to produce the $[\text{Ru}(\text{bpy})_3]^{2+*}$ triplet **48** which is about 2.04 eV above the ground state.



One of the first ideas for exploitation of the ECL from $[\text{Ru}(\text{bpy})_3]^{2+}$ involved the inclusion of the complex in a polymer-coated modified electrode.⁵¹ The electrode was constructed from platinum coated with a layer of Nafion ion-exchange polymer into which a large amount of $[\text{Ru}(\text{bpy})_3]^{2+}$ was incorporated by electrostatic binding. Electrogenerated chemiluminescence was observed from this electrode once the potential was stepped to the oxidation potential of $[\text{Ru}(\text{bpy})_3]^{2+}$ in an aqueous solution at a pH of 4-8 and in the presence of oxalate ions. The resulting intense orange luminescence is due to a complex sequence of reactions which are outlined below **49**.



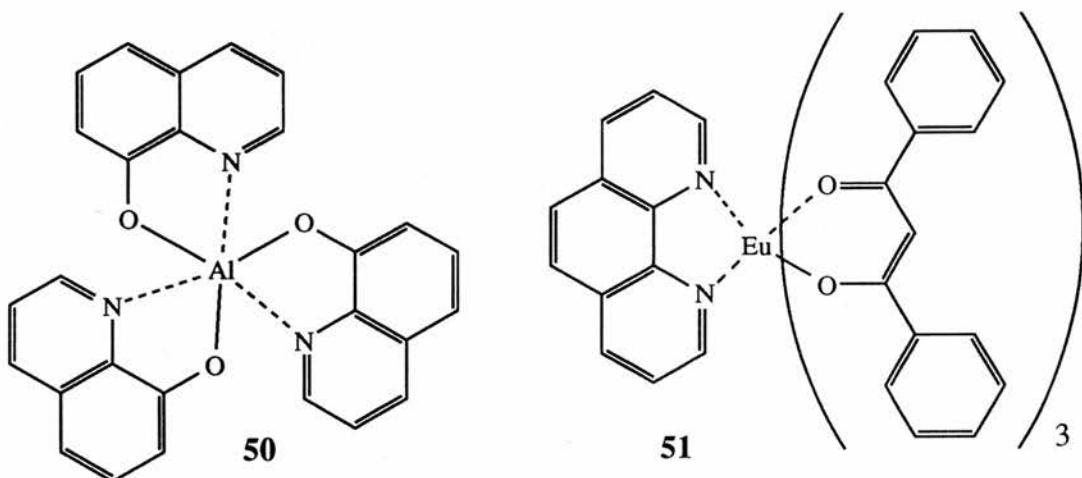
As can clearly be seen, only one stage in this complex sequence of reactions **49** results in ECL emission **49f**. This happens as detailed before on the radiative decay of the

triplet species. However, in order to maintain this reaction the oxalate ions are used up and converted into CO₂ which is lost as gas. Thus in order to maintain the ECL the system must be constantly fuelled with oxalate and this would severely limit the electrode's potential as a commercial light emitting device.

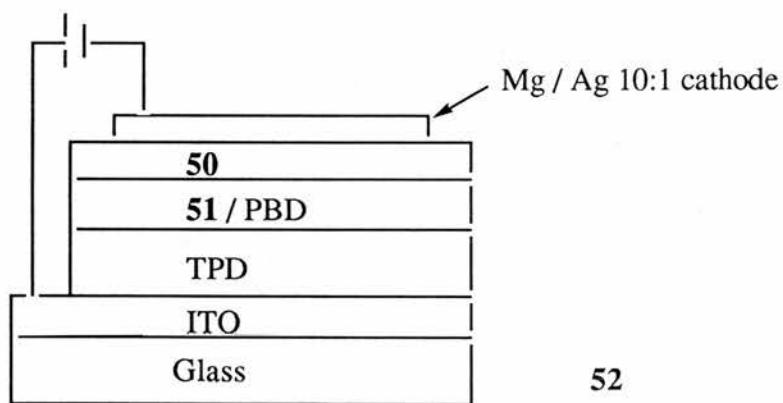
A further scheme for possible sustained ECL from [Ru(bpy)₃]²⁺ was developed by Bartlett, Drew and Wightman⁵² involving band array electrodes. In this device the anode and cathode are fine wires of width 4 μm and held a similar distance apart. The length of the array is about 5 mm. From this array a solution of [Ru(bpy)₃]²⁺ is both oxidised and reduced within a very small volume. The resultant charge transfer reactions are concentrated within this volume to produce bright and sustainable ECL. In practice the light intensity remained stable for several minutes but after this time had elapsed the process of convection that is set off by the small amount of heat generated upsets the flow of ions. The device is therefore unlikely to find any commercial applications as some efficient means of stabilising the temperature at the electrode would be required to allow long term operation.

Interest has developed in the use of metal complexes as the emissive layers in LED devices. Much of this has been inspired by Tang and VanSlyke⁵³ who pioneered the use of multi layer devices. Previously metal complexes had been regarded as relatively poor candidates for emissive layers due to processability problems associated with the deposition of thin films, the poor charge carrier transport properties of the complexes and the tendency for the complexes to crystallise with use leading to device failure. The use of an organic hole transporting layer between the anode and the emissive tris(8-quinolinolato)Al³⁺ **50** complex resulted in a device with a significant increase in luminescence efficiency compared to monolayer devices. The increased efficiency is due to the improved balance of electron and hole injection. The aluminium complex **50** is known to have electron transport properties⁵⁴ and the incorporation of an organic hole injection / electron blocking

layer increases the number of recombinations within the emissive layer giving rise to increased luminescence.



Developing the multilayer idea, Kido et al ⁵⁵ manufactured a multi layer device using the Europium complex tris(1,3-diphenyl-1,3-propanediono)(monophenanthroline) Eu³⁺ [Eu(DBM)₃Phen] **51** mixed in a 1:3 ratio with electron transporting PBD **30** as the emissive layer. Electron injection is provided by a layer of **50** applied before the cathode. Hole injection / electron blocking is provided by a layer of TPD **29**.

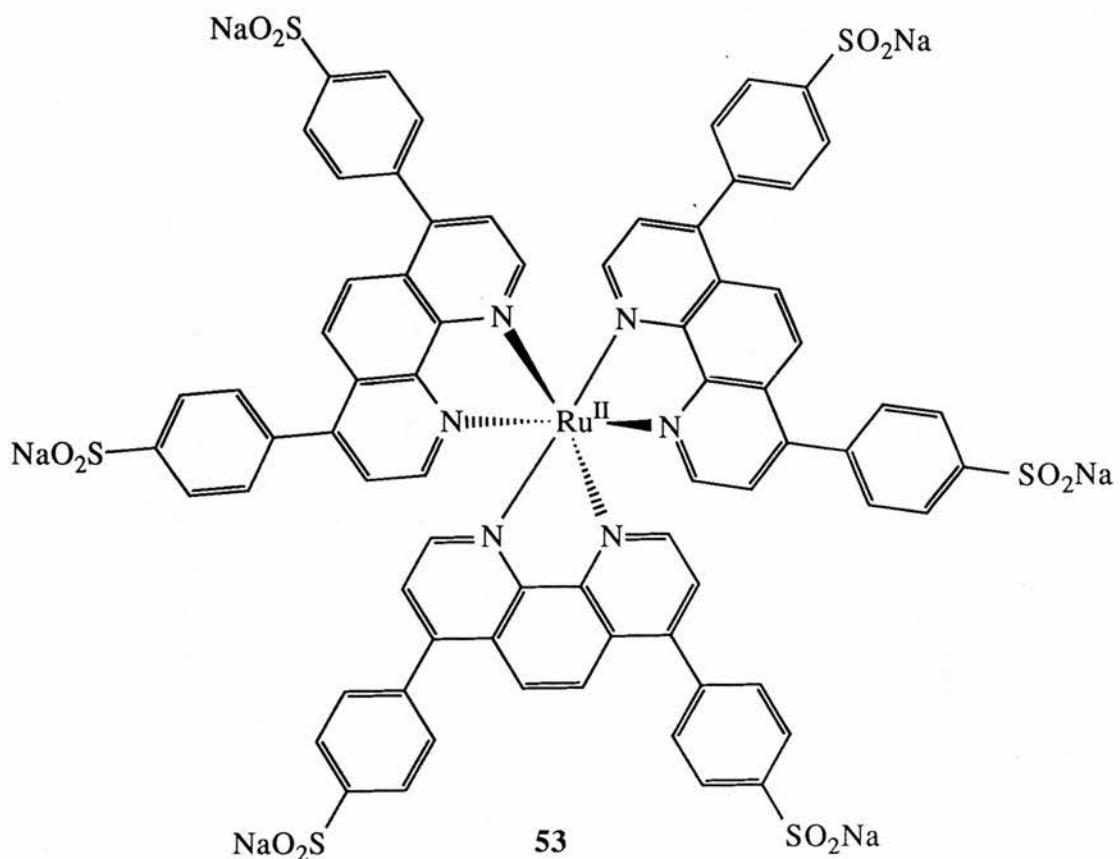


On applying a voltage across the device **52** red electroluminescence was observed from the cell. This is an extremely sharp emission band at 614 nm characteristic of the ⁵D₀ to ⁷F₂ transition of Eu³⁺. This excitation is expected to be due to energy transfer from the host PBD to the guest Eu complex. Generally, in lanthanide metal complexes, a central

metal ion is excited through the excitation of the ligand. In this case the excited energy at the π conjugation of the ligand is transferred to the central ion through the ligands triplet energy level. Therefore under EL operation it is expected that PBD is first excited by the recombination of the carriers then the excited energy is transferred to the ligand and finally to the central Eu ion. This is supported by the fact that on PL measurements, excitation of PBD in a mixture of **50** / PBD results in luminescence from **50**.

With such a complex multi-layer device **52**, variations in behaviour are to be expected dependent on the individual thicknesses of the layers. By using a 40 nm layer of **51** / PBD and a 30 nm layer of **50**, the device gave EL only from the Eu complex layer **51**. By thickening the Al complex layer **50** to 40 nm and reducing the thickness of the Eu complex layer **51** to 10 nm a broad EL peak at 520 nm was also observed attributed to the electron transport layer **50**. Such complex devices can thus be engineered to provide a range of EL emission as well as provide highly monochromatic light.

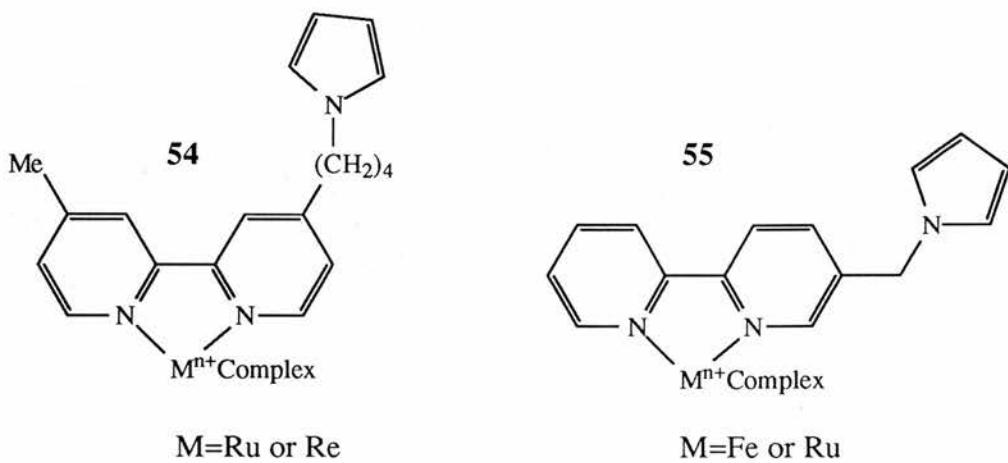
In a more recent advancement Lee et al⁵⁶ succeeded in manufacturing an LED using an electroluminescent Ru complex via simple solution processing techniques. The key to this breakthrough lies in the synthesis of a solution processable polypyridyl complex **53** that does not easily crystallise.



Simple spin coating of a solution of **53** onto ITO followed by evaporation of an Al cathode on top of the complex layer led to a device that gave EL at 628 nm under an applied voltage of 3.5 V. Perhaps the most interesting characteristic of this device is that it shows a distinct "charging effect", i.e. it takes between 30 s to 2 min to produce its maximum luminescence at a set potential. This, in conjunction with the fact that the turn-on voltages are apparently unrelated to film thickness leads to the conclusion that the charge injection is electrochemical in origin although further studies are necessary to investigate charge injection and transport in these devices.

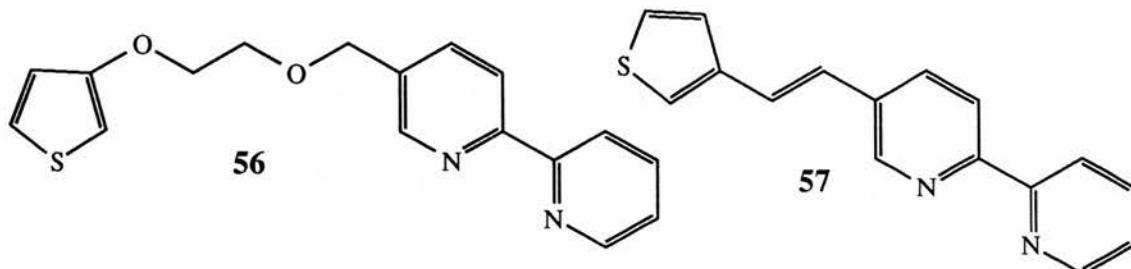
1.5. Conducting Polymers Containing Redox-active Metal Complexes

There has been growing interest in the area of polymer modified electrodes containing metal centres. Ruthenium centres in polymer modified electrodes have been examined for possible use in the catalysis of organic oxidation. Rhenium centred polymers have received interest in the field of the catalytic reduction of carbon dioxide. These polymers are commonly based on N-substituted polypyrroles and metal chelation is provided by a bipyridyl group. Two examples of the monomer complexes used in the modified electrode studies by Deronzier *et al*^{57,58} **54** and Parker *et al*⁵⁹ **55** are shown below.



The polypyrrole based polymers of the complexes **54** and **55** were easily obtained by electrochemical polymerisation onto platinum. Once made, a modified electrode coated with a layer of **46** ($M=Re(CO)_3Cl$) was found to be capable of reducing in high efficiency a saturated solution of CO_2 to carbon monoxide and carbonate ion via a two electron process while the modified electrode was maintained at -1.85 V. Similarly a modified electrode prepared with $[Fe(55)_3]^{2+}$ was found to be capable of one electron oxidations of ferrocene and dichloro-5,6-dicyano-p-benzoquinone.

The field of metallocopolymer modified electrodes is rapidly expanding with some interesting results. A very intriguing example has been described by Parker et al⁶⁰ using the thienyl substituted ligands **56** and **57** shown below.



Once chelated to form $[\text{Fe}(\mathbf{56})_3]^{2+}$ and $[\text{Fe}(\mathbf{57})_3]^{2+}$, these complexes show unusual behaviour on electropolymerisation. Starting with cycling onto a Pt electrode at 0 to +1.7 V polymer growth occurs at the high anodic potentials required to oxidise the thiophene. Once a thin layer of polymer had been established polymer growth was found to continue during cycling to between 0 and 1.25 V, which is below the apparent oxidation potential of the monomer. It is thought the Fe(III) centres in the growing film may mediate hole transfer to the proximate thiophene aiding sustained film growth. Although this is not fully resolved, it is attractive to consider that electronic communication between a chelated metal centre and a conducting polymer backbone is being seen and this may have important implications and possible applications for many molecular electronic fields.

1.6 Programme of Research

Following on the recent and tremendous surge of interest in the field of electroluminescent polymers, a main objective of the project is the synthesis of electroluminescent polymers with metal complex derivative side chains. As discussed earlier, metal complexes alone make poor candidates as emitters in LED devices due to poor charge carrier properties and a tendency towards crystallisation. It is possible that these problems may be circumvented by the synthesis of electroluminescent metallo polymers since it has been shown that there is precedent for the following factors:

1. Electronic communication (electron hopping) may be possible between a conjugated polymer backbone and a metal complex side chain.
2. Metal complexes have been demonstrated to produce EL when incorporated into device structures similar to polymer LEDs.
3. Metal complexes, when admixed with luminescent organic molecules, apparently accept energy from the excited states of the luminescent organic molecules and in turn display characteristic emission.
4. Synthetic strategies may be devised to provide processable precursor metallo-polymers with qualities advantageous to the manufacture of device quality films.

As has been discussed in the Introduction, $[\text{Ru}(\text{bpy})_3]^{2+}$ has been demonstrated to produce ECL electrochemically both in solution and immobilised in a modified electrode. In the solid EL polymers, the EL mechanism involves the transport of holes and electrons in an applied electric field, thus redox reactions of the metal complex bound to the polymer are likely to occur, perhaps resulting in ECL. Such a metallo polymer may give high

luminescence efficiency through excitation of the metal centre via the normally non-emissive triplet excitons generated on passing a current through the device.

Since the metal complex polymers may be capable of producing ECL in addition to the EL known to be generated from conjugated polymer backbones, an investigation can be undertaken to differentiate between the two possible sources of emission. As part of this investigation, and also a test of the facilities for device construction and PL / EL measurement, poly-3-alkyl thiophenes are prepared as models for the metal complexes. Comparison of the characteristics of these models against the literature on these polymers and looking for differences in the PL/EL spectra between the models and metal complex polymers should show up the effect of ECL from the metal centre should it occur.

The eventual aim of the project is to evaluate the potential of such materials as candidates for the light emitting layer in organic LED's. This may be achieved by electrochemical polymerisation and / or spin coating of the metal containing polymers onto transparent indium tin oxide coated glass slides. It must be noted that although electrochemical polymerisation leads to conducting polymers in the "doped" form (undesirable for maximum EL efficiency) the polymer may be de-doped by holding the electrode at a reducing potential. These slides may then be used for photoluminescence studies to gain valuable information on the bandgap of the materials and the PL intensity. Such measurements may give an insight into the possible colour and efficiency of the material's EL spectrum if this is obtainable. The same slides may then be used directly for EL measurements by evaporation of a metal cathode over the polymer surface and applying a variable potential through the polymer to the ITO anode. Since this practice will provide simple polymer LED devices, then any working devices can be maintained to answer other questions such as the stability of the polymer (relating to the working lifetime of the device) and allow further work in the field of improving efficiency and lifetime by chemical and mechanical alterations.

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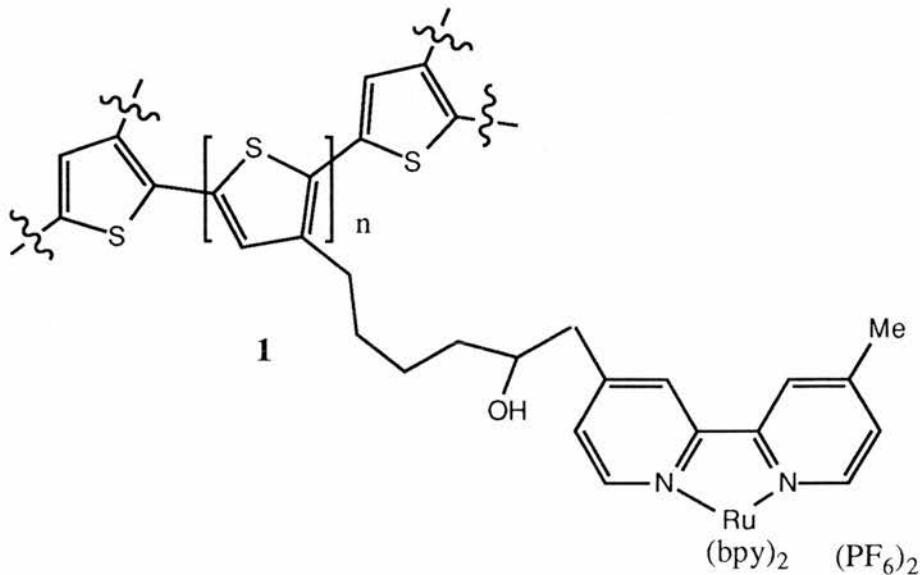
Chapter 2

Synthesis, Chelation and Polymerisation of a Monothienyl Ligand 4-[6-(3-thienyl)hexan-2-oyl]-4'methyl-2,2'- bipyridine

2.1 Introduction

The main objective of the work described in this chapter was to provide a polymer with a fully conjugated polythiophene backbone which is functionalised with luminescent metal complexes. It is hoped that this strategy will provide a material that can be used as an emissive layer when incorporated into a polymer LED device. A synthetic strategy was designed to leave thiophene units free for polymerisation through the 2,5-positions and allow metal chelation to a bipyridine attached via an alkyl chain. Two examples are synthesised based on ruthenium and rhenium, both of which are chosen not only for the luminescent properties of their complexes but also for their diamagnetic nature which aids NMR characterisation.

The first objective of polymer design and synthesis had already been pursued in this department by Dr A. Iraqi¹ and this involved a 3-substituted thiophene with an attached ligand consisting of a spacer group (to avoid steric congestion on polymerisation of the thiophene) and a 2,2'-bipyridine metal co-ordinating group. The ligand was firstly reacted with Ru(bpy)₂Cl₂ to give a metal complex monomer and then electrochemically polymerised onto a platinum electrode to give polymer **1** illustrated in Figure below.



Once polymerised and transferred to a solution of the same electrolyte in the absence of the monomer the electroactivity of the Ru(II/III) couple was apparently maintained showing the capability of redox reactions within the polymer.

In this work the synthesis of the ligand is repeated, improved, and also applied to the co-ordination of metals other than ruthenium with the intention of studying the ability of these materials in EL and ECL devices. As well as changing the metal centres, there is also great scope for experimenting with different ligands. For example, increasing the conjugation in the spacer group may promote conduction from the polymer chain to the metal centre, possibly affecting the redox reactions of the metal. Alternatively, or additionally, increasing chain length of the alkyl spacer groups (or attaching a long alkyl group to some other part of the complex) should result in greater solubility of the polymer which may aid the processability of a chemically polymerised complex. During the study of the electrochemical and luminescence properties of these complexes and their polymers we also made comparative measurements on 3-alkylthiophenes in order to highlight differences in properties due to the inclusion of the metal complexes.

2.2 Instrumentation and General Techniques

NMR Spectroscopy

¹H NMR

Routine spectra were obtained at 60 MHz on a Varian EM-360 spectrometer. Spectra of new compounds were obtained at 80 MHz on a Bruker WP80 or at 200 MHz on a Varian Gemini 200. High resolution spectra were obtained at 300 MHz on a Bruker AM-300 spectrometer operated by Mrs M Smith or at 300 MHz on a Varian Gemini 2000 by the author.

¹³C NMR

Spectra were obtained at 75 MHz on a Bruker AM-300 spectrometer operated by Mrs M Smith. Spectra at 50 MHz on a Varian Gemini 200 and at 75 MHz on a Varian Gemini 2000 were run by the author. All spectra were obtained from solutions in deuteriochloroform except where indicated otherwise and chemical shifts are expressed in parts per million to high frequency of tetramethylsilane or by other standard indicated.

Infrared Spectroscopy

Spectra were obtained on a Perkin-Elmer 1710 Fourier transform spectrophotometer. Solution spectra were run in methylene chloride, deuteriochloroform or other stated solvents using matched sodium chloride cells of path length 0.1mm or a solid suspension in KBr disc. Spectra were calibrated with the polystyrene peak at 1603 cm⁻¹.

Mass Spectrometry

Accurate mass measurements and mass spectra were obtained on a Fisons VG Autospec mass spectrometer operated by Mr C Millar. Fast Atom Bombardment ionisation MS was run using the SERC facility in Swansea and the Fisons VG Autospec mass spectrometer in house.

Gas Chromatography-Mass Spectrometry

Gas chromatography-mass spectrometry studies were carried out on a Hewlett-Packard 5890A gas chromatograph coupled to a Finnigan Incos mass spectrometer. Mass spectra obtained were matched against the mass spectra of authentic samples.

Elemental Analysis

Microanalysis for carbon, hydrogen and nitrogen were carried out on a Carlo-Erba 1106 elemental analyser operated by Mrs S Smith.

Melting points

Melting points, both routine and for new compounds were determined on a Reichert hot-stage microscope. All melting points are uncorrected.

Thin Layer Chromatography

This was carried out using 0.2 mm layers of silica (Merck, Kieselgel 60F₂₅₄) on aluminium sheets. The components were observed under ultraviolet light.

Preparative Thin Layer Chromatography

This was carried out using 1.0 mm layers of silica (Merck, Kieselgel 60-80 mesh), containing 0.5% Woelm fluorescent green indicator, on glass plates. After locating the components with ultraviolet light, the bands were scraped off and the products removed from the support by soaking in methylene chloride for 30 min.

Drying and Evaporation of Organic Solutions

Organic solutions were dried by standing over anhydrous magnesium sulphate and were evaporated under reduced pressure on a rotary evaporator.

Drying and Purification of Solvents

For the synthetic work commercially available solvents were used without further purification unless otherwise indicated.

Dry ethyl acetate was prepared by storing over molecular sieves. Dry toluene was prepared by the addition of sodium wire. Extra dry THF was prepared by preliminary drying with sodium wire and then distilling from potassium benzophenone ketyl. Dry 1,4-dioxane was provided by the same procedure substituting sodium for potassium. Dry dichloromethane was distilled from phosphorus pentoxide and stored over molecular sieves. Triethylamine was dried by heating under reflux with potassium hydroxide for 2 h then distilling onto molecular sieves. A commercial solution of n-butyl lithium in hexanes was used. Where necessary, the strength of this solution was checked by titration with diphenylacetic acid under nitrogen.

Ozonolysis

Ozone was generated using a Fischer model 500 ozone generator. The excess ozone escaping from the reaction vessel was destroyed by bubbling the exhaust through a solution of 5% potassium iodide in 50% acetic acid (100 cm³).

Electrochemistry

Polymer growth and cyclic voltammetry were carried out using a Pine Instruments RDE 4 potentiostat connected to a Graphtec XYY' chart recorder. All potentials are stated vs the standard calomel electrode (SCE) unless otherwise indicated.

2.3 Experimental

2.3.1 Synthesis

Hex-1-ene-5-ol 2

1,2,6-Trihydroxyhexane (415 g, 3.1 mol) was stirred under nitrogen and an equivalent of triethylorthoformate (458 g, 3.1 mol) was added. The mixture was stirred under reflux for 30 min then allowed to cool before distilling off ethanol at 79 °C (245 cm³). Acetic acid (1 cm³) was then added before continuing to distil off the ethanol (530 cm³) followed by fitting a Vigreux column and distilling over the product hex-1-ene-6-ol (275.75 g, 89 %), bp 156 °C; δ_H 5.95-5.80 (1H, m, vinyl), 5.28 (1H, s, OH), 5.17-5.00 (2H, m, vinyl), 3.55 (2H, t, methylene), 2.22-2.10 (2H, m, methylene) and 1.74-1.45 (4H, m, methylenes); δ_C 138.7 (C-2), 114.4 (C-1), 61.8 (C-6), 33.8 (CH₂), 32.2 (CH₂) and 20.6 (CH₂).

1-Bromohex-5-ene 3

Hex-1-ene-6-ol (100 g, 1 mol) and pyridine (10 cm³) were added to ether (600 cm³) and stirred under N₂ over a CO₂ / acetone bath for 30 min. Phosphorus tribromide (135.3 g, 0.5 mol) in ether (100 cm³) was then added dropwise to the cold mixture with the precipitation of a white solid, phosphorus acid : pyridine. The mixture was allowed to stir for 2 h, then the precipitate was filtered off and the liquors washed with water and dilute NaHCO₃ solution, followed by several further water washes until neutral. The organic layer was then dried and evaporated, then distilled to give the product 1-bromohex-6-ene (80 g, 49 %) bp 152-154 °C; δ_H 5.92-5.75 (1H, m, vinyl), 5.15-5.03 (2H, m, vinyl), 3.33 (2H, t, methylene), 2.17-2.03 (2H, m, methylene), 1.87-1.75 (2H, m, methylene) and 1.60-1.45 (2H, m, methylene); δ_C 137.7 (C-5), 114.5 (C-6), 32.9 (CH₂), 33.6 (CH₂) (CH₂), 31.9 (CH₂) and 27.1 (CH₂).

1-(3-Thienyl)hex-5-ene **4**

a. *Hex-6-ene-1-magnesium bromide*

1-Bromohex-6-ene (39 g, 240 mmol) in dry ether (50 cm³) was added dropwise to dry magnesium turnings (6.32 g, 260 mmol) in dry ether (100 cm³) under nitrogen. The reaction was initiated by the addition of a few grains of iodine, then continued for 10 min after the last of the alkenyl halide was added. The mixture was then heated under reflux for 1.5 h and the hex-6-ene-1-magnesium bromide used directly for the reaction below.

b. *1-(3-Thienyl)hex-5-ene*

This was prepared by modification of the method of Kumada *et al*²

3-Bromothiophene (39.1 g, 240 mmol) and [Ni(dppp)Cl₂] (200 mg, 0.17 mol %) in dry ether (50 cm³) were stirred under nitrogen and over ice for 20 min. Hex-6-ene-1-magnesium bromide (240 mmol) described above was transferred slowly to the stirred mixture via a cannula over 1 h. The mixture was then left to stir for a further 1 h then heated to reflux for 16 h. The products were poured into crushed ice (100 cm³) and HCl (250 cm³ of 0.5 M) was added. The mixture was extracted with ether (3 x 200 cm³ aliquots) and the combined extracts were washed with water until neutrality. The liquor was then dried and evaporated after which distillation gave 1-(3-thienyl)hex-6-ene (21.29 g, 53 %) bp 93-96 °C / 8 torr; δ_H 7.26-7.16 (1H, m, ArH), 6.96-6.85 (2H, m, ArH), 5.92-5.70 (1H, m, vinyl), 5.15-4.85 (2H, m, vinyl), 2.70-2.56 (2H, t, *J* 7, methylene) 2.18-1.98 (2H, m, methylene) and 1.74-1.42 (4H, m, methylenes); δ_C 142.9 (ArC), 138.8 (C-5), 128.2 (ArC), 125.1 (ArC), 119.8 (ArC), 114.4 (C-6), 33.6, (CH₂) 33.8 (CH₂), 30.1 (CH₂), 30.0 (CH₂), and 28.5 (CH₂).

1-(3-Thienyl)pentan-5-al **5**

This compound was pepared by a modification of the method of Dev *et al*³

1-(3-thienyl)hex-6-ene (6.00 g, 36 mmol) in dry methanol (60 cm³) was maintained at -78 °C and stirred briskly while ozone was bubbled through the solution (40 l / h for 4 h). Nitrogen was then bubbled through the mixture for 10 min to displace any residual ozone

then a solution of thiourea (1.37 g, 18 mmol) in dry methanol (20 cm³) was added with vigorous stirring and the mixture left to stir for 1 h. During this period a white precipitate of thiourea-S-dioxide developed which was filtered off. The liquors were then poured into HCl (100 cm³ of 1 M) and stirred for 30 min. The mixture was extracted with ether (3 x 100 cm³) and the combined extracts dried and evaporated, then distilled to provide 1-(3-thienyl)pentan-5-al (3.00 g, 49 %) bp 90 °C / 1.5 torr.; δ_H 9.77 (1H, t, J 2, CHO), 7.31-7.19 (1H, m, ArH), 6.98-6.88 (2H, m, ArH), 2.74-2.58 (2H, m, ArCH₂), 2.56-2.40 (2H, m, methylene) and 1.76-1.55 (4H, m, methylenes); δ_C 202.6 (C-5), 142.2 (ArC), 128.1 (ArC), 125.4 (ArC), 120.1 (ArC), 43.7 (CH₂), 30.0 (2CH₂), and 21.6 (CH₂).

4-[6-(3-Thienyl)hexan-2-oyl],4'-methylbis-2,2'-bipyridine 6

Diisopropylamine (1.8 g, 17.6 mmol) was stirred under N₂ in dry THF (60 cm³) at -78 °C for 10 min. n-Butyllithium (8 cm³, 2.2 M) was added via syringe and the mixture was allowed to slowly reach room temperature. The resulting LDA solution was then cooled to -78 °C and transferred slowly via cannula to a solution of 4,4'-dimethyl-2,2'-bipyridine (3.24 g, 17.6 mmol) in THF (60 cm³) that was also previously cooled to -78 °C. The mixture was left to stir at -30 °C for 1h then the resulting lithiated bipyridine was again cooled to -78 °C. 1-(3-Thienyl)pentan-5-al (3.00 g, 17.6 mmol) in dry THF (20 cm³) was cooled to -78 °C and added dropwise via cannula to the lithiated bipyridine. The mixture was stirred under N₂ for 12 h slowly allowing the temperature to reach RT. The mixture was then added to water (100 cm³) and stirred for 10 min then extracted with ether (3 x 200 cm³), washed with water then dried and evaporated. The products were then subjected to vacuum sublimation (90 °C / 2x10⁻² torr) for 2h to remove unreacted starting materials to yield 4-[6-(3-thienyl)hexan-2-oyl],4'-methylbis-2,2'-bipyridine (3.60 g, 58 %); δ_H 8.56-8.42 (2H, m, ArH), 8.25-8.12 (2H, m, ArH), 7.28-7.02 (3H, m, ArH), 6.95-6.80 (2H, m, ArH), 3.98-3.83 (1H, m, OH), 2.95-2.47 (5H, m, methylenes and methine), 2.44 (3H, s, ArMe) and 1.75-1.20 (6H, m, methylenes); δ_C 156.0 (4ry) (ArC), 155.7 (4ry) (ArC), 149.1 (4ry) (ArC), 149.0 (ArC), 148.8 (ArC), 148.2 (4ry) (ArC), 142.7 (4ry) (ArC), 128.2 (ArC), 125.2 (ArC), 125.0 (ArC), 124.7 (ArC), 122.1 (ArC), 122.0 (ArC),

119.9 (ArC), 71.7 (CHOH), 43.6 (CH₂), 37.0 (CH₂), 30.4 (CH₂), 30.1 (CH₂), 25.4 (CH₂), and 21.2 (CH₂).

4-[6-(3-Thienyl)-2-methoxyhexyl],4'-methylbis-2,2'-bipyridine 7

This preparation was attempted by modification of the method of Johnstone and Rose.⁴

Finely powdered KOH (0.224 g, 4 mmol) was added to DMSO (1 cm³) and allowed to stir for 15 m. 4-[6-(3-Thienyl)hexan-2-oyl],4'-methylbis-2,2'-bipyridine (0.337 g, 1 mmol) was dissolved in DMSO (1 cm³) and added to the alkali solution immediately followed by iodomethane (0.284 g, 2 mmol). The mixture was stirred for 40 min then poured into water (20 cm³). The organics were extracted with methylene chloride (3 x 20 cm³) then washed with water (5 x 30 cm³). Evaporation of the solvent followed by drying in a vacuum oven (60 °C / 20 torr / 1 h) gave a mixture comprised of the original alcohol and the sought ether. δ_H 8.56-8.42 (2H, m, ArH), 8.25-8.12 (2H, m, ArH), 7.28-7.02 (3H, m, ArH), 6.95-6.80 (2H, m, ArH), 3.31 (3H, s, OMe), 2.95-2.47 (5H, m, methylenes and methine), 2.44 (3H, s, ArMe) and 1.75-1.20 (6H, m, methylenes); δ_C 156.2 (4ry) (ArC), 155.9 (4ry) (ArC), 149.3 (4ry) (ArC), 149.0 (ArC), 148.9 (ArC), 148.1 (4ry) (ArC), 142.7 (4ry) (ArC), 128.2 (ArC), 125.1 (ArC), 125.0 (ArC), 124.9 (ArC), 122.0 (2C) (ArC), 119.9 (ArC), 81.3 (CHOMe), 57.1 (CH₂), 48.8 (CH₂), 39.8 (CH₂), 33.4 (CH₂), 30.5 (CH₂), 30.2 (CH₂), and 21.2 (CH₂) in a 7:3 ratio.

N, N' [4-[6-(3-Thienyl)hexan-2-oyl],4'-methylbis-2,2'-bipyridine] ruthenium bis-2,2'-bipyridine dihexafluorophosphate 8

This compound was prepared by modification of the method of Ward *et al*⁵

Ruthenium bis-2,2' bipyridine dichloride (0.75 g, 1.5 mmol) and 4-[6-(3-thienyl)hexan-2-oyl],4'-methylbis-2,2'-bipyridine (0.53 g, 1.5 mmol) were heated to reflux in ethylene glycol (100 cm³) under nitrogen for 1h. The mixture was allowed to cool slowly to RT with stirring then potassium hexafluorophosphate (0.87 g, 6 mmol) was added producing an orange precipitate which was filtered off and washed thoroughly with distilled water and dried in a vacuum oven to give the title metal complex (1.10 g, 69 %); (Found C,46.27; H,

3.72; N, 7.47. C₄₁H₄₀N₆F₁₂P₂OSRu Requires C, 46.03; H, 3.86; N, 8.05); δ_H (d₆-acetone) 8.88-8.58 (7H, m, ArH), 8.27-7.75 (10H, m, ArH), 7.68-7.28 (7H, m, ArH), 7.11-6.90 (1H, m, ArH), 3.98-3.83 (1H, m, OH), 3.18-2.60 (5H, m, methylenes and methine), 2.54 (3H, s, ArMe) and 1.78-1.20 (6H, m, methylene); δ_C (d₆-acetone) 158.0 (ArC), 157.5 (4ry) (ArC), 157.2 (4ry) (ArC), 153.0 (ArC), 152.5 (ArC), 152.4 (ArC), 152.3 (ArC), 151.5 (ArC), 151.4 (ArC), 151.2 (ArC), 143.7 (4ry) (ArC), 138.6 (4C) (ArC), 129.8 (ArC), 129.4 (ArC), 129.0 (ArC), 128.6 (4C) (ArC), 126.2 (ArC), 125.9 (ArC), 125.8 (ArC), 125.2 (4C) (ArC), 120.7 (ArC), 71.5 (CHOH), 43.7 (CH₂), 38.0 (CH₂), 31.2 (CH₂), 30.6 (CH₂), 25.9 (CH₂) and 21.1 (CH₂). (2 extra peaks in aromatic region); λ_{max} 456.8 nm; m/z 911 (M⁺-PF₆⁻ 100%), 783 (13), 766 (30), 743 (15), 597 (31), 441 (24), 413 (41) and 257 (27).

*N, N' [4-[6-(3-Thienyl)hexan-2-oyl],4'-methylbis-2,2'-bipyridine] rhenium tricarbonyl chloride **9***

This compound was prepared by modification of the method of Wrighton *et al*⁶. Rhenium pentacarbonyl chloride (1 g, 2.76 mmol) and 4-[6-(3-thienyl)hexan-2-oyl],4'-methylbis-2,2'-bipyridine (0.98 g, 2.78 mmol) were stirred in hexane (100 cm³) and heated to reflux for 2 h. During this period a sticky pale yellow solid formed which seized the stirrer. DMF (30 cm³) was added to the mixture to dissolve the solid then the contents were returned to reflux for 1 h. The solvents were evaporated off to yield a yellow oil which was dissolved in acetone and residual solid material then filtered off. Evaporation of the acetone solution gave bright yellow crystals of the title compound (1.78 g, 89 %); (Found: M⁺, 658.068747. C₂₄H₂₄N₂O₄S³⁵Cl¹⁸⁷Re requires M⁺, 658.070297); δ_H (d₆-acetone) 8.94-8.68 (2H, m, ArH), 8.50-8.25 (12H, m, ArH), 7.58-7.32 (2H, m, ArH), 7.29-7.02 (1H, m, ArH), 7.00-7.74 (2H, m, ArH), 4.00-3.70 (1H, m, OH), 2.99-2.47 (5H, m, methylenes and methine), 2.45 (3H, s, ArMe) and 1.70-1.27 (6H, m, methylenes); δ_C (d₆-acetone) 199.0 (2 CO), 191.1 (CO) 156.4 (4ry) (ArC), 156.0 (4ry) (ArC), 155.0 (4ry) (ArC), 153.0 (ArC), 152.8 (ArC), 143.7 (4ry) (ArC), 129.5 (ArC), 129.3 (ArC), 129.1 (ArC), 128.9 (ArC), 126.0 (ArC), 125.9 (ArC), 125.7 (ArC), 125.4

(ArC), 120.7 (ArC), 71.5 (CHOH), 44.0 (CH₂), 38.2 (CH₂), 31.3 (CH₂), 30.7 (CH₂), 26.0 (CH₂), and 21.5 (CH₂). (1 extra peak in aromatic region); λ_{max} 380.6 nm; *m/z* 658 (³⁵Cl – M⁺, 23%), 623 (100), 574 (18), 539 (19), 453 (32), 426 (31), 353 (62) and 185 (61).

3-n-Octylthiophene 10

a. n-Octyl-1-magnesium bromide

1-Bromooctane (2.13 g, 11 mmol) in dry ether (50 cm³) was added dropwise to dry magnesium turnings (0.29 g, 12 mmol) in dry ether (100 cm³) under nitrogen. The reaction was initiated by the addition of a few grains of iodine, then continued for 10 min after the last of the alkyl halide was added. The mixture was then heated under reflux for 1.5 h and the n-octyl-1-magnesium bromide used directly for the reaction below.

b. 3-n-Octylthiophene

This was prepared by modification of the method of Kumada *et al*²

3-Bromothiophene (1.63 g, 10 mmol) and [Ni(dppp)Cl₂] (10 mg, 0.2 mol %) in dry ether (50 cm³) were stirred under nitrogen and over ice for 20 min. n-octyl-1-magnesium bromide (11 mmol) described above was transferred slowly to the stirred mixture via a cannula over 1 h. The mixture was then left to stir for a further 1 h then heated to reflux for 16 h. The products were poured into crushed ice (50 cm³) and HCl (100 cm³ of 0.5 M) was added. The mixture was extracted with ether (3 x 100 cm³ aliquots) and the combined extracts were washed to neutrality with water. The liquor was then dried and evaporated after which Kugelrhor distillation (80 mtorr / 90 °C) gave 3-n-octylthiophene (1.06 g, 54 %); δ_{H} 7.28-7.20 (1H, m, ArH), 6.96-6.87 (2H, m, ArH), 2.62 (2H, t, *J* 7, ArCH₂), 1.63 (2H, pentet, *J* 7, methylene), 1.45-1.25 (10H, m, methylenes) and 0.92 (3H, t, *J* 7, Me); δ_{C} 143.2 (4ry) (ArC), 128.3 (ArC), 125.0 (ArC), 149.7 (ArC), 31.9 (ArCH₂), 30.6 (CH₂), 30.3 (CH₂), 29.5 (CH₂), 29.4 (CH₂), 29.3 (CH₂), 22.7 (CH₂) and 14.1 (CH₃).

Poly(3-n-octyl thiophene) 11

This was prepared by the method of Hotta *et al*⁷

3-n-Octylthiophene (0.67 g, 3.4 mmol) was dissolved in Analar chloroform (15 cm³) and slowly added dropwise to a solution of iron (III) chloride (2.26 g, 13.9 mmol) in chloroform (80 cm³) under nitrogen. The mixture was left to stir for 24 h at RT then the resulting polymer was filtered and washed on the sinter with chloroform (100 cm³) then methanol (3 x 100 cm³). The polymer was then left to reflux in methanol (400 cm³) for 10 h after which the methanol was replaced with clean solvent and the reflux repeated. The polymer was then de-doped by stirring in a solution of hydrazine hydrate (2 cm³ in 20 cm³ water) for 48 hours. Once filtered off the polymer was washed thoroughly with water (200 cm³), methanol (100 cm³) and ether (100 cm³). After drying in a vacuum oven the polymer (0.58 g, 86 %) was analysed and found to still contain considerable amounts of impurities; (Found C, 71.12; H, 8.92. (C₁₂H₁₈S)_n Requires C, 74.16; H, 9.34.). Analysis of the polymer under a microscope revealed contamination with glass fragments which were removed by filtration of the polymer dissolved in hot CHCl₃. The residual insoluble polymer displayed considerable swelling. As the polymer was only sparingly soluble in hot CHCl₃, two further extractions were removed by reflux firstly in toluene followed by filtration, then the process repeated with o-xylene. After evaporation of the solvents the yields of polymer obtained from the original mass of 0.58 g were 50 mg (9%) from CHCl₃, 70 mg (12%) from toluene and 145 mg (25%) from o-xylene.

Attempted chemical polymerisation of N, N' [4-[6-(3-Thienyl)hexan-2-oyl],4'-methylbis-2,2' bipyridine]ruthenium bis(2,2'-bipyridine) dihexafluorophosphate

Using the method described above the Ru complex (0.25 g, 0.236 mmol) was suspended in Analar chloroform (25 cm³). HPLC grade acetonitrile (25 cm³) was added to dissolve the complex, and then it was slowly added dropwise to a solution of iron(III) chloride (0.115 g, 0.78 mmol) in chloroform (40 cm³) under nitrogen to give a dull red mixture. The flask was left to stir for 72 h after which time the contents displayed no darkening of colouration that would indicate polymerisation was taking place. The solvents were

evaporated off to give a viscous brown oil. Water was added to give a red precipitate which was filtered off and on washing the precipitate with water it displayed the same hydrophobic nature as the metal complex monomer. The precipitate was also highly soluble in acetone, again suggesting that only the monomer alone was present.

2.3.2 Electrode Preparation and Electrochemistry

*Spin coating of poly(3-n-octyl thiophene) **11***

This was done by modification of the procedures of Janata and Chin⁸ and I. D. W Samuel.⁹

ITO / Glass slides (approx. 2 cm²) were fixed to the motor of a Rotating Disc Electrode and a drop of poly(3-n-octyl thiophene) solution in CHCl₃ (1% w/v) was placed on the middle of the slide. The slide was then rotated under rapid acceleration to reach 1500 rpm within 5 s. The slide was held at this rate of rotation for 1 min then stopped. This procedure was run twice using the poly(3-n-octyl thiophene) obtained from reprecipitation from CHCl₃ and gave different thicknesses of films as indicated by a difference in intensity of the colour of the red-orange polymer. The procedure was run again using the material obtained from reprecipitation from toluene and resulted in a polymer coating of a darker coloration than that found from the earlier two slides . The slides were submitted to Prof. Allen of the Physics Dept, University of St. Andrews for PL and EL measurements. All three samples gave poor PL intensities and different peak maxima coresponding to the colour intensity / thickness of the polymer layer. The thinnest layer gave a peak maximum of 510 nm and the two thicker layers gave maxima at 520 and 530 nm respectively.

*Electrochemical polymerisation of poly(3-n-octyl thiophene) **11***

This was done by modification of the procedure of Clemenson *et al.*¹⁰

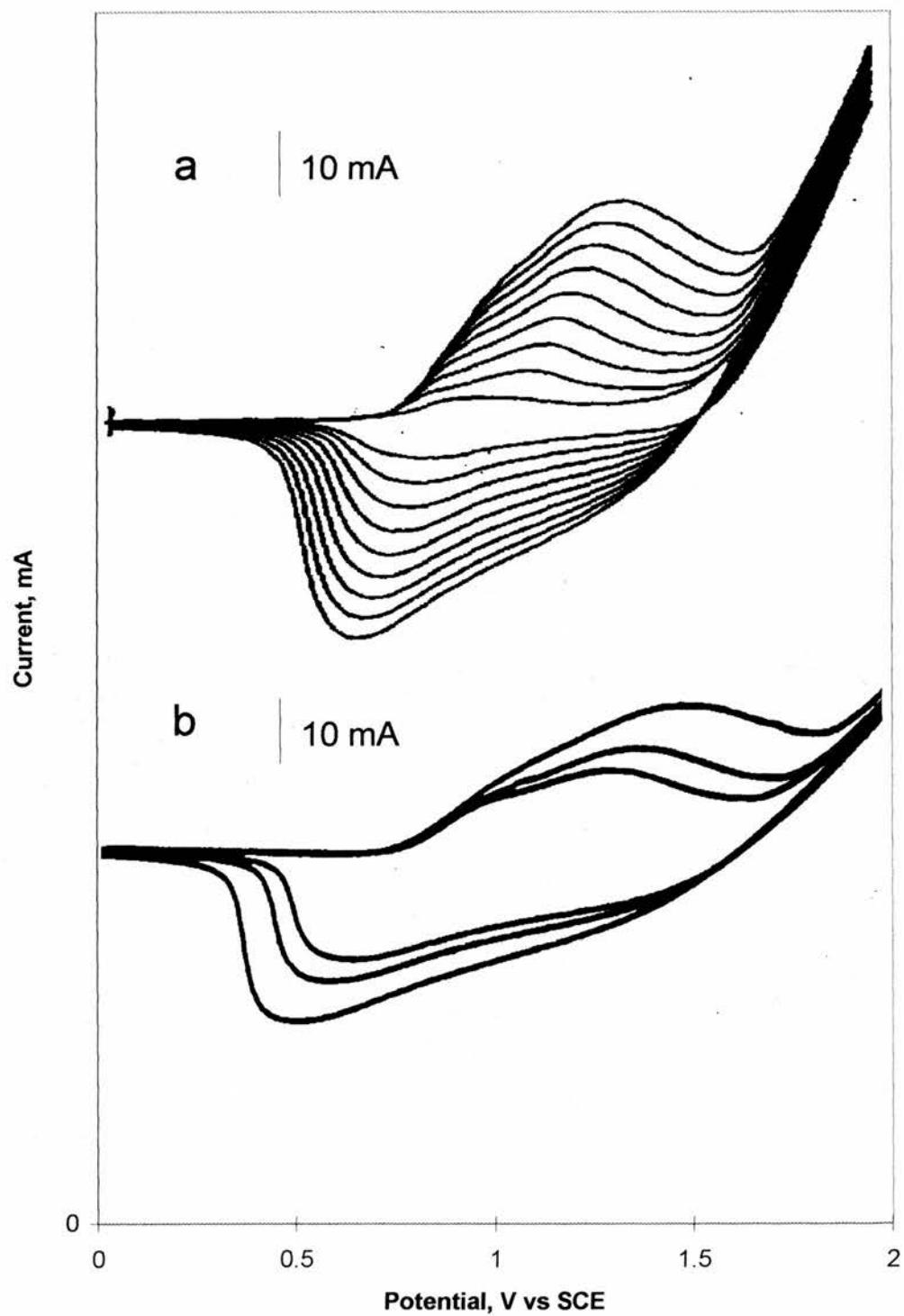
Films of poly(3-n-octyl thiophene) were grown electrochemically in a three electrode cell with an ITO coated glass slide as the working electrode, a saturated calomel reference electrode and a 2 cm² platinum foil counter electrode. The electrolytic medium consisted of

acetonitrile (HPLC grade), 0.1 M TBAT as supporting salt and 30 mM monomer (3-n-octyl thiophene) **10**. Prior to use, the prepared solution was degassed by bubbling with argon for 15 min.

The films were grown on an area of about 1 cm² of the ITO slide by the following method. The working electrode was held at a potential of 2.5 V for 40 min at RT followed by cycling the potential from 0 to +2.0 V for 5 min to allow the polymerisation reaction to be followed by cyclic voltammetry. During this cycling, polymer growth was evident as is displayed by the increasing currents in the C. V. scans Figure 2.1 (a) and (b).

As the scans are run the peak in the polymer growth wave is found to shift to an increasingly anodic potential, starting at +1.1 V and increasing to a final value of +1.3 V Figure 2.1 (a). This is due to the increasing resistance of the polymer on growth.

The high potential of 2.5 V was found to be necessary to initiate the polymerisation which took place rapidly under these conditions to give a visible coating within a few minutes. Previous attempts at growing the polymer by cycling the potential from 0 to +2.5 V failed and it was also discovered that the resistivity of the ITO electrode in the electrolytic medium led to overloading of the potentiostat when the area of the electrode immersed exceeded about 1 cm³. The above procedure was repeated to provide two further polymer coated slides, one grown for 15 min and a further one grown for 5 min at +2.5 V. The slides were submitted to the Physics Dept. for PL and EL measurements. All three samples gave improved PL intensities over that found for the equivalent chemically polymerised polymers and the PL peak maxima again varied according to the thickness of the polymer layer. The thinnest layers (from slides prepared by growing the polymer for 5 and 15 min) gave a peak maximum of 490 nm and the thicker layer gave a maximum at 540 nm. A slide that displayed blue shifted PL (at 490 nm) was prepared for EL measurements by vacuum deposition of aluminium on the polymer. The aluminium was used as a cathode and the ITO used as the anode. The polymer had a varied potential passed through it of up to 20 V.



*Figure 2.1: (a) CV of Polymer growth of 3-n-octyl thiophene (10 mA/cm, 0-2 V, Scan rate 100mV/s).
(b) CV Scan rate dependence in supporting Electrolyte (1, 2 and 3×10^2 mV/s).*

At 20 V the device shorted showing that the polymer had decomposed. At no time through the potential increase was any EL observed (as estimated by eye in a darkened room).

Electrochemical polymerisation of N,N' [4-[6-(3-Thienyl)hexan-2-oyl],4'-methylbis-2,2'-bipyridine] ruthenium bis-2,2' bipyridine dihexafluorophosphate 8

Using the same set up and methods as those used above no polymer growth was observed on the ITO coated glass electrode from a 30 mmol dm⁻³ solution of the Ru complex. The same set up and methods were attempted using a 1 cm² area platinum flag working electrode. After holding at +2.5 V for 30 min the cyclic voltammogram Figure 2.2 shows increasing conductivity on cycling from 0 to +3.25 V.

On removal of the electrode from the Ru complex solution a bright orange colouration was observed on the Pt surface which did not dissolve off on dipping into acetone. On transferring the Pt electrode to a blank 0.1 M solution of TBAT in MeCN for electrochemical studies the orange solid on the electrode completely dissolved over 10 min while the cell was being purged with Ar gas. The loss of the solid due to complete dissolution into the MeCN indicated that the complex had been adsorbed onto the electrode rather than polymerised.

Further attempts to polymerise the Ru complex onto platinum were made. Firstly the same solution of the Ru complex in MeCN was used with a freshly polished 0.8 mm diameter Pt working electrode. The potential was cycled from 0 to +2.5 V Figure 2.3 (a) for 10 min then held at +2.5 V for 30 min. After this period a further scan Figure 2.3 (b) was obtained. With this smaller, cleaner electrode more detail was obtained on the CV than that found with the earlier study using the larger Pt electrode. Common to both studies there is a Ru²⁺ to Ru³⁺ oxidation wave at +1.22 V with a cathodic peak at +1.18 V. On repeated cycling using the smaller electrode the height of the waves is reduced indicating that the electrode surface is becoming more resistive and with this decrease in the height of the waves a further irreversible oxidation wave becomes evident at a potential of 1.95 V.

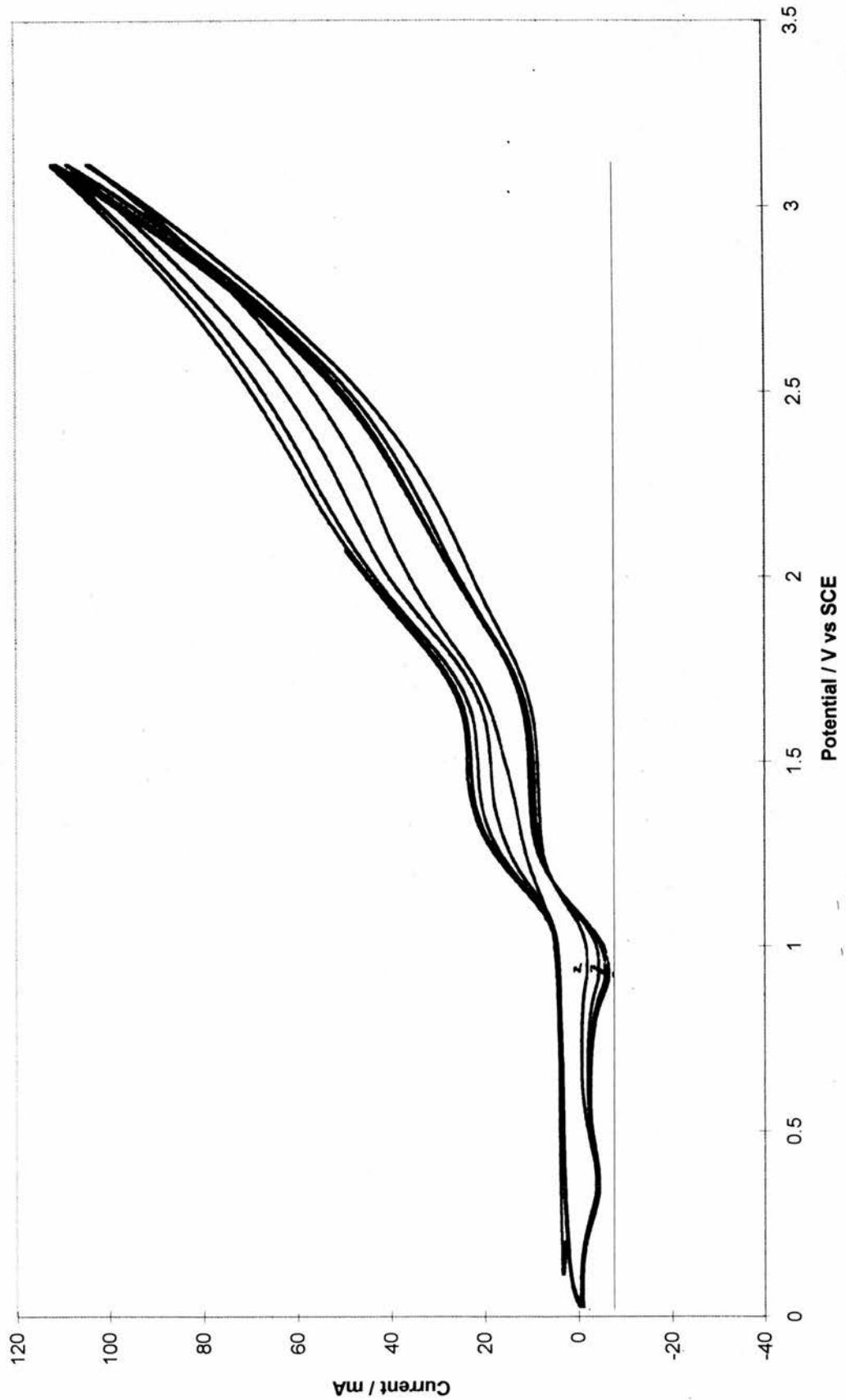


Figure 2.2: Pt electrode in 30 mmol dm⁻³ ruthenium complex (10 mA/cm, 0 to +3.5 V, Scan rate 100mV/s)

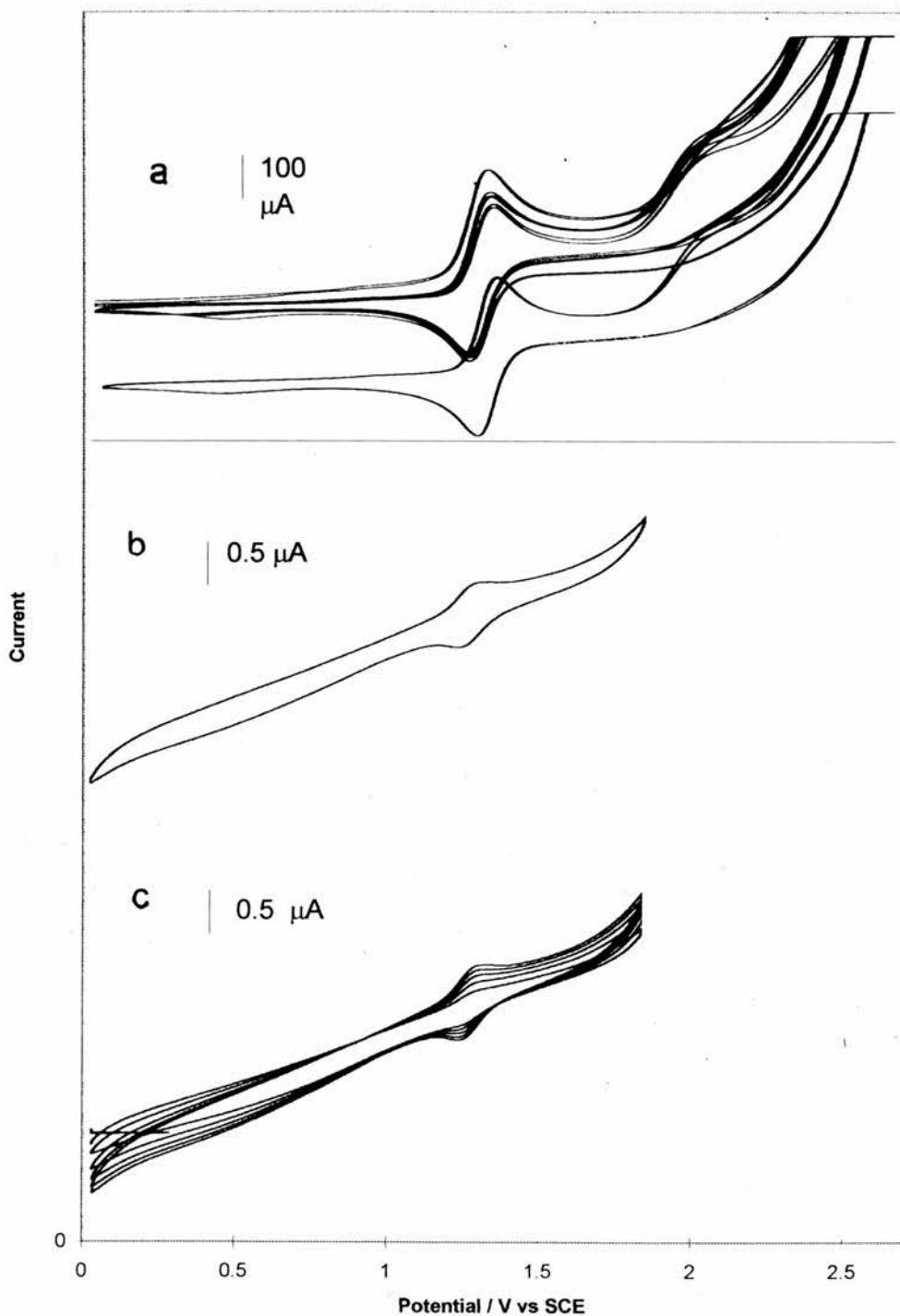


Figure 2.3: (a) Electrochemistry of the Ruthenium complex (30 mmol dm⁻³ in 0.1M TBAT in MeCN) using a 0.8 mm diameter Pt electrode (0.1 mA/cm, 0-2.5 V, Scan rate 100mV/s). Bottom scan shows CV after holding at a potential of +2.5 V for 30 min.

(b) CV and scan-rate dependence of the Pt electrode used above in fresh 0.1 M TBAT / MeCN,500 nA/cm, 0-+1.8 V,Scan rate 100 mV/s.

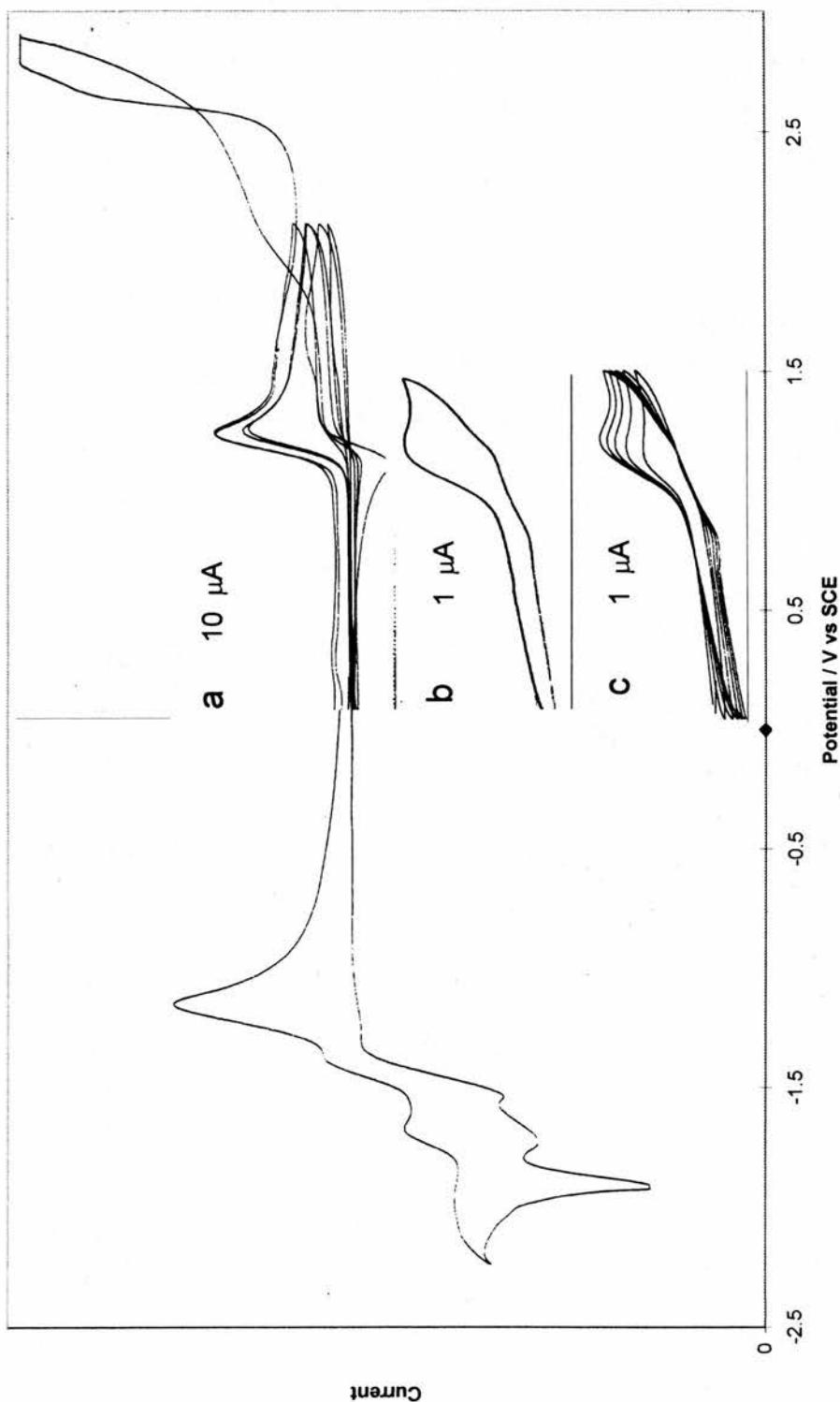
(c) CV and scan-rate dependence of the Pt electrode used above in fresh 0.1 M TBAT / MeCN, 500 nA/cm, 0-+1.8 V,Scan rate 20-100 mV/s

At cathodic potentials four reversible reduction waves are observed at $E_{\text{a}} = -0.75$ (300), -1.395 (60), -1.615 (70) and -1.69 V (70 mV peak to peak separation) attributed to the three bipyridine reductions and the Ru^{2+} to Ru^+ reductions.

On removal of the electrode from the cell an orange solid was found on the Pt surface which persisted on washing with acetone. Cyclic voltammetry of the electrode in a blank solution Figure 2.3 (b) and subsequent scan rate dependence Figure 2.3 (c) showed an oxidation wave at $+1.22$ V with a reduction at $+1.18$ V showing that the Ru^{2+} to Ru^{3+} process was occurring externally from the Ru complex solution. On application of an anodic potential of $+2$ V to look for the second oxidation wave at $+1.95$ V the electrode surface broke down and the previously observed oxidation wave was lost.

A further attempt at polymerising the Ru complex **8** was done using the same method as described above and using a new solution of the complex prepared from vacuum oven dried TBAT and Ru complex and fresh HPLC grade MeCN. Electrochemistry of this solution Figure 2.4 (a) gave significantly different results. As before the Ru^{2+} to Ru^{3+} oxidation wave was observed at $+1.22$ V but in this case it is reversible at $+1.18$ V only for the first few scans. On cycling from 0 to $+2.2$ V without holding at a high anodic potential as before a bright orange solid developed on the electrode surface. Also, the conductivity of the electrode decreased rapidly on cycling (growth current decreasing) indicating that rapid insulative polymer growth was taking place.

On transferring the electrode to a blank solution Figure 2.4 (b) and (c) the oxidation wave was observed at $+1.22$ V but again it was found to be not so reversible as that seen in the earlier attempts at polymer growth. The solid material on the electrode appeared to be thicker than that found on earlier attempts and was insoluble in the blank solution and showed no deterioration over two days.



*Figure 2.4: (a) Ru complex cyclic voltammetry and polymer growth (10 μ A/cm, 0-+2.2 V, Scan rate 100 mV/s).
(b) Inset shows polymer CV (2 μ A/cm, 0 to +1.5 V, Scan rate 100 mV/s).
(c) Scan rate dependence (2 μ A/cm, 0 to +1.5 V, Scan rate 100-1000 mV/s). Scale is at 5 V/cm on 1cm grid.*

Due to the rapid polymerisation of the complex onto platinum that was observed using dry reagents, the same solution of Ru complex was used in a second attempt to polymerise the complex onto ITO. The electrochemistry Figure 2.5 (a) displays polymer growth on a 0.5 cm² ITO electrode by cycling from 0 to +2.7 V (20µA/cm, Scan rate 100 mV/s) for 15 min. The CV shows an oxidation that is reversible at +1.0 V and the current through the electrode is increasing with growth suggesting that the polymer is less resistive than the ITO electrode.

On removing the electrode from the Ru complex solution a pale orange transparent film was found on the ITO electrode. On examining the electrode electrochemically in a blank solution Figure 2.5 (b) and (c) the same Ru²⁺ to Ru³⁺ oxidation wave was observed at +1.22 V as had been seen with the Ru complex polymerised onto Pt.

Using a Pt electrode (0.8 mm diameter) and a fresh, dry solution of 30 mmol dm⁻³ Re complex **9** in 0.1 M TBAT in MeCN, polymerisation by the same method as that which was used with the Ru complex was attempted. The CVs Figure 2.6 (a) and (b) show the progress of the electrochemistry which was found to be quite complex. Figure 2.6 (a) (displaying the behaviour at cathodic potentials on the 2nd scan) shows the 6 cycles after the 3rd scan and here the height of the oxidation waves decreases with time. Figure 2.6 (b) was recorded after scanning for 30 min and here the oxidation waves are increasing in height over time. On the first few scans Figure 2.6 (a) two oxidation waves are clearly defined, while a third at +2.20 V is poorly defined and is lost with repeated scans. The better resolved waves are at +1.33 and +1.88 V; however, these also deteriorate with time and their positions shift anodically for the first wave and cathodically in the case of the second wave. With the later scans Figure 2.6 (b) the three oxidation waves are more clearly defined at +1.31, +1.88 and +2.20 V and are of fixed potentials over time.

At cathodic potentials Figure 2.6 (a) a complex system of reductions is displayed with the best defined waves showing cathodic peaks at -1.52, -1.74, -1.95 and -2.68 and

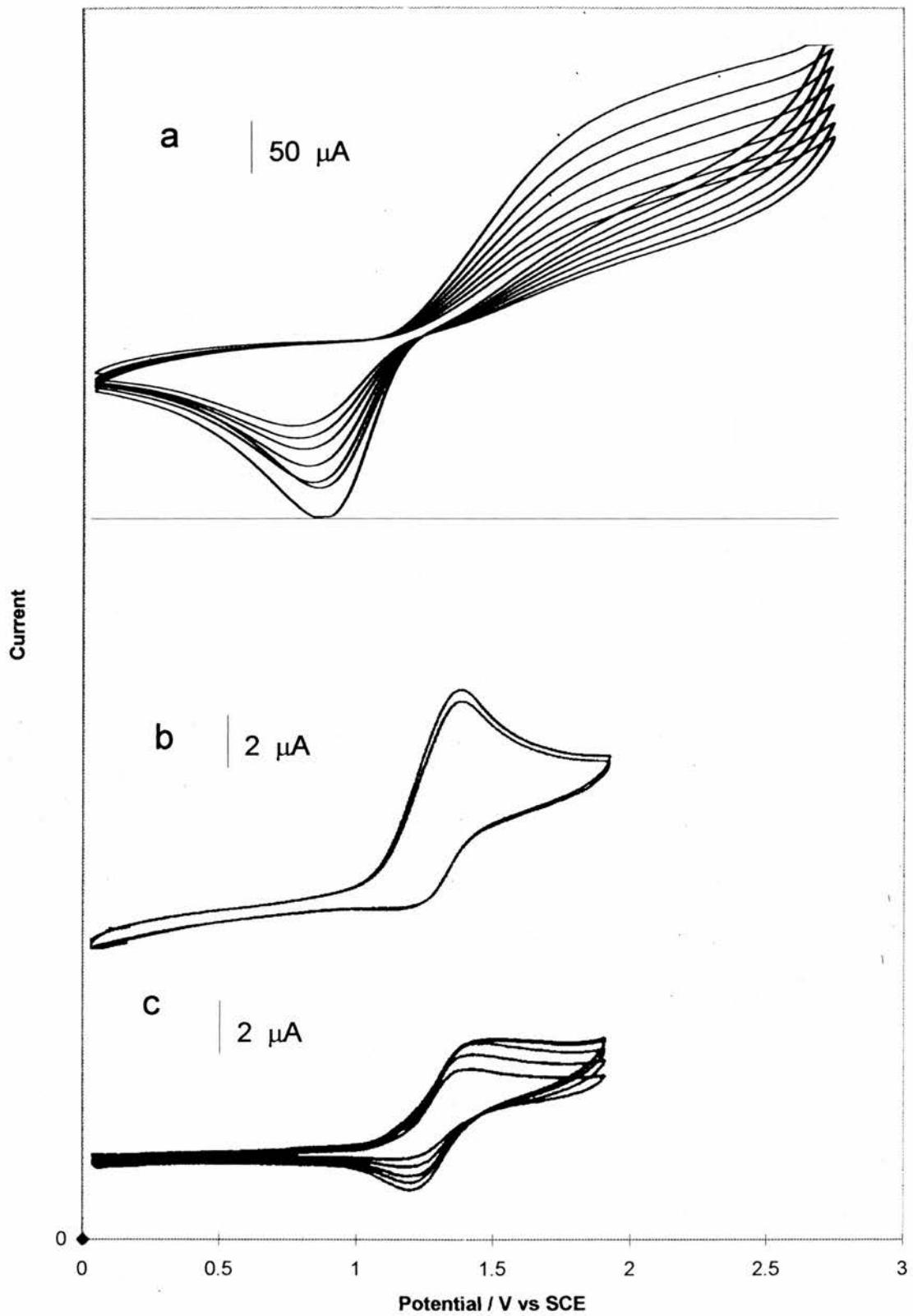


Figure 2.5: (a) Dry Ru complex on ITO electrode.(2 mA/cm, 0 to +1.5 V, Scan rate 100 mV/s).

(b) Scan rate dependence from 20 to 100 mV/s.

Electrochemical polymerisation of *N,N'* [4-[6-(3-Thienyl)hexan-2-oyl],4'-methylbis-2,2'-bipyridine] rhenium tricarbonyl chloride **9**

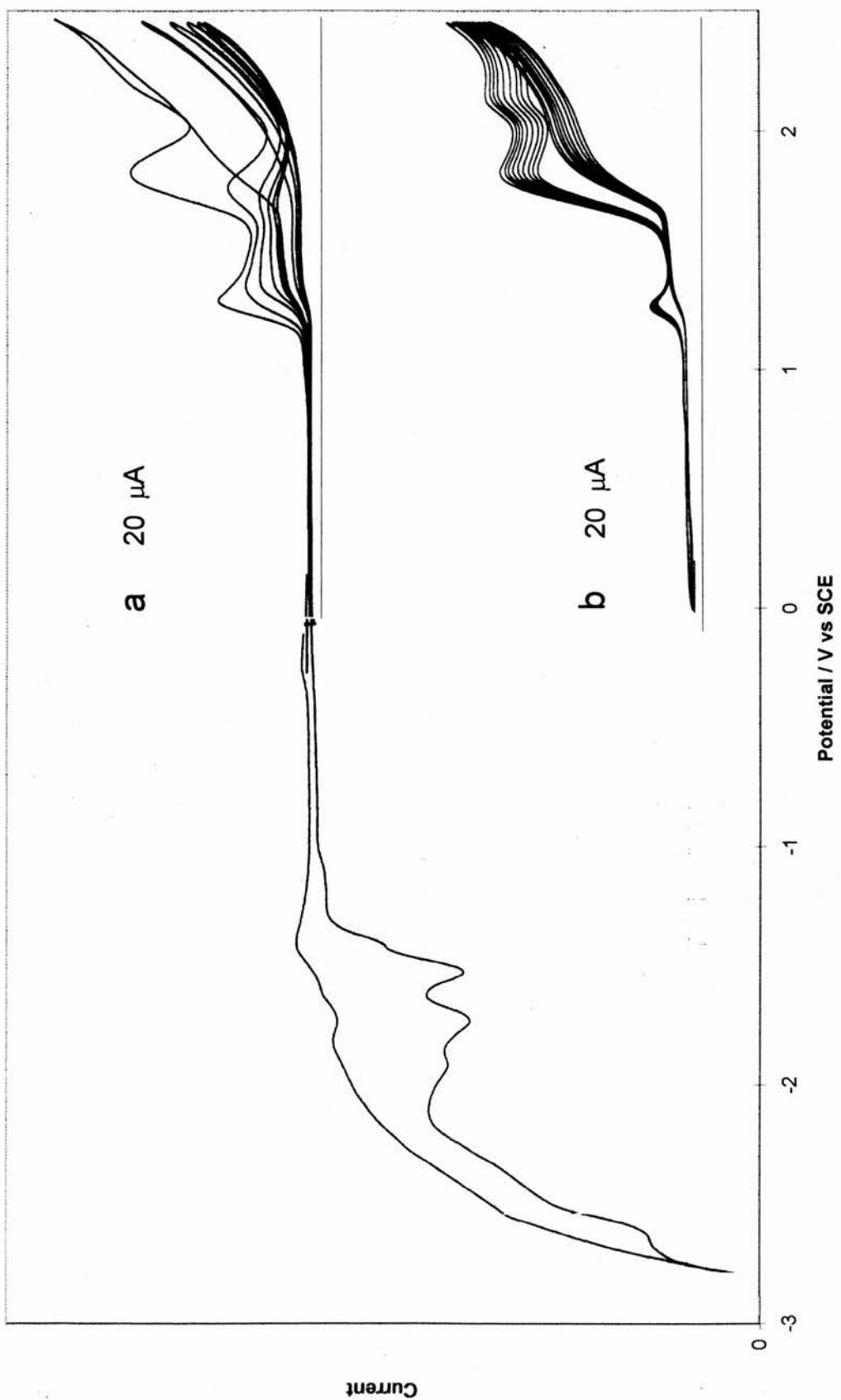


Figure 2.6: (a) and (b) CV of Re complex on Pt ($20\mu\text{A}/\text{cm}^2$, 0 to 2.5V, Scan rate 100 mV/s).

anodic peaks at -1.40, -1.60, -1.74 and -1.82 V. The complexity of the CV at these potentials may be partly explained by the reduction of the bipyridine groups complementing the Re^+ to Re^0 reduction.

After the cycling had run for 1 h, the Pt surface was coated with a bright yellow solid. The electrode was washed with acetone then transferred to a blank electrolyte solution. The cyclic voltammetry Figure 2.7 (a) showed an oxidation wave at +1.30 V which is similar to the oxidation wave at +1.33 V found in the Re complex **9** solution. On scanning to cathodic potentials Figure 2.7 (b) the expected reduction waves analogous to those observed for the monomer **9** were absent. On removing the electrode from the blank solution the yellow colouration had gone revealing a shiny Pt surface. The electrode was replaced in the cell and a further scan revealed much the same trace as before, indicating that some material was still lightly coating the electrode as the high current on the scans could not be due to insignificant transfer of soluble Re complex from the electrode.

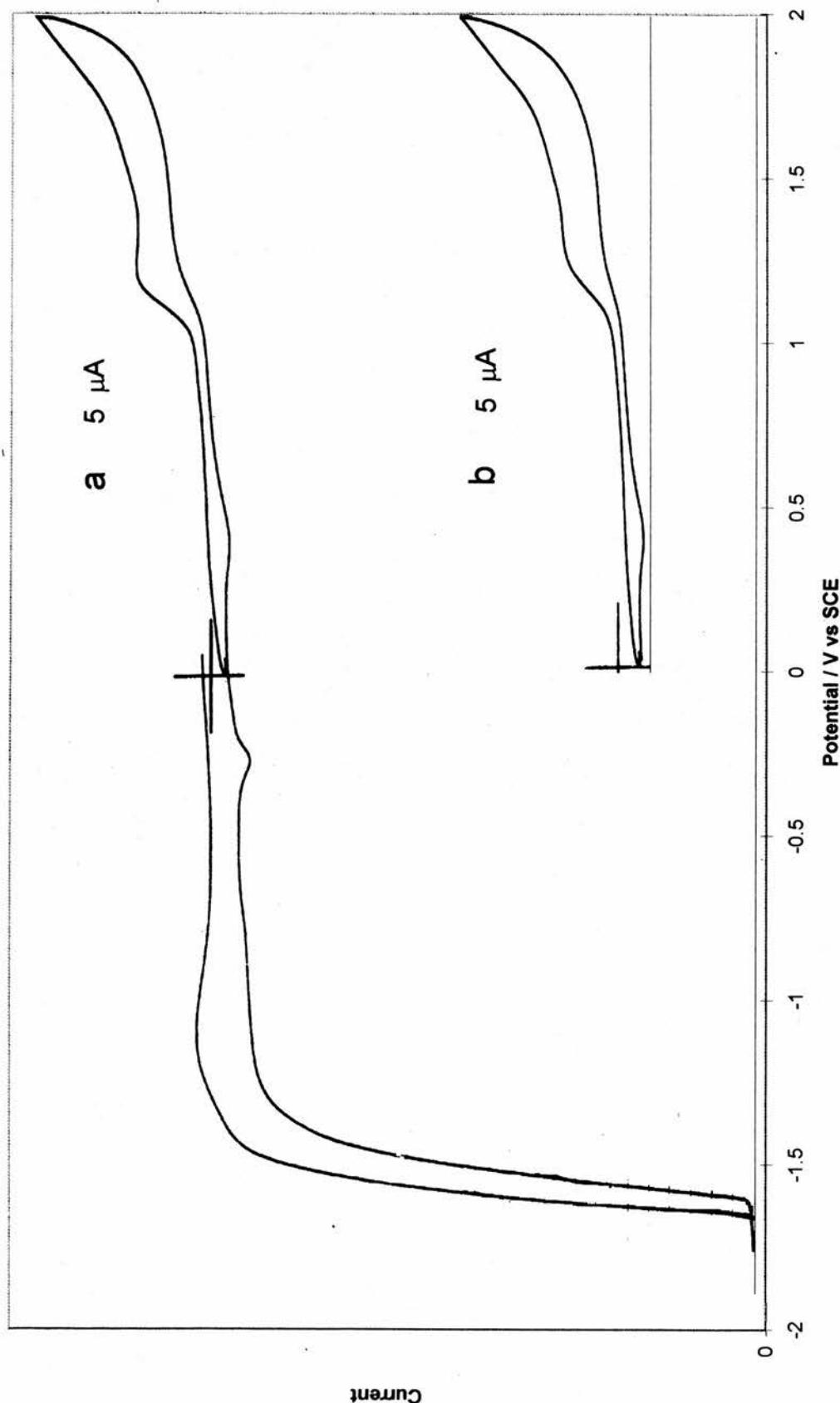


Figure 2.7: (a) and (b) Re complex on Pt in blank solution (Current as scale, 0 to 2.0V, Scan rate 100 mV/s)

2.4 Discussion

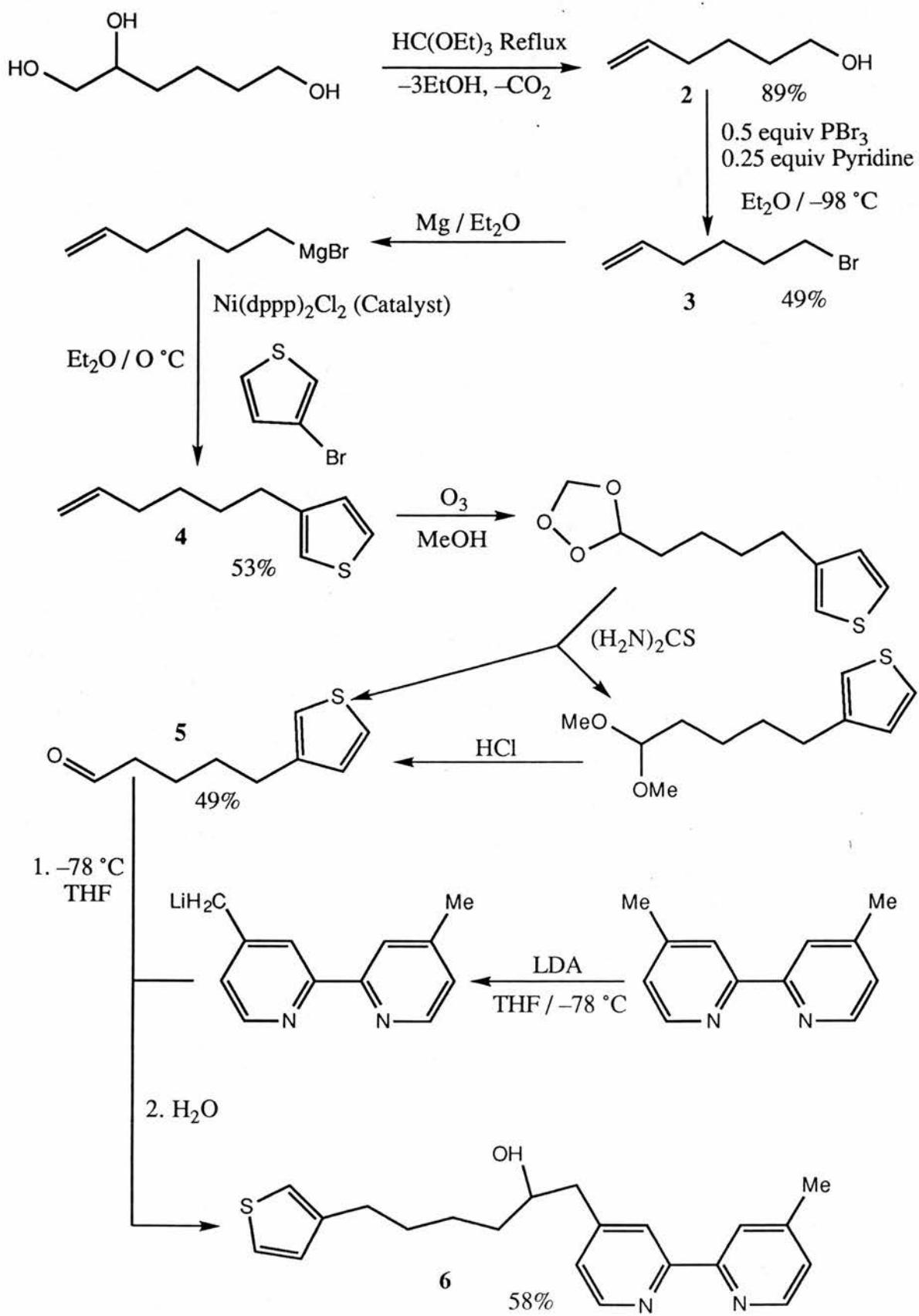
2.4.1 Synthesis

Preparation of 4-[6-(3-thienyl)hexan-2-oyl],4'-methylbis-2,2'-bipyridine 6

The synthesis of the title compound and its subsequent coordination to ruthenium bis(2,2'-bipyridine) dichloride had earlier been achieved by the work of A. Iraqi¹. Problems encountered included low yields of complex (leading to insufficient material for a full electrochemical study) and poor polymerisation behaviour. A major objective remained in the repetition and scaling up of the multi-stage synthesis and attempts were made at every opportunity to maximise the yields and provide as high a purity as allowed by practically viable routes.

The first stage required the conversion of the terminal diol 1,2,6-trihydroxyhexane into the corresponding alkene **2** via the action of triethylorthoformate; the latter stage of the reaction (loss of CO₂) is catalysed by the addition of a small quantity of acid. This conversion ran cleanly and in high yield throughout several attempts. The alkenol was then converted to the corresponding alkenyl halide **3** by the action of phosphorus tribromide. The phosphorous acid by-product generated in the latter stages of the reaction was to be isolated by formation of the insoluble phosphorous acid : pyridine adduct. This factor was found to be the cause of very low product yields as the stocks of pyridine used in early attempts were found to contain impurities such as water. The use of distilled pyridine brought the reaction yield up to 49% as stated in the Experimental section.

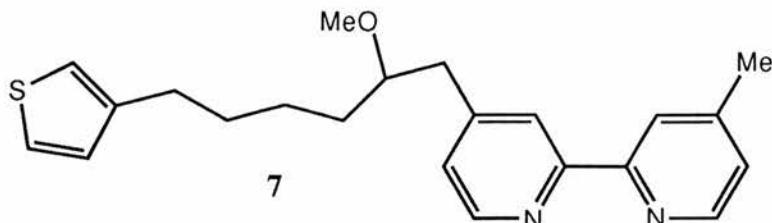
1-(3-Thienyl)hex-1-ene (or hexenylthiophene) **4** was prepared firstly by generation of the Grignard equivalent of **3** and transfer of the Grignard to a solution of 3-bromothiophene containing a catalytic quantity of a dihalodiphosphinenickel(II) cross-coupling catalyst. Initial attempts at this reaction either resulted in failure or very low yields



due to the use of an old stock of catalyst which had been allowed to undergo substantial aerobic oxidation with consequent loss of activity. On using a better preserved catalyst and taking great care over the slow addition of the Grignard to the mixture (to avoid overloading the catalyst) a respectable yield of 53% was achieved. This was then converted to the ozonide which was subjected to reductive cleavage by thiourea. The thiourea is conveniently converted to thiourea S-dioxide which is easily removed by filtration to leave a solution of the required aldehyde as a mixture with the corresponding acetal. The acetal is readily converted to the product 1-(3-thienyl)pentan-5-al **5** by the action of acid; subsequent workup provided this aldehyde in an overall yield of 49%.

The ligand 4-[6-(3-thienyl)hexan-2-oyl],4'-methylbis-2,2'-bipyridine is produced in 2 major steps starting with the lithiation of 4,4'-dimethyl-2,2'-bipyridine. The lithiation is achieved by generating LDA in a THF solution and transferring it at -78 °C to the equivalent of the bipyridine in THF maintained at the same temperature. Warming to -30°C gives the lithiated 4,4'-dimethyl-2,2'-bipyridine which is then cooled again before slowly adding to the aldehyde **5** also maintained at -78 °C in THF. As the mixture warmed to RT the reactants undergo a reductive alkylation to give the required secondary alcohol functionalised ligand and other products. Subsequent work up and vacuum sublimation gave the clean ligand **6** in an overall yield of 58%.

An attempt was made to prepare a modified ligand by conversion of the hydroxy group in **6** to a methyl ether function **7**. Although successful in converting 30 % of **6** to **7** the product was difficult to separate and this attempt was abandoned.

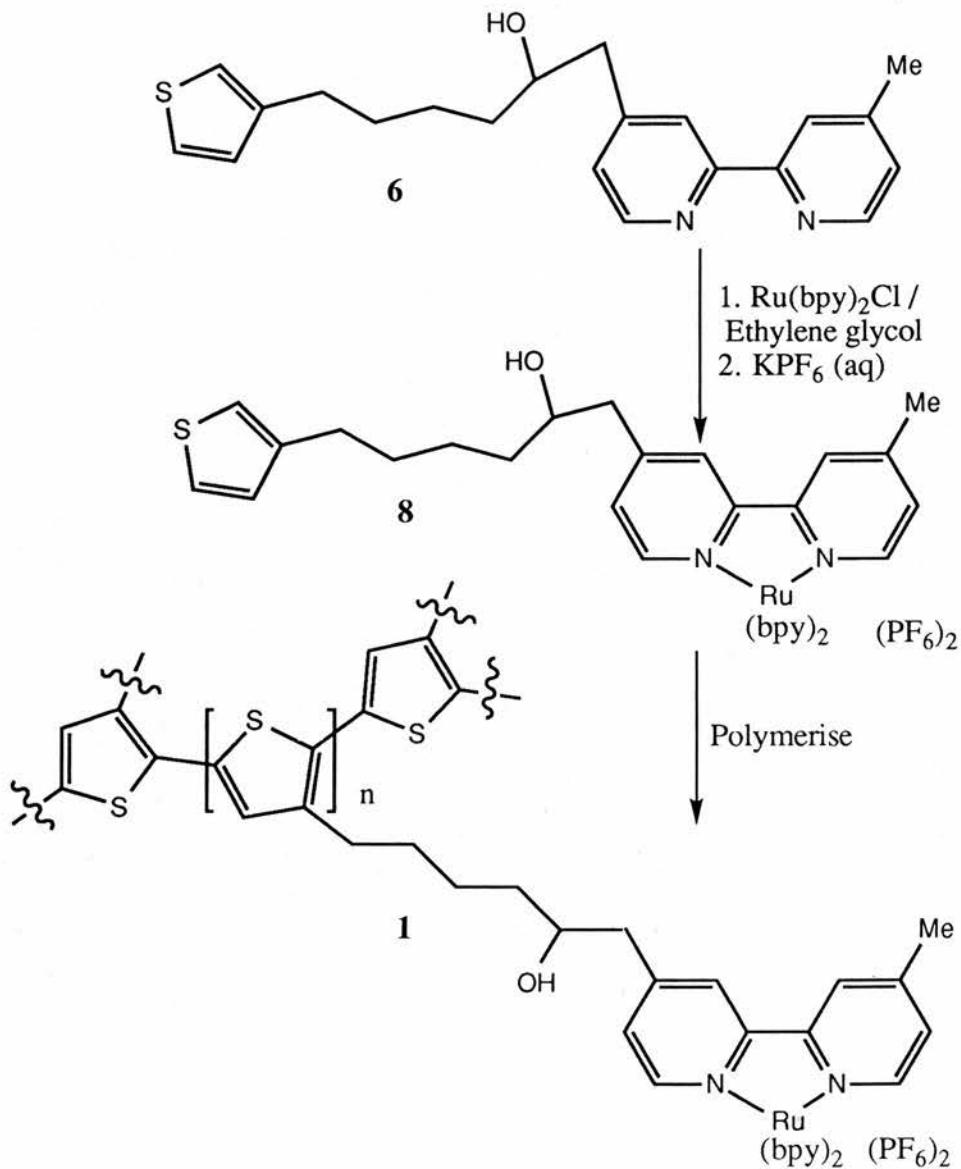


Preparation of the Bipyridine-derivatised Thiophene Metal Complexes .

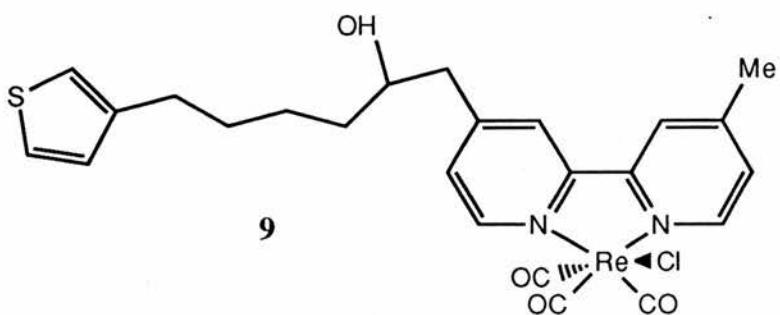
The ligand discussed above was coordinated successfully to two metal centres (ruthenium and rhenium) by the following methods. However, preliminary experiments to provide coordination with first row metals have both run into difficulties which have been troublesome to solve due to the paramagnetic nature of the complexes. This has made the task of characterising the products of these reactions difficult since NMR of the species is not available and the complexity of the products sought requires such a powerful technique in order to gain information on the course of the reaction. The uncertainty as to the results of this series of experiments has led to them being omitted from this report.

The first complex made was [4-[6-(3-thienyl)hexan-2-oyl],4'-methylbis-2,2'-bipyridine]ruthenium bis(2,2'-bipyridine) dihexafluorophosphate **8**. This compound was prepared by heating a mixture of equivalents of **6** and dichlorobis-2,2'-bipyridine ruthenium(II) to reflux in ethylene glycol. After workup this reaction yielded the Ru complex **8** (69%) in almost pure form, as estimated by CHN MICROANALYSIS, but with an observable but unknown impurity indicated by the appearance of two extra carbon signals on the ^{13}C spectrum in the aromatic region. This synthesis represents an advance on previous work where a different synthetic route led to a less pure Ru complex (3 extra ^{13}C signals on spectrum). The diagram below shows the structure of the product and the structure of the intended polymerisation product **poly 1**.

The Ru complex **8** is a bright orange solid that is highly soluble in polar organic solvents. Unfortunately, the Ru complex does not exhibit obvious luminescence under UV light which is a quick and easy test to find out if the material may display EL or not. The reason for the lack of luminescence may lie in the ability of the thiophene substituent to offer a route to non-radiative charge transfer or relaxation of the Ru triplet excited state (if this exists in the solid!) or by other factors not yet envisaged.



The second complex made was [4-[6-(3-thienyl)hexan-2-oyl],4'-methylbis-2,2'-bipyridine] rhenium tricarbonyl chloride **9**. This complex was prepared by the displacement reaction of the ligand **6** on rhenium pentacarbonyl chloride in boiling hexane. The reaction resulted in the fast development of an insoluble sticky pale yellow



solid and at this point dimethylformamide was added to the reaction mixture to take the material into solution and the reflux continued. This action has been successful in providing the title compound **9** in 89% yield without significant organic impurities as observed from the ^{13}C and ^1H spectra of the product.

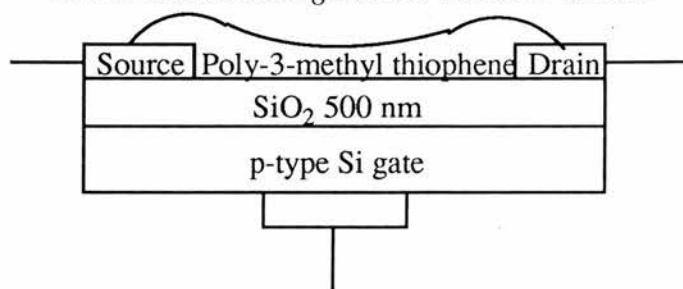
The yellow crystals of the Re complex **9** have been examined under UV light and observed to produce an yellow orange fluorescence. UV / Vis spectra show a maximum absorption at 380 nm. This is considerably blue shifted from the λ_{max} of 456.8 nm for the Ru complex **8** and this in turn is expected to give rise to blue shifted luminescence characteristics.

One of the greatest differences between this material and the Ru complex is the absence of an external counter ion in the former. The Re centre has a coordinated chloride ion on one of the octahedral sites and so exists as a neutral molecule hence avoiding the possibilities of “quenching” of luminescence reactions. For this reason the Re complex is perhaps a more promising precursor to the goal of producing an electroluminescent metal containing polymer.

2.4.2 Electrochemical and chemical polymerisation studies on poly-3-alkylthiophenes

In an additional line of study the factors involved in luminescence from the thiophene metal complexes are compared against results obtained from electrodes coated with poly-3-alkylthiophenes fashioned in the same way, i.e. by electrochemical polymerisation. The reasons behind this study are twofold. Firstly, most of the work done on polymer LED devices to date have concentrated on spin coating of the polymer film onto the electrode. This may be mainly due to the amount of work being reported on PPV based devices where the use of the precursor polymers (as discussed in the Introduction) precludes other methods of polymer handling. Another reason is that even soluble PPV based polymers seem to give a better surface contact on spin coating than by electrochemical methods.¹¹ This however may not be the case with electrochemically polymerised 3-alkyl thiophenes^{12,13,14} since so far this method has been successful in the construction of field effect devices such as transistors which require the same qualities of precise thickness of polymer growth and adhesion as that in polymer LED's.

Cross Section through a PAT MISFET device.



The further purpose is to investigate the PL and EL spectral characteristics of these polymers in a polymer LED device identical to those to be tried on the metal thiophene complexes. Such experiments will help to answer whether any luminescence observed from the complexes is due to the polymer backbone or the metal centre.

So far, 3-n-octyl thiophene **10** has been prepared from n-octyl bromide and 3-bromothiophene by the method discussed as for hexenyl thiophene **4**. Chemical polymerisation of this material using ferric chloride in chloroform has yielded after workup and hydrazine dedoping, poly(3-n-octylthiophene) **11** (86%). CHN MICROANALYSIS of this material had shown it to contain considerable impurities and so further reprecipitation prior to spin coating of this material was done using chloroform. The polymer was found to be only sparingly soluble (9% dissolved) in chloroform with the remaining solid material undergoing considerable swelling and taking on a bright red colouration which is in common with that of the poly(3-alkylthiophene) gel reported by Sugimoto *et al.*¹⁵ Further polymer was dissolved in toluene (12%) but again the solubility was limited. The greatest quantity (25%) was dissolved into o-xylene. Once the solvents had been evaporated off in each case the polymer recovered from chloroform was made up to a 10 mg/ml solution as was the polymer recovered from toluene. These chloroform solutions were then spin coated onto ITO covered glass slides using the motor of a rotating disc electrode as the spinner. This teCHN microanalysisique involved difficulties in setting the slide level and on centring the pipette on the slide. On accelerating the rotation the drop of polymer solution tended to fly off the slide rather than level out to give a smooth coating. This effect was minimised by slowing the rate of acceleration and stopping the rotation once or twice to make light adjustments to level of the slide. This enabled greater coverage of the slide, however, since the polymer solution spent more time on some areas of the slide as droplets, the possibility of adhesion during this time lends doubt to the uniformity of the polymer layers after spinning. These effects could be minimised by the use of a commercial spin coating device which would provide greater accuracy in the levelling of the slide and addition of the polymer solution.

The electrochemical polymerisation of 3-n-octyl thiophene **12** described in the Experimental section was successful in growing different thicknesses of poly-3-n-octyl thiophene film onto ITO coated glass electrodes. These experiments were rudimentary and the method of polymer growth (holding the working electrode at a +2.5 V potential for

alternating periods of time) was designed only as a qualitative measure with the main purpose being that of obtaining the PL spectra of the polymer produced by this method to look for differences between this and the spin coated polymer PL spectra.

The PL spectra of both the chemically **11** and electrochemically **12** polymerised poly-3-n-octyl thiophenes was run in the Dept. of Physics by Prof. Allen and Dr. Zheng. The results of the spectroscopy are shown in Figure 2.8.

The intensity of the spectra are displayed in arbitrary units and have been scaled simply to show the PL maxima. Perhaps the most interesting point that is not detailed by the spectra is that the electrochemically polymerised polymer films exhibited significantly higher PL intensities than the spin-coated films. This could, of course, be due to the spin-coating process used to make the films which is inferior to the process used in other laboratories and in industry. However the fact that greater PL intensities were found for the electrochemically polymerised films suggests that continuing to manufacure films by this method may be a fruitful area for further studies as the method is largely ignored in the literature with a strong preference being directed to spin-coated films for polymer LED's.

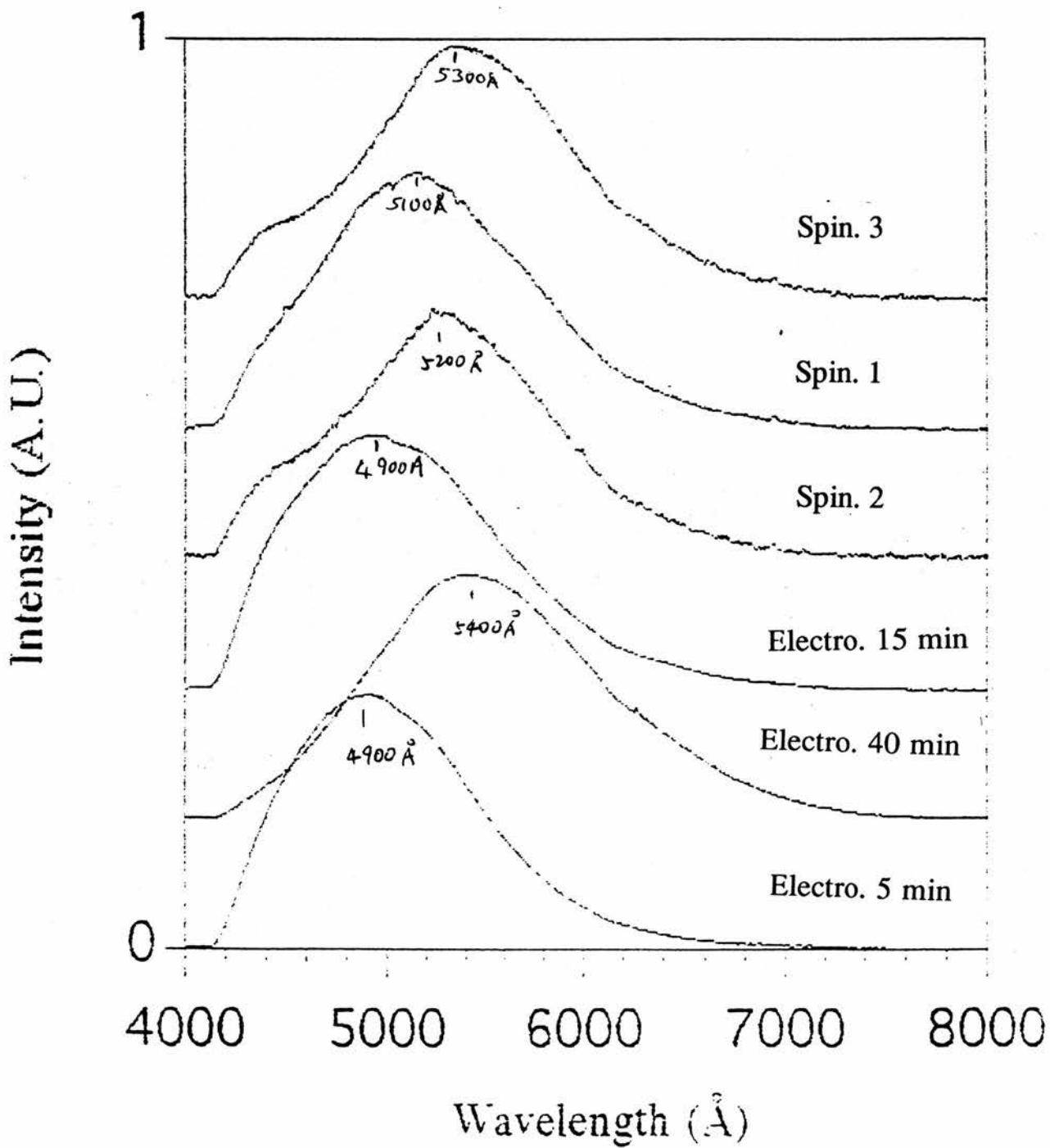


Figure 2.8: Photoluminescence spectroscopy of poly-3-n-octylthiophene coated ITO.

The wavelengths of the photoluminescence maxima from the polymer films studied showed considerable variation (490 to 540 nm), especially in the case of the electrochemically prepared films. Dealing with the electrochemically coated films the variation in maxima may be rationalised in terms of the average chain length of the polymer. As mentioned in Chapter 1, work by Hadzioannou *et al*¹⁶ showed that alteration of the polymer chain length (in that case controlled by co-polymerisation) leads to different PL and EL maxima from the polymer. Shortening the chain length leads to a blue shift and this may be the reason for the difference in the PL maxima from the electrochemically polymerised films since the polymer obtained in the films grown for 5 and 15 mins are likely to have shorter average chain lengths than the film grown over 40 mins.

The differences in the chemically polymerised films PL spectra may also be rationalised in the same way. Due to the difficulty found in dissolving the polymer into chloroform it was found that toluene was a better solvent and xylene better still. The latter two solvents may be better at dissolving longer chain lengths of polymer so the polymer reprecipitated from toluene would exhibit a red shifted PL maximum and this is found to be the case. This could be further supported in future by preparation of a spin-coated film from the polymer reprecipitated from xylene which should also display an even greater red shift of the PL maximum.

The above argument is not the only possible reason for the shifting PL maxima; a further correlation is found on looking at the thickness of the polymer coating. Although no physical measurements of the thickness of the polymer coatings was made, a simple observation of the intensity of the colouration of the polymer films by eye shows that the thicker films are associated with a PL maximum at longer wavelength. The thickness alone should not change this physical characteristic but the presence of impurities or dopants in the polymer may be more concentrated in the thicker polymer films due to greater difficulty of their removal by washing them out or by electrochemical de-doping. This factor is another area requiring further investigation.

One of the electrochemically polymerised poly 3-n-octyl thiophene/ITO/glass slides was used in an electroluminescence study. This involved vacuum deposition of an aluminium cathode onto the polymer surface passing a stepped potential of up to 20 V via the Al cathode and the ITO anode. At a potential of 20 V the device failed without any EL being observed. Although it is disappointing that no EL was observed from the device it is encouraging that the polymer layer was robust enough to withstand the high potential since literature reports on EL from 3-polyalkyl thiophenes normally use lower potentials of between 6 to 14 V.^{17,18} The absence of EL from our device could be due to the film being too thick, requiring excessive applied voltages.

2.4.3 Electrochemical polymerisation studies on the Ruthenium and Rhenium complexes (8 and 9).

The first attempts at the polymerisation of the Ru complex **8** onto ITO failed. Following on from our experience from the electrochemical polymerisation of 3-n-octylthiophene onto ITO where it was found that using a large ITO electrode surface area caused overloading of the potentiostat, it was decided to try a different electrode material initially and return to an ITO electrode once favourable conditions for the electrochemical polymerisation had been established.

As with the earlier attempts at polymerisation of **8** on ITO, the complex failed to deposit onto the Pt electrode on cycling alone. It was decided to try holding the potential at +2.5 V for 30 min as this strategy was successful in the growth of poly 3-n-octyl thiophene. Using this technique microanalysisique the cyclic voltammetry (shown in Figure 2.2 of the Experimental) was obtained. Polymer growth was found to be initiated by holding the electrode at +2.5 V and once a layer had been formed growth continued on cycling from 0 to +2.5 V. The continuation of growth was indicated both by observation of the visible darkening of the red-orange colouration of the electrode and by the height of the Ru²⁺ to Ru³⁺ oxidation wave at +1.22 V. On repeated cycling the height of the waves

is reduced indicating that the electrode surface is becoming more resistive.

An important feature of the electrochemistry of the complex **8** is the absence of a polymer growth peak. Comparison to earlier work by Dr. Iraqi¹⁹ gives an explanation for this absence. Electropolymerisation of the tetrafluororoborate salt of **8** onto Pt via cycling from 0 to +1.7 V in methylene chloride was found to display a polymer growth wave at 1.05 V Figure 2.9. The wave was found to diminish on repeated cycling and eventually disappear. It may be the case that on holding the potential at +2.5 V prior to cycling, the polymer has passed the stage of growth which indicates the polymer growth peak.

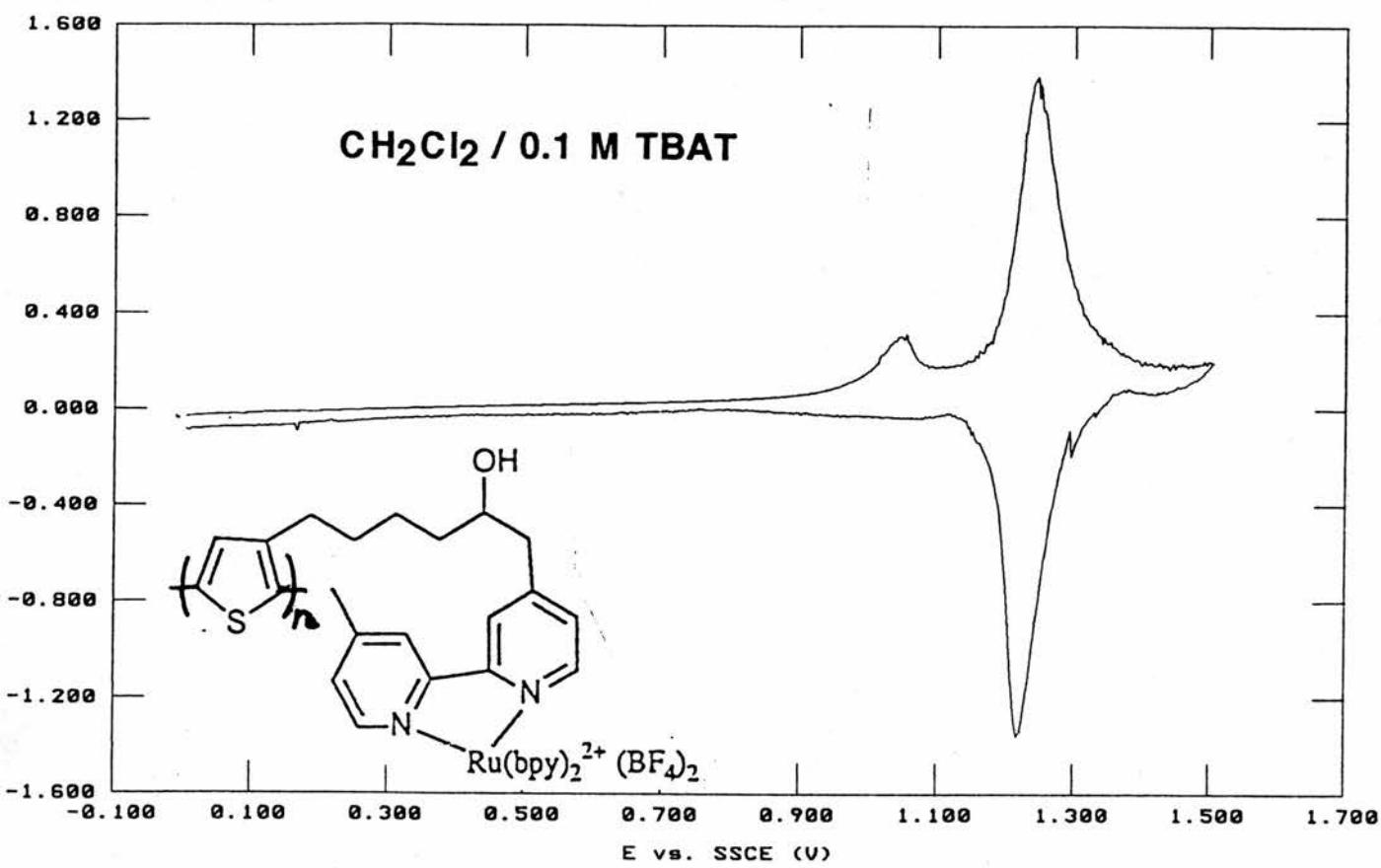


Figure 2.9 : Electropolymerisation of the tetrafluororoborate salt of **8** onto Pt via cycling from 0 to +1.7 V in methylene chloride

Using chronocoulometry, other group members¹⁹ have determined that for polymer **1** prepared in dichloromethane the ratio of charge under the polythiophene peak (at 1.05 V) to that under the Ru²⁺ to Ru³⁺ oxidation peak (at +1.22 V) indicates the ratio of Ru oxidisable centres vs. polarons is 4:1, consistent with the idea that on average the polaron is delocalised over 4 thiophene rings and providing good evidence that conjugated polythiophene segments are present in the film. This high population of Ru³⁺ promotes the well known over-oxidation of the polymer backbone with a consequent decrease in the polymer growth wave.

The presence of water in the electrolyte solution has long been known to have an important effect on the electrochemical polymerisation of thiophene²⁰. Since it was believed that the presence of water was partly responsible for the difference in CVs observed in the current and previous work, both the Ru complex **8** and the TBAT were thoroughly dried under vacuo and a fresh stock of HPLC grade acetonitrile was used to make a water free electrolyte solution. Electrochemistry of this solution using the same sized Pt working electrode as before made a dramatic difference to the CVs. The two most notable factors were the loss of reversibility of the Ru²⁺ to Ru³⁺ oxidation on repeated scans and with this change there was the observation of the fast growth of a robust film on the Pt electrode. The drop in reversibility of the Ru oxidation is maintained on transfer of the electrode to a blank solution and this change in nature is believed to be due to the thick film formed impeding electron exchange with the electrolyte.

The change in reversibility indicates that substantial coverages of polymer growth have occurred in this case whereas in the previous efforts using acetonitrile electrolyte the apparent lower coverages may have been simply due to adsorbed or crystallised material. This possibility is supported by the later sucessful attempts at growing films onto ITO, the more demanding substrate, from the same dry electrolyte solution.

A Ru complex polymer coated ITO electrode was submitted to the Physics Department for PL spectroscopy. The spectra obtained is shown in Figure 2.10 and displays three distinct bands at 450, 540 and 580 nm. The peak at 540 nm is believed to be caused by PL from the polythiophene backbone since a similar λ_{max} was obtained from the poly(3-n-octylthiophenes) **11**, **12** discussed earlier. The peak at 580 nm is due to PL of the Ru complex. PL spectra of the monomer showed one peak at the same wavelength. The peak at 450 nm was initially a source of confusion which was resolved satisfactorily; the ITO electrode had been contaminated with a fluorescent dyestuff from a paper label attached to the slide. The Physics Department had previously found this to be a common contaminant in PL spectroscopy and so the peak is almost certainly unconnected with the metallo-polymer.

This PL study shows that the Ru complex is capable of luminescence within the polymer matrix and is an encouraging result. Had no PL from the Ru complex been found, no excitation of the metal complex would be expected if the polymer were incorporated into a polymer LED device.

The attempted electrochemical polymerisation of the Re complex **9** using the same method as that which was found successful for the Ru equivalent **8** failed to give a robust film of polymer. The nature of the material grown on the electrode and the interpretation of the complex cyclic voltammetry have not yet been fully established. Work done by Deronzier *et al*^{19,20} may offer a reason for these changes over time. The CV shows firstly a decrease Figure 2.7 (a) in the current drawn, then a change to an increasingly more resistive electrode reaction that looks like polymer growth Figure 2.7 (b) (see Figure 2.7 in the Experimental).

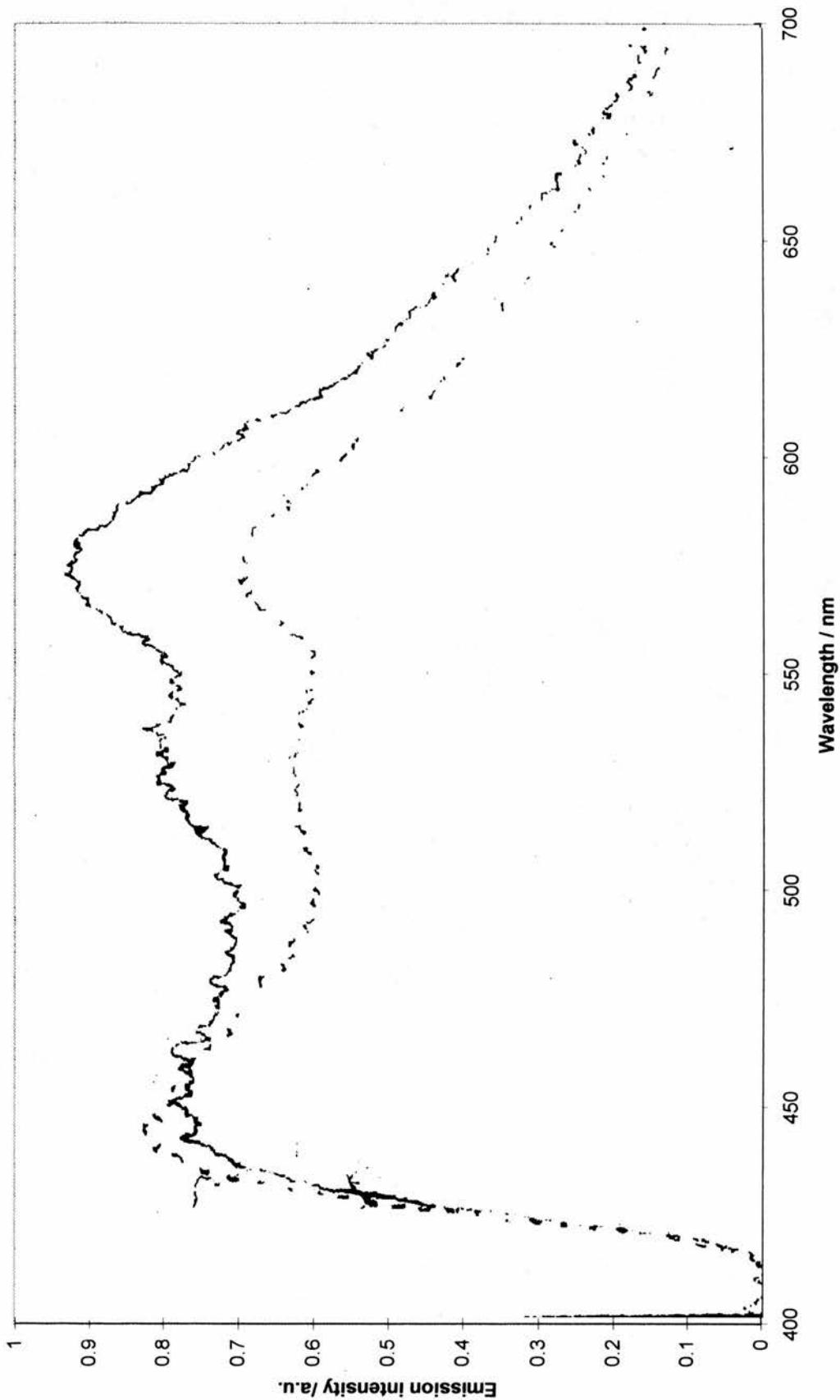
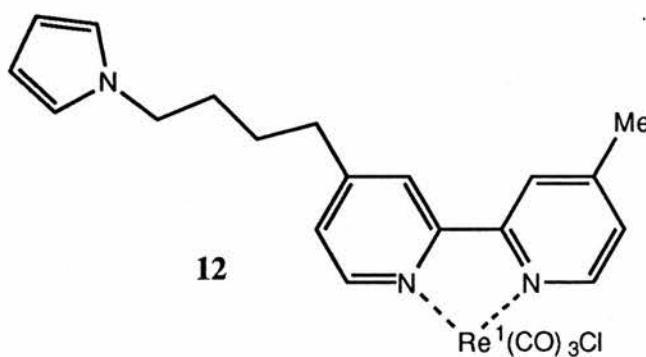
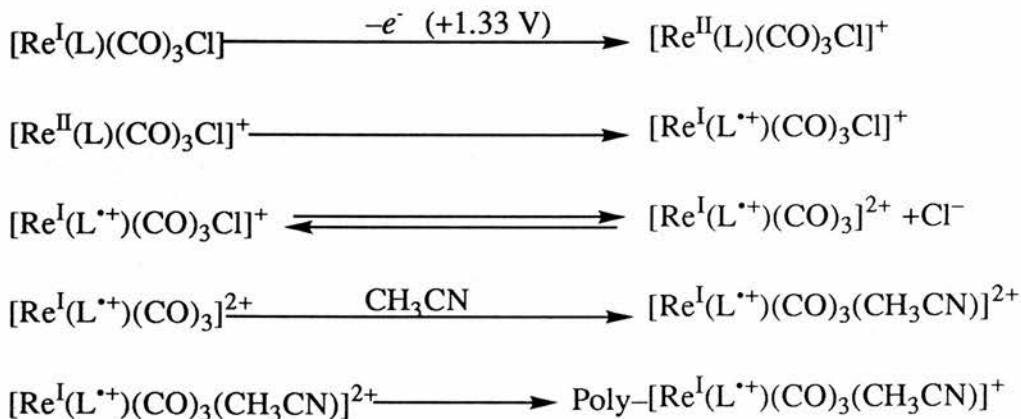


Figure 2.10: PL spectra of the polymer of [4-[6-(3-Thienyl)hexan-2-oyl],4'-methylbis-2,2'-bipyridine] ruthenium bis-2,2' bipyridine dihexafluorophosphate polymer **I**



Working with a pyrrole based complex **12**²¹ it was found that the following exchange reaction with the MeCN solvent takes place in the cell during polymerisation (L^+ refers to the pyrrole cation):



It should be noted that the redox potential of $[Re(L^+)(CO)_3(CH_3CN)]^{2+}$ ($E_p^a = +1.88$ V) is more positive than for $[Re^I(L)(CO)_3Cl]$. This means that the substituted complex can catalyse further oxidatively induced substitution away from the electrode. This is called "electron transfer chain" (ETC) catalysis.

A similar exchange reaction may be taking place in the case of the Re complex **9** used in this work except that in our case the $[Re^I(L)(CO)_3Cl]$ oxidations ($E_p^a = +1.33$ V) may not be quite positive enough to oxidise the thiophene ligand. This could possibly explain the dramatic change in the cyclic voltammetry. If it is considered that the first few cycles promote the exchange reaction, once a significant amount of the complex has

coordinated with MeCN a second electrode reaction (such as polymerisation of the MeCN co-ordinated complex) may begin.

The fragility of the film found on the electrode on transfer to the blank solution suggests that the material was not a polymer. One possibility that would account for the increase in resistivity of the electrode on cycling in the Re complex solution may be the crystallisation of the complex onto the electrode. The complex could be in either the chloride or MeCN coordinated forms.

A disturbing factor brought up by the possibility of the exchange reaction is that in the exchanged form the Re complex has lost its neutrality and exists as a charged complex. This change loses one of the main advantages of using **9** since the lack of a counter ion may lead to a greater opportunity for the complex to produce EL as discussed earlier.

To conclude, the Ru monomer **8** may be successfully polymerised electrochemically provided extreme precautions are taken to ensure dryness of the solvents and electrolytes. PL from both the backbone and complex is observed with comparable intensity. However, more work is required to address the problems associated with the uniformity of thickness of the polymer films before such complexes may be used as the emissive layers in polymer LEDs.

On attempts to polymerise the Re complex **9** in coordinating solvents the Cl⁻ is thought to be readily replaced by solvent. This leads to an 'induction period' before polymerisation. Further exploration of polymerisation in non-coordinating solvents will be necessary before a truly ion-dopant free metal containing polymer is obtained.

2.5 References

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Chapter 3

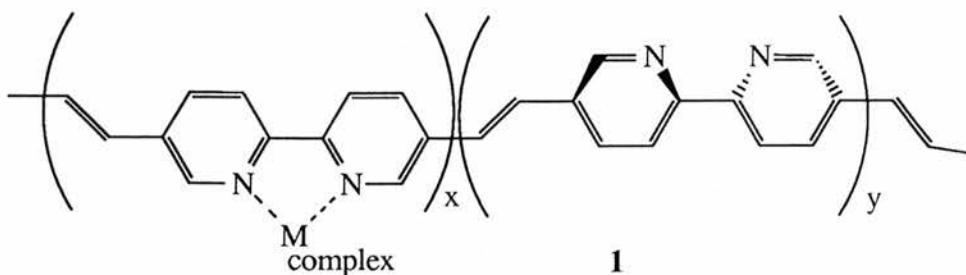
Synthesis of monomers for Poly(bipyridinevinylene) and their Polymerisation Behaviour

3.1 Introduction

The objective of this study was to synthesise a series of novel polymers, poly(bipyridinevinylenes). As with the objectives set out for the thiophene based metallo-polymers described in Chapter 2, such a polymer would have a fully conjugated backbone which would provide opportunities for charge transport and perhaps EL combined with sites for the chelation of luminescent metal complexes.

To date, LED devices which rely upon metal complexes as the emissive layer have either been based upon mixtures of the complex with organic charge carriers¹ or based upon monomeric complexes designed to have reasonable processability and charge carrier properties.^{2,3,4} The metallo-polymers discussed in Chapter 2 were studied with the main aim of finding a way around some of the problems associated with the design of metal complex LED's. However, before attempting to manufacture a device from these thiophene based polymers, problems with the uniformity of their electrochemically grown films will have to be addressed.

A most interesting factor in the design of poly(bipyridinevinylene) **1** is the position of the chelation sites which lie along the conjugated backbone of the polymer. Rather than attachment to the polymer backbone via an alkyl spacer group, the metal centre is bonded directly to the polymer backbone. Indeed, since the mutual repulsion of the nitrogen lone pairs naturally twist the bipyridine rings out of planarity, a factor which disturbs conjugation, the presence of the metal centre brings the rings back into planarity. Thus the metal complex becomes an integral part of the conjugated backbone.



In a study by Parker *et al*^{6,7} on metal functionalised polymer modified electrodes it was found that conjugation between a polymerisable thiophene and a metal bipyridyl complex via an ethylene group significantly lowered the oxidation potential of the thiophene. It is thus reasonable to assume that incorporation of a metal complex into a conjugated polymer backbone will lead to alteration in the polymer's redox properties with related effects on the polymer's band gap.

Where a luminescent metal complex is employed in this way the luminescent properties of the metallo polymer are of great interest. On applying a voltage through such a material within a polymer LED device, charge carriers migrate through the polymer and meet to form excitons on the polymer backbone. If the excitation energy of the metal complex is lower than the bandgap of the polymer then it is reasonable to assume that energy transfer may occur from the polymer-based excitation to the metal complex. Luminescence from the excited state of the metal complex would then be observed. Moreover, since EL from conjugated polymers may be argued to arise mainly *via* intrachain processes,⁸ chelating the metal complex on the polymer backbone could promote such energy transfer and associated luminescence.

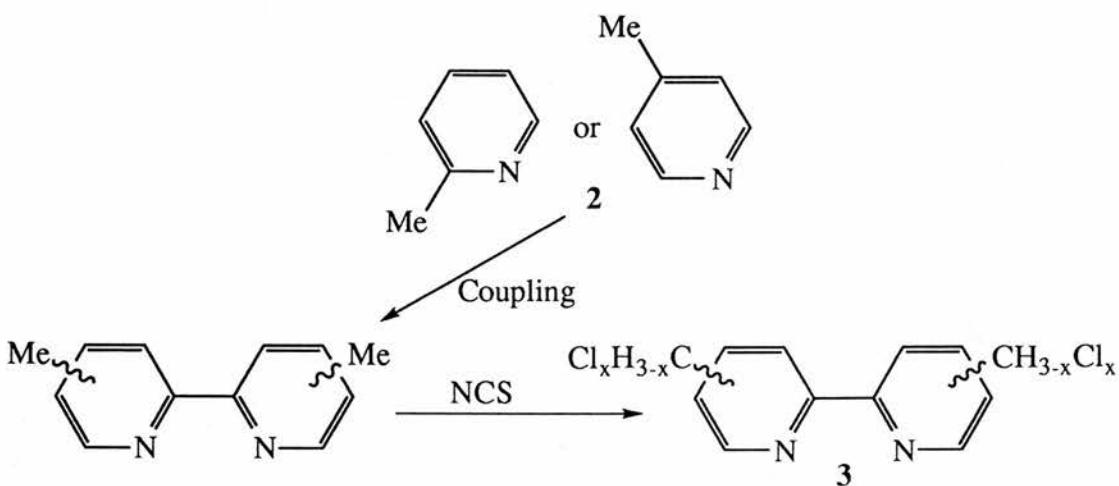
The synthetic work is aimed towards providing the polymer **1** by a variety of routes. The first consideration is the attainment of functionalisation on the bipyridyl rings. 5,5'-functionalisation was sought on simple steric grounds. It is believed to be the best option since this would avoid blocking up the nitrogen chelation sites (a possible outcome of 6,6'-functionalisation) and also provides an open site for polymer growth. Steric competition for growth could arise from functionalisation on the 4,4'-(or worse, the 3,3')-sites. This aim complicated the synthesis, since whereas 4,4'- and 6,6'-functionalised bipyridines (eg. 4,4'-dimethyl-2,2'-bipyridyl) are readily available commercially, the 5,5'-versions are generally not. The reason for this lack of commercial precursors may be due to the lack of reactivity of the 5,5'-site. Thus 2,2'-bipyridine can be N-oxidised and nitrated to obtain intermediates from which many 4-substituted⁹ and 4,4'-disubstituted

derivatives^{10,11} can be synthesised. In addition 6-substituted^{12,13} and 6,6'-disubstituted bipyridyls^{12,14,15,16} can be prepared by direct substitution of the 2,2'-bipyridyl ring system. However, the 5,5'-positions are unreactive towards electrophilic attack save for low yielding sulphonation¹⁷ and bromination¹⁸ reactions achieved under vigorous conditions.

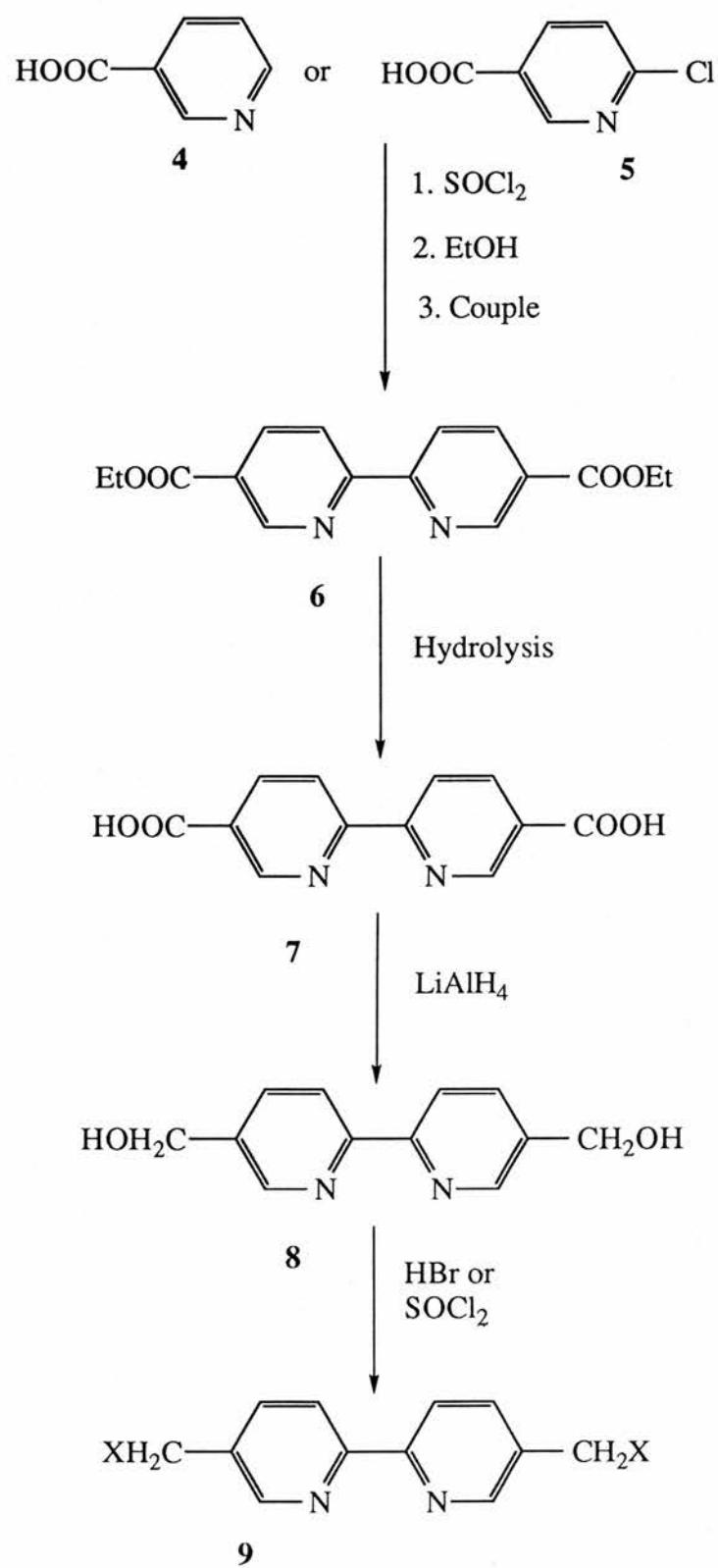
This lack of reactivity at the 5,5'-sites means that 2,2'-bipyridyl is a poor candidate as a starting material in the synthesis of **1**. The synthesis therefore was planned to start with the coupling of 3-functionalised pyridines. This choice of functionality is dictated by the effect that the coupling reaction will have upon the functional group and by the eventual target molecule in later synthetic steps. For this study it was decided that a similar approach to the synthesis of the eventual vinylene linkage as that used by Holmes *et al*¹⁹ in their synthesis of PPV would be employed. In this route 1,4-bis(halomethyl) benzene is a key intermediate in the synthesis of a processable precursor polymer. Since precursor methodology was found to be important in the production of device quality films of PPV, it should be of paramount importance in the bipyridyl analogue **1** which would be expected to present greater processing problems due to the polar nature of the pyridine units. A further impetus for the use of the precursor method is down to the great difficulty in devising a synthetic strategy that would allow the attachment of solubilising groups on poly(bipyridinevinylene) without introducing steric barriers towards chelation or polymerisation.

A synthetic strategy was devised to provide 5,5-bis(halomethyl)-2,2'-bipyridyl from readily available materials and proven techniques. The 2,2-bipyridine linkage has traditionally been achieved using Raney Nickel by the method of Badger and Sasse.²⁰ However, more recently a number of methods utilising Pd on charcoal^{21,22,23} or a Ni triphenylphosphine complex²⁴ have been developed and these are favoured due to the considerable risk of explosion during the preparation of degassed Raney Nickel.²⁵

Previous work on the synthesis of 4,4'-²⁶ and 6,6'-bis(halomethyl)-2,2'-bipyridines²⁷ by free radical halogenation of the corresponding dimethyl bipyridyls was found to be problematic. Monohalogenation of the methyl groups of 4,4'-²⁶ and 6,6'-dimethyl-2,2'-bipyridines²⁷ under free radical conditions did not occur selectively, rendering ineffective the potentially simple route *via* picolines **2** to bis(halomethyl)-2,2'-bipyridines **3** shown below.

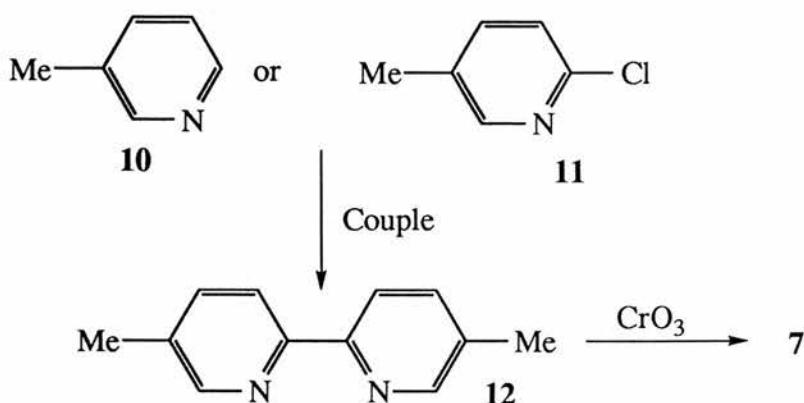


Instead, 3-nicotinic acid **4** was chosen as a starting material due to its low cost and versatile carboxylic acid function. In addition, the 6-chloro-3-nicotinic acid **5** is also commercially available and this may be used for regiospecific coupling.^{22,24} Previous experience with the synthesis and handling of 4,4'-dicarboxy-2,2'-bipyridine²⁸ has shown that such diacids are difficult to isolate and purify due to poor solubility. For this reason it was decided to attempt coupling of the easily attainable ethyl esters **6** of the nicotinic acids. This was intended to ease the separation of the product from the coupling reaction residues and provide a soluble and hence more easily characterisable material. Once isolated the diester may be easily converted to the diacid **7** by hydrolysis. Two further steps are then required to provide the target 5,5'-dimonohalomethyl-2,2'-bipyridyl. Reduction of the diacid **7** by lithium aluminium hydride has been reported by Whittle²⁹ to provide 5,5'-bis(hydroxymethyl)-2,2'-bipyridyl **8**. The alcohol may be conveniently converted to the target bis(halomethyl) derivative by conventional reagents such as HBr or SOCl₂.



Several variations on this scheme are available. A most obvious alternative would be to start with the coupling of 3-picoline **10** or 6-chloro-3-picoline **11** to give 5,5'-dimethyl-2,2'-bipyridine. Subsequent oxidations of 4,4'-dimethyl-2,2'-bipyridine to give

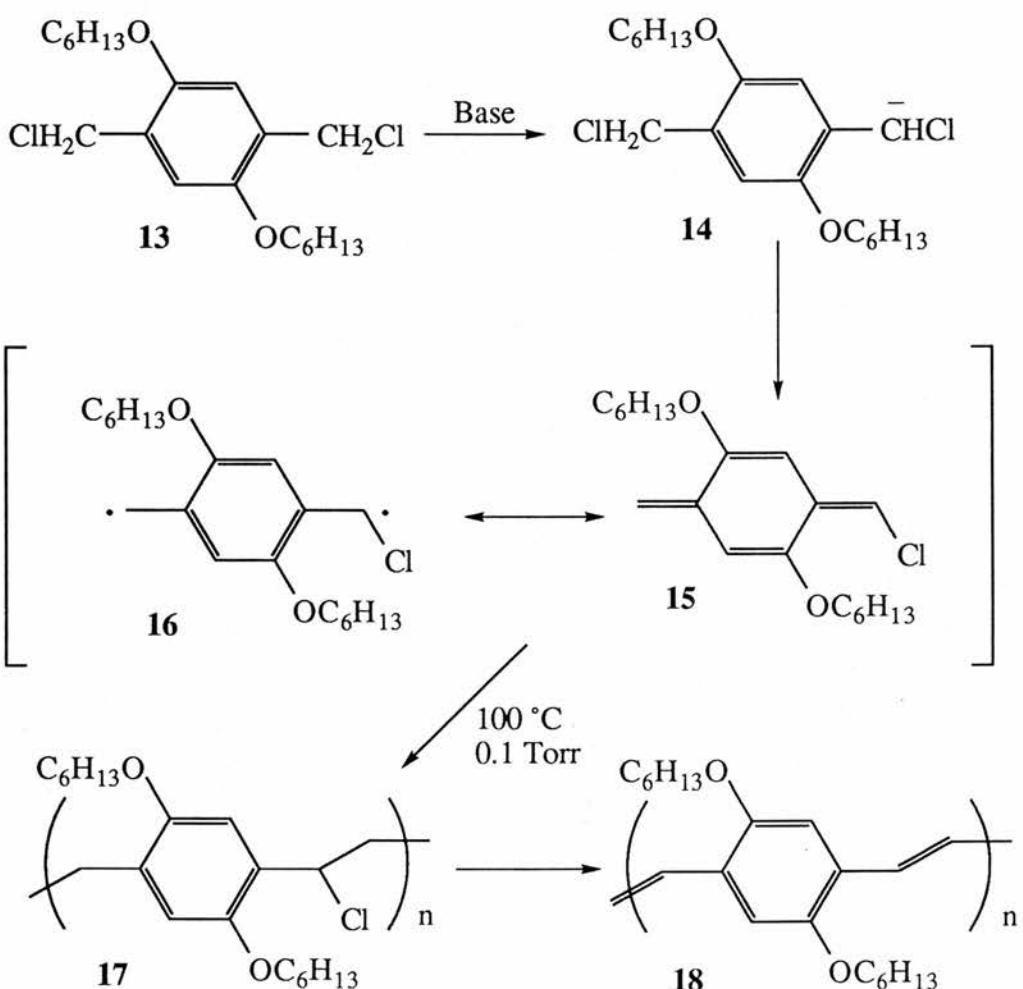
the diacids have been successful using permanganate^{21,28} and have also been run with 5,5'-dimethyl-2,2'-bipyridine.²⁹ However in all these cases only moderate yields have been obtained. Vierling and Garelli³⁰ accomplished the oxidation of 4,4'-dimethyl-2,2'-bipyridine to give the diacid in 90% yield using Cr₂O₇ and so attempting this reaction with the 5,5'- equivalent **12** would seem a sensible aim.



Once prepared, the 5,5'-dihalomethyl-2,2'-bipyridine **9** is to be used for polymerisation studies. The most straightforward of these was first investigated by Gilsch et al³¹ and recently applied to PPV synthesis by Swatos and Gordon³². Here 2,5-di-*n*-hexyloxy-1,6-bis(chloromethyl)benzene **13** was prepared and polymerised by the action of potassium-*t*-butoxide base. The base operates by abstraction of a benzyl proton to form the anion **14**. This is stabilised by loss of chloride on the formation of the quinoid **15** which has a diradical character **16**. The quinoid proceeds to polymerise to the precursor polymer **17** which maintains flexibility and hence good processing qualities due to the retention of the flexible alkyl linkages. After the precursor polymer is processed into films (e.g. by spin coating), heating in vacuo gives the fully conjugated PPV **18**.

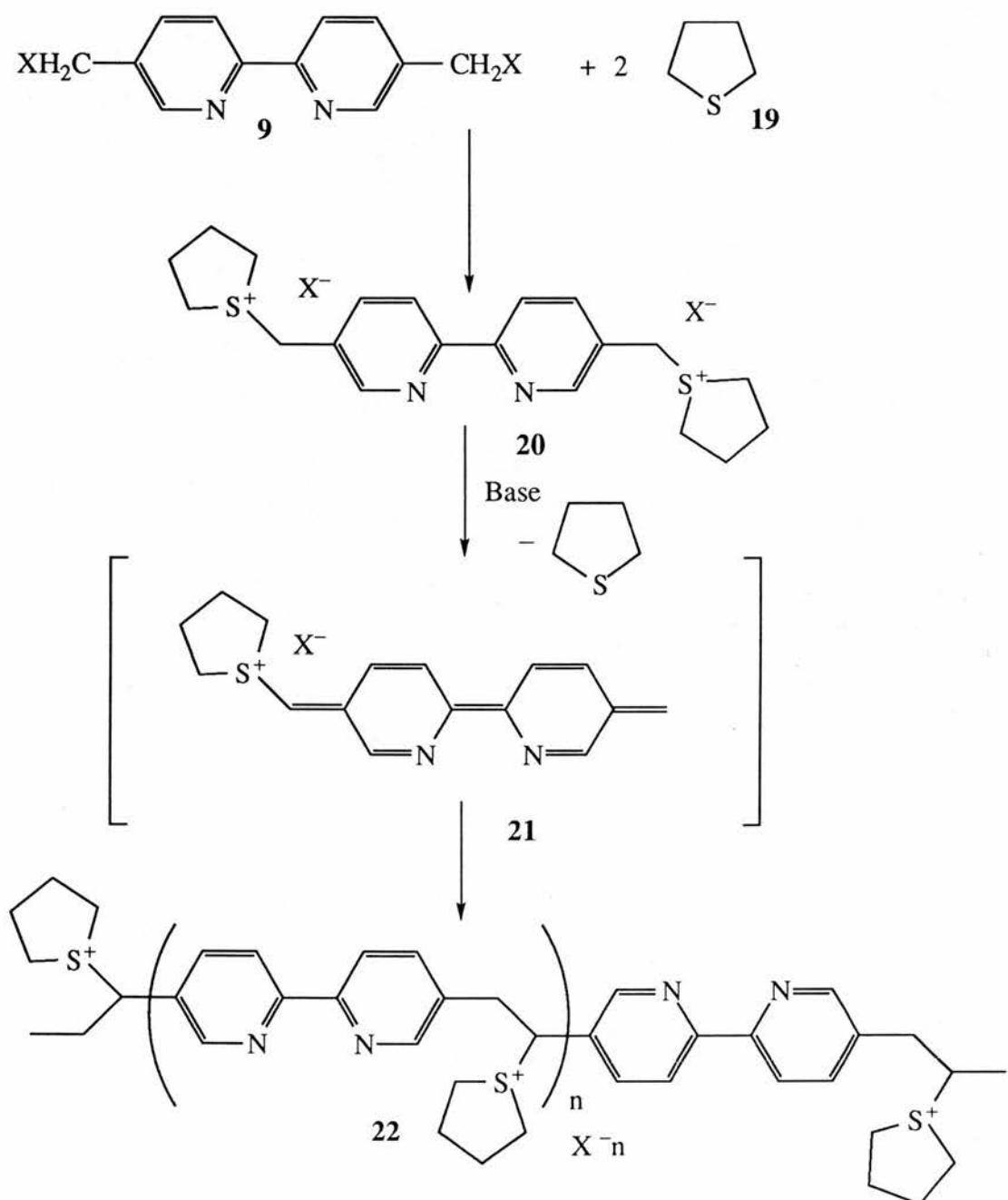
Although the Gilsch strategy may directly provide a poly(bipyridinevinylene) by substituting 5,5'-dihalomethyl-2,2'-bipyridine **9** for the alkoxy-substituted bis(chloromethyl)benzene **13**, it must be noted that the lack of solubilising groups on **9**

such as the alkoxy groups on **13** mean that in all likelihood such a polymer will be difficult to dissolve in common solvents and so other routes will be investigated.



In their synthesis of PPV Holmes *et al*¹⁹ utilised a precursor polymer route first devised by Wessling³³. The synthesis and base polymerisation steps operate in a very similar fashion to the Gilsch route detailed above save that the processability of the precursor is maintained via the use of tetrahydrothienyl salts. Rather than involving the use of alkoxy derivatives as solubilising units a simpler synthesis based on 1,4-bis(chloromethyl)benzene and its reaction with tetrahydrothiophene produced a water soluble dication monomer. Action of base produced a precursor polymer which maintained its processability through flexible aliphatic links along the backbone and the retention of one tetrahydrothienyl solubilising group per repeat unit.

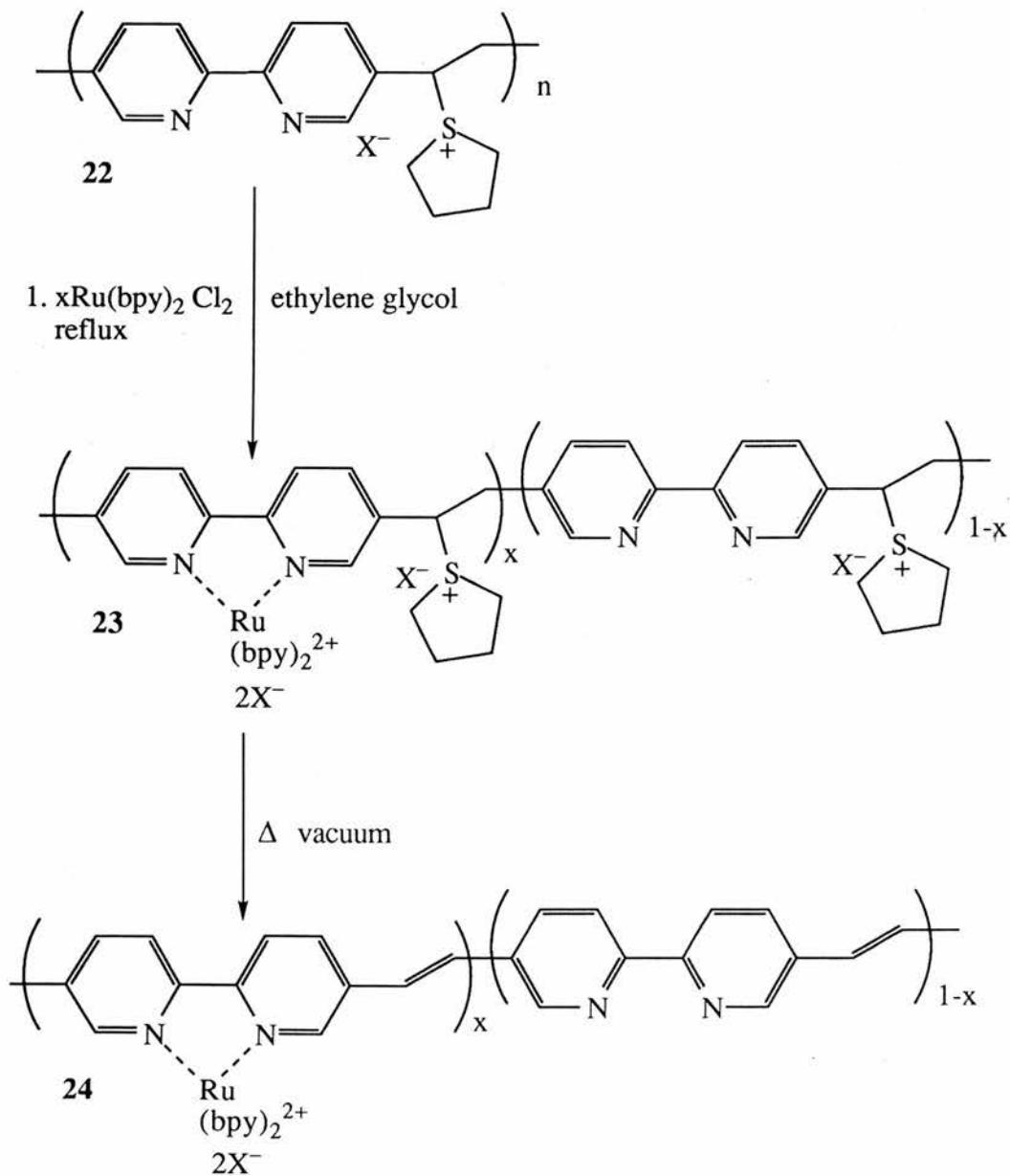
Taking this idea and utilising a 5,5'-dihalomethyl-2,2'-bipyridine **9** it may be expected that the polymerisation could take place as illustrated below. Reaction of **9** with two equivalents of tetrahydrothiophene **19** would lead to the dication **20**.



Action of base upon the dication **20** may lead to benzylic hydrogen abstraction as seen before and this in turn could trigger the loss of tetrahydrothiophene due to stabilisation

through quinoid formation **21**. The quinoid may then polymerise to form the precursor polymer **22**.

If such a precursor polymer **22** is achieved then many of its qualities will be worthy of study. Of primary concern would be the solubility of the polymer since at this point, processing of the PPV analogues into device structures normally take place. In the case of **22** however this may be a good stage in which to chelate luminescent metal complexes onto the bipyridyl sites



Metal chelation may be possible via the same route as found to be successful for the thiophene metal complexes discussed in Chapter 2. Here, however, solubility of the precursor polymer is of great concern as are the effects on solubility of the chelation of the metal complexes. The approach illustrated assumes solubility of the precursor polymer **22** under ethylene glycol reflux for chelation of $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$. Loading of the metal complex onto the polymer may be controlled by simple addition of the required mole fraction of the $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$ to the reaction mixture. Ideally, high levels of loading should provide a metal centre at every bipyridyl site ($x=1$) although this may be constrained by steric and solubility factors and thus it is more reasonable to assume that a copolymer may be formed **23**.

The copolymer **23** should at this stage still have flexible aliphatic linkages and solubilising tetrahydrothienyl groups, provided that these groups are not found to be so thermally labile as to be lost in the chelation step. If the synthesis is successful to this extent, further processing to provide films of the polymer may be achievable using suitable solvents. This may then be followed by heat treatment in vacuo to provide the fully conjugated metallo polymer **24**.

3.2 Experimental

General experimental techniques remain the same as for Chapter 2 save for the following exceptions. 3-picoline (BDH) was purified by distillation onto 4 A sieves. 3-Ethyl nicotinate and 6-chloro-3-nicotinic acid were used as supplied by Aldrich.

6-chloro-3-ethylnicotinate

6-Chloro-3-nicotinic acid (12.0g, 76 mmol) was refluxed in thionyl chloride (30 cm³) for 4 h. The excess thionyl chloride was evaporated off and the residues cooled to 0 °C under N₂. Dry ethanol (20 cm³) was added and the mixture slowly warmed to reflux for 1 h. During this period HCl gas was evolved. Vacuum distillation of the products gave the title compound (11.0 g, 78%) as a colourless oil bp 92 °C / 0.7 torr; δ_H 8.99 (1H, d, *J*9, ArH), 8.31 (1H, d, *J*9, ArH), 7.02 (1H, s, ArH), 4.54 (2H, q, *J*7, CO₂CH₂) and 1.52 (3H, t, *J*7, Me); δ_C 168.66 (ArCO₂Et), 151.40 (ArC), 139.78 (ArC), 124.32 (ArC), 110.82 (ArC), 61.84 (OCH₂) and 14.29 (CH₃).

Pd-catalysed coupling Method (1) of 3-ethyl nicotinate (synthesis of 5,5'-diethoxycarbonyl-2,2-bipyridine).

This was based on the method of Whitten *et al.*²¹ 3-Ethyl nicotinate (50 g, 327 mmol) and Pd on charcoal (2 g, 10 % Pd) were refluxed for 72 h. Toluene (20 cm³) was added and the mixture refluxed for a further 30 min. Attempts were made to filter the products while hot but these failed due to persistent clogging of the sinter by a black tar like residue. The toluene was evaporated off to leave a black tar. Distillation of the tar gave a fraction at 58 °C / 0.4 torr. found by ¹H NMR to be the starting material (40.8 g). Attempts at extraction of the tar with further aliquots of toluene, ethyl acetate and DMF failed to separate any further components.

Pd-catalysed coupling Method (2) of 6-chloro-3-ethylnicotinate (synthesis of 5,5'-diethoxycarbonyl-2,2-bipyridine).

This was run by modification of the method of Bamfield and Quan.²² 6-chloro-3-ethylnicotinate (9.38 g, 50 mmol), triethylbenzylammonium chloride (2 g), Pd on charcoal (0.15g, 10% Pd), sodium hydroxide (6.8 g in 22 cm³ water) and sodium formate (3.8 g) were mixed and refluxed with the addition of a further 60 cm³ of water for 4 h with stirring. After a further addition of sodium formate (3.8 g) the mixture was left to reflux for a further 20 h. The products were extracted with chloroform (3 x 100 cm³) and the solvent dried and evaporated to yield 5,5'-diethoxycarbonyl-2,2-bipyridine (0.2 g, 2.6 %) as white needles m.p.148-150 °C, (lit³⁴ 149-150 °C); δ_H 9.35 (1H, s, ArH), 8.59 (1H, d, J9, ArH), 8.46 (1H, d, J9, ArH), 4.55 (2H, q, J7, CO₂CH₂) and 1.53 (3H, t, J7, Me); δ_C 165.15 (ArCO₂Et), 158.21 (ArC), 150.58 (ArC), 138.10 (ArC), 125.51 (ArC), 121.24 (ArC), 61.56 (OCH₂) and 14.30 (Me).

Ni complex catalysed coupling of 6-chloro-3-ethylnicotinate (synthesis of 5,5'-diethoxycarbonyl-2,2-bipyridine).

This was run by modification of the method of Iyoda *et al.*²⁴ To a stirred, deep blue solution of nickel(II) chloride hexahydrate (11.8 g, 50 mmol) and triphenylphosphine (52 g, 200 mmol) in DMF (250 cm³) under nitrogen at 50 °C, zinc powder (3.2 g, 50 mmol) was added. After 1 h the colour of the mixture changed to a rich red-brown. 6-Chloro-3-ethylnicotinate (9.38 g, 50 mmol) was then added and the mixture was continually stirred at 50 °C for a further 2.5 h. The mixture was then poured into an ammonia solution (250 cm³, 2 M) and extracted with chloroform (3 x 250 cm³). The organic layer was washed with water (3 x 250 cm³), dried and evaporated to yield a white solid (52.4 g) mixed with many plate-like crystals of triphenyl phosphine. The solid was recrystallised from petroleum ether (b.p. 100-120 °C) and 3 crops of white needles removed on cooling of the solution (0.92g). The product was found by TLC (chloroform : methanol 3 : 2) to be a mixture of 5,5'-diethoxycarbonyl-2,2-bipyridine, triphenylphosphine oxide and triphenyl phosphine. Two further recrystallisations of the product gave 5,5'-diethoxycarbonyl-2,2-

bipyridine (0.57 g, 7.4 %); m.p. 147-149 °C; ^1H NMR as 3 above, free from impurites by TLC. Further recrystallisations from the mother liquor indicated some 5,5'-diethoxycarbonyl-2,2-bipyridine was still present by TLC. Further purification would have required a laborious series of column chromatography and was not continued.

Raney nickel catalysed coupling of 3-ethylnicotinate (synthesis of 5,5'-diethoxycarbonyl-2,2-bipyridine).

This was run by modification of the method of Sasse and Whittle.³⁴ Commercial Raney nickel (Aldrich, slurry in water) was converted to the ethanol slurry by flooding and decanting off excess ethanol 8 times. Great care was taken to avoid spillages as the dried particles of Ni spontaneously burst into flame and threatened to ignite the solvent. 3-Ethylnicotinate (50 g, 267 mmol) was added and the mixture allowed to reflux for 72 h. On cooling, a small quantity of white needles was observed on the Raney nickel surface. These were redissolved by heating the mixture and the Raney nickel was removed by hot filtration on a 10 cm sinter through Supra-cell using a water pump and variable air leak. Care was taken to always ensure a layer of liquid was retained over the Ni surface and to this end extra ethanol was occasionally added to the filter. On one occasion the air leak failed and the solution briskly flowed through the filter exposing the Ni briefly. On flooding with ethanol the Ni sparked and caused a small explosion and resultant fire. The fire was extinguished by flooding the area with water and washing all residues down the drain.

The above was repeated, substituting chloroform for ethanol in all cases. This reduced the risk of fire and aided the filtration of the products since these are more soluble in chloroform than ethanol. After filtration the chloroform was evaporated off and unreacted 3-ethylnicotinate was distilled off under reduced pressure until only 5 cm³ of residues remained. These residues were treated with chloroform (20 cm³) and filtered hot to remove insoluble material. Evaporation of the solvent yielded dull yellow crystals. Recrystallisation from petroleum ether (b.p. 100-120 °C) yielded 5,5'-diethoxycarbonyl-2,2-bipyridine (0.88 g, 2.2 %); m.p. 147-149 °C; ^1H NMR as 3 above.

Synthesis of 5,5-dimethyl-2,2'-bipyridine

a. *Preparation of W7-J Raney Nickel*

This was run by the modification of the method of Sasse.³⁶ Using an efficient magnetic stirrer in a 2 l flask surrounded by a large water bath sodium hydroxide (160 g) is dissolved by portionwise addition to 600 cm³ of distilled water. Under fast stirring, 1:1 aluminium-nickel alloy (125 g) was added portionwise as fast as possible but at such a rate that none of the material is lost by the vigorous frothing that occurs on these additions. When all the alloy had been added and the frothing subsided, the stirrer was slowed and all catalyst run down the sides of the flask with distilled water. Digestion of the catalyst was continued for 6 hrs by filling the water bath with boiling water and topping up the water level above the catalyst to ensure that it was covered and not exposed to air at any time. After this period the catalyst was allowed to stand for 15 h. at room temperature.

The catalyst was then washed by decantation with 10 x 250 cm³ portions of distilled water and transferred to a 1 l round bottomed 3 neck flask by washing with distilled water. The total volume of water and catalyst was adjusted to about 300 cm³ and the flask placed in a cold water bath. The central neck was fitted with a dropping funnel and the other two necks were connected to 3 l Buchner flasks by short lengths of thick walled rubber tubing via a T-piece. These in turn were connected to two equally efficient water pumps and at one side the T-piece was linked to a vacuum gauge and the other side a positive pressure argon line. The argon line was provided to purge the system if evidence of a leak was found during evacuation of the apparatus or during degassing. To control the pressure inside the apparatus, a screw clamp was placed between each Buchner flask and each pump. With the clamps completely closed and the tap at the argon line turned off the two pumps are turned on.

Pressure inside the apparatus is slowly reduced by partial opening of the clamps at such a rate that no excessive frothing of the catalyst occurs. When both clamps were fully open the pressure was closely monitored and held at around 12 torr. Occasionally, either

pump would back up due to fluctuations in water pressure in which case the screw clamp at that end would be closed until normal flow was resumed.

After holding the apparatus under reduced pressure for 30 min. the temperature of the water bath was increased gently and gradually to boil off the water in the flask. This took 2 h. at 50 °C then the water bath was raised to 100 °C over 20 minutes and maintained at this temperature for a further 2 h. The W7-J Raney nickel catalyst was then cooled to 60 °C ready for use.

b. *Coupling of 3-picoline (Synthesis of 5,5'-dimethyl-2,2'-bipyridine)*

With the clamps closed at both sides, 3-picoline (80 cm³) was run into the W7-J Raney nickel catalyst via the dropping funnel with care to ensure that no air entered the apparatus. The flask was carefully shaken to wet the catalyst thoroughly before a further 80 cm³ of 3-picoline is introduced in the same way. The catalyst was now well covered with the picoline and after a further 40 cm³ was added the flask was opened to the air and disconnected from the vacuum system.

The mixture was set up to reflux for 72 h then cooled to 60 °C. Most of the liquid was then decanted and filtered through a sinter with care being taken to maintain some liquid above the catalyst as in preparation 5 (above). Additional 3-picoline was used where necessary for this purpose. A further 50 cm³ of 3-picoline was added to the flask and the mixture heated to reflux for 10 min. before cooling to 60 °C and decanting as before. This was repeated twice and the remaining catalyst in the flask was flooded with water and set aside.

The filtrates were set up for vacuum distillation and 3-picoline started to distil off at 42 °C / 3 torr. However, the solution was bumping very badly and so the 3-picoline was finally slowly removed on an evaporator at 100 °C / 20 torr. The residues were recrystallised from petroleum ether (600 cm³ of b.p. 40-60 °C). Two crops (29.9 g and

1.3 g) of 5,5-dimethyl-2,2'-bipyridyne were isolated without need for further purification; m.p. 114 - 115 °C (lit³⁴ 114.5 - 115 °C); δ_H 8.49 (2H, s, ArH), 8.27 (2H, d, *J*9, ArH), 7.60 (2H, d, *J*9, ArH), and 2.35 (6H, s, 2Me); δ_C 154.00 (ArC), 149.74 (ArC), 137.58 (ArC), 133.17 (ArC), 120.46 (ArC) and 18.33 (CH₃)

Subsequent repeat of the above procedure again with freshly prepared degassed W7-J Raney nickel furnished a further 45 g of **12**.

Synthesis of 5,5'-dibromomethyl-2,2'-bipyridine.

This was run by modification of a method supplied by Moore.³⁷ 5,5'-Dimethyl-2,2'-bipyridine (0.92 g, 5 mmol) and N-bromosuccinimide ((1.78 g, 10 mmol) were stirred vigorously in carbon tetrachloride (100 cm³). The solution was heated to 65 °C and irradiated with a mercury vapour lamp for 2 h. During this time the NBS is converted to the succinimide which precipitates out of the solution and floats to the top. The mixture was filtered at about 50 °C then half the volume of solvent was evaporated off. The product was filtered off after slow cooling and recrystallised from chloroform to give the title compound 5,5'-dibromomethyl-2,2'-bipyridine as light yellow-white crystals (0.60 g, 35 %); m.p. 210 - 211 °C (lit³⁸ 212 °C); δ_H 8.70 (2H, s, ArH), 8.40 (2H, d, *J*9, ArH), 7.88 (2H, d, *J*9, ArH), and 4.52 (4H, s, ArCH₂Br); δ_C 155.67 (ArC), 149.61 (ArC), 137.87 (ArC), 134.12 (ArC), 121.39 (ArC) and 29.57 (ArCH₂Cl).

The above reaction was scaled up to use 10 mmol of the bipyridine and 20 mmol of NBS in 200 cm³ carbon tetrachloride. Work up as before provided 1.80 g of 5,5'-dibromomethyl-2,2'-bipyridine (53 % yield). A subsequent scale up to 20 mmol of the bipyridine and 40 mmol of NBS in 300 cm³ carbon tetrachloride gave 3.79 g 5,5'-dibromomethyl-2,2'-bipyridine (55 % yield). Subsequent repeats at this scale reliably returned product yields of 53-56 %.

Synthesis of 5,5'-dimethyltetrahydrothiophenium-2,2'-bipyridine

This was run by modification of the method of Lenz *et al.*³⁷ 5,5'-Dibromomethyl-2,2'-bipyridine (1.04 g, 3 mmol) and tetrahydrothiophene (0.9 g, 10 mmol) were stirred in methanol / water (5 cm³ 8 / 2) at 50 °C for 24 hours. During this time the suspension of the bipyridine gradually dissolved as it was converted to the soluble salt. The mixture was poured into acetone (10 cm³) at 0 °C in a failed attempt at precipitation. The solvents and excess tetrahydrothiophene was evaporated off to give a crude product as a dull yellow waxy solid. Routine ¹H NMR (60 MHz) of the crude material was similar to that of the bipyridine starting material with further major peaks in the aliphatic region. Integration suggested the presence of tetrahydrothiophene units in the expected 2:1 ratio against the bipyridine.

Attempts at purification by recrystallisation or precipitation of the crude product from ether, acetone, ethanol and methylene chloride failed. The crude material was dissolved up in methanol (10 cm³) and saturated sodium perchlorate was added dropwise with stirring. A light brown sticky immiscible oil crashed out of the solution and surrounding the oil traces of a yellow precipitate formed which cleared on shaking the flask. Water (10 cm³) was added and the mixture heated to 60 °C to dissolve the products. After 10 min a small quantity of insoluble brown solid was filtered off then the flask was cooled slowly to yield further sticky immiscible brown oil. Evaporation of the solvent left sticky brown tarry residues. These were abandoned without further characterisation.

The above reaction was repeated using 5,5'-bisbromomethyl-2,2'-bipyridine (2.08 g, 6 mmol) and tetrahydrothiophene (1.8 g, 20 mmol) in methanol / water (10 cm³ 8 / 2) again at 50 °C for 24 hours. Once cooled the solution was stirred and a saturated solution of potassium hexafluorophosphate in methanol was added dropwise resulting in the formation of pink crystals.

These were filtered and washed with cold methanol then recrystallised from acetone / water (1 : 1) to give the product 5,5'-bis(tetrahydrothiopheniummethyl)-2,2'-bipyridine hexafluorophosphate(3.03 g, 78 %); mp 230 °C dec; δ_H (DMSO) 8.89 (2H, s, ArH), 8.50 (2H, d, *J*9, ArH), 8.18 (2H, d, *J*9, ArH), 4.67 (4H, s, ArCH₂), 3.52 (8H, m, S-methylenes) and 2.26 (8H, m, methylenes); δ_C 155.97 (ArC), 151.45 (ArC), 140.03 (ArC), 127.58 (ArC), 121.70 (ArC), 43.64, 42.98 and 28.65 (2CH₂); ν_{max} 3005, 2962, 1607, 1542, 1470, 1381, 1255, 1058, 1026, 818 and 562; M⁺ (EI) 544 (5), 394 (7), 364 (36), 214 (8), 183 (59), 169 (12), 120 (20) and 107 (100).

Synthesis of 5,5'-bis(ethoxythiocarbonylthiomethyl)-2,2'-bipyridine.

This was run by modification of the method of Son *et al.*⁴⁰ 5,5'-Dibromomethyl-2,2'-bipyridine (0.50 g, 1.5 mmol) and potassium ethyl xanthate (0.48 g, 3 mmol) were stirred under reflux in methylene chloride (15 cm³) for 2 h. with benzyl tributylammonium chloride (10 mg) as a surfactant. The products were washed with water (3 x 10 cm³) then the organic layer dried and evaporated to yield a white powder that was recrystallised from methanol to give white crystals of 5,5'-bis(ethoxythiocarbonylthiomethyl)-2,2'-bipyridine (0.45 g, 71 %); m.p. 95.0 - 96.5 °C; Found C 50.87, H 4.94, N 6.58, C₁₈H₂₀N₂O₂S₄ requires C 50.91, H 4.75, N 6.60; δ_H 8.68 (2H, s, ArH), 8.36 (2H, d, *J*9, ArH), 7.83 (2H, d, *J*9, ArH), 4.69 (4H, q, OCH₂), 4.40 (4H, s, ArCH₂) and 1.44 (6H, t, Me); δ_C 213.40 (SCOS), 155.15 (ArC), 149.80 (ArC), 137.68, (ArC) 132.43 (ArC), 121.04 (ArC), 70.52 (ArCH₂S), 37.33 (OCH₂) and 13.81 (CH₃); M.S (EI) 424 (10), 364 (15), 303 (64), 243 (100), 214 (20), 197 (22) and 182 (95).

Attempted Gilsch polymerisation of 5,5'-dibromomethyl-2,2'-bipyridine.

This was run by modification of the method of Swatos *et al.*³²

5,5'-Dibromomethyl-2,2'-bipyridine (0.251 g, 1 mmol) was added to dry THF (30 cm³) and stirred under nitrogen at RT. A suspension resulted which was dissolved by the addition of dry dioxane (20 cm³) with stirring. Potassium-*t*-butoxide (0.112 g, 1 mmol) was dissolved in dry dioxane (10 cm³) and added via syringe. No reaction was observed

during stirring for 2 h. The solvents were then evaporated off and the residues treated with chloroform. Recrystallisation from chloroform (50 cm³) gave the unchanged starting material 5,5'-dibromomethyl-2,2'-bipyridine (0.210 g, 0.8 mmol) mp 209 - 211 °C with subsequent crops contaminated with *t*-butanol (δ_H 1.27).

A further attempt was run by modification of the method of Lenz *et al.*⁴¹ 5,5'-Dibromomethyl-2,2'-bipyridine (0.251 g, 1 mmol) was added to dry DMF (20 cm³) and stirred under nitrogen at RT. Potassium-*t*-butoxide (0.112 g, 1 mmol) was dissolved in dry DMF (5 cm³) and added via syringe. No reaction was observed during stirring for 2 h. The products were poured into methanol (100 ml) and a white precipitate formed on cooling to 0 °C. Filtration of the precipitate and copious washing with methanol and ether gave the unchanged starting material 5,5'-dibromomethyl-2,2'-bipyridine (0.212 g, 0.8 mmol) mp 208 - 210 °C, mp 227 °C dec.

Attempted Wessling type polymerisation of 5,5'-bis(tetrahydrothiopheniummethyl)-2,2'-bipyridine hexafluorophosphate.

This was run by modification of the method of Wessling.³³ 5,5'-Bis(tetrahydrothiopheniummethyl)-2,2'-bipyridine hexafluorophosphate (0.26 g, 0.4 mmol) was suspended and stirred in water (25 cm³). Sodium hydroxide solution (4 cm³, 0.1 M, 0.4 mmol) was placed in a pressure equalising funnel over the suspension and the apparatus was degassed and flushed with argon. The NaOH solution was added with efficient stirring which was continued for 1 h. at room temperature. No reaction was observed during this period so the mixture was refluxed for 2 h. Again no reaction was observed and the starting material failed to fully dissolve in the boiling water. The mixture was cooled and filtered then recrystallised from chloroform to obtain unchanged 5,5'-bis(tetrahydrothiopheniummethyl)-2,2'-bipyridine hexafluorophosphate(0.19 g, 0.3 mmol).

Further modification of the above method with DMF / t-butoxide.

5,5'-Bis(tetrahydrothiopheniummethyl-2,2'-bipyridine hexafluorophosphate(0.654 g, 1 mmol) was dissolved in DMF (10 cm³) and stirred at room temperature. Potassium t-butoxide (0.112 g, 1 mmol) was dissolved in DMSO (5 cm³) and added after degassing as described above. Immediately after addition of the base the solution turned a deep red colour (λ_{max} 368.5 nm) which persisted for 1h then faded during stirring overnight. The products were poured into methanol (50 cm³) and left to precipitate for 8 h. A pale yellow precipitate **A** was then filtered off (7 mg) and washed thoroughly with methanol and ether. The remaining solvent was evaporated down to 5 cm³ and treated with methanol (20 cm³) then cooled to 0 °C. A further pale yellow precipitate **B** (22 mg) evolved which was filtered off and washed with methanol and ether as before.

The precipitate **A** was dissolved in d⁶-DMSO (1 cm³). On addition of the solvent the solid was observed to undergo considerable swelling to become a transparent gel and was only fully dissolved after sonication for several hours. The solution was exposed to UV-light and found to produce an intense bright blue fluorescence. λ_{max} 368.5 nm; δ_{H} 9.00 - 8.00 (~6H, br, m, ArH), 7.70 - 7.55 (~0.5H, br, m, ArH), 5.32 - 5.20 (~0.5H, br, m, vinyl), 4.90 - 4.30 (~2H, br, m), 3.65 - 3.15 (br, s, H₂O in DMSO) 3.12 - 2.90 (~1H, br, s), 2.87 and 2.70 (DMF solvent singlets) 2.50 (DMSO, s) ,2.37 - 2.00 (~2 H, m), all integration is approximate due to the poor baseline obtained on running the spectra for 3000 transients at 300 MHz. Zinc acetate was added to a DMSO solution of **A** and this did not shift the absorption maximum.

The precipitate **B** was dissolved in d⁶-DMSO (1 cm³). On addition of the solvent the solid was observed to undergo less swelling than **A** and was fully dissolved after sonication for 1 h. The solution was exposed to UV-light and found to produce an intense bright blue fluorescence. λ_{max} 368.5 nm; δ_{H} 9.00 - 8.80 (2H, m, ArH), 8.75 - 8.5 (2H, m, ArH), 8.50 - 8.18 (2H, m, ArH), 4.78 (~3H, br, s), 4.62 (~1H, br, s), 3.60 - 3.40 (1H, m), 3.30 (br, s, H₂O in DMSO) 3.02 (~3H, s), 2.87 and 2.70 (DMF solvent singlets)

2.50 (DMSO, s), 2.37 - 2.00 (~1H, m), all integration is stated in fractions compared to the total integral for the aromatic protons; ν_{max} 3021, 2962, 1608, 1544, 1471, 1253, 1058, 1025, 819 and 561. Zinc acetate was added to a DMSO solution of A and this did not shift the absorption maximum.

Attempted Son type polymerisation of 5,5'-bis(ethoxythiocarbonylthiomethyl)-2,2'-bipyridine

This was run by modification of the method of Son *et al.*⁴⁰ 5,5'-Bis(ethoxythiocarbonylthiomethyl)-2,2'-bipyridine (0.120 g, 0.3 mmol) was dissolved in dry THF (10 cm³) and stirred at room temperature under argon. Potassium *t*-butoxide (0.033 g, 0.3 mmol) was dissolved in dry THF (2 cm³) and added to the bipyridine solution. Immediately on base addition the solution turned yellow then gradually to a deep red. The red colouration continued for 2 hours then returned to yellow. The mixture was then added to methanol (50 cm³) and a yellow solid precipitated out (15.5 mg). NMR spectroscopy found that this was composed of the starting material and a further component with signals at δ_{H} 8.52 (1H, s, ArH), 8.38 (1H, m, ArH), 7.70 (1H, d, *J*9, ArH) and 3.65 (2H, s, ArCH₂S); δ_{C} 149.69, 137.46, 133.32 and 40.11 found by comparing the spectrum of the mixture with that of the starting material. Assuming this component is a related bipyridine, integration indicates that the ratio of the products are 3:2 unknown : xanthate.

The above reaction was repeated using 0.6 mmol (0.254 g) of 5,5'-bis(ethoxythiocarbonylthiomethyl)-2,2'-bipyridine and 0.6 mmol (0.073 g) of potassium *t*-butoxide in a total of 20 cm³ dry THF. On addition of the base the solution turned deep red and a dark precipitate formed. The precipitate did not redissolve while stirring at room temperature even after the addition of a further 20 cm³ of dry THF. The mixture was gently warmed with stirring under argon to reflux for 2 h. During this period the red colouration subsided and changed to yellow. The products were then poured into methanol

(100 ml) and no precipitate was observed. The solvents were then evaporated off to leave a yellow solid that was reprecipitated from methanol. The precipitate (34 mg) was found to consist of the same components as before but in the ratio 2:3 unknown : xanthate.

3.3 Discussion

3.3.1 Coupling reactions of 3-substituted pyridines

As previously noted in the introduction, a traditional and effective method of forming 2,2-bipyridyls has been via a coupling reaction on degassed Raney Nickel. Due to the highly pyrophoric nature of this catalyst and the time consuming preparation involved, more recently developed methods utilising palladium on charcoal or homogenous catalysis by nickel triphenylphosphine complex were preferred and these were the first to be attempted.

The rationale behind using 3-substituted pyridines has also already been discussed and the results of the following reactions will now be illustrated, starting with the coupling of 3-ethyl nicotinate to form 5,5'-diethoxycarbonyl-2,2-bipyridyl **6**.

Sasse *et al*⁴² and Whitten *et al*²¹ were successful in coupling 4-methyl pyridine to form 4,4-dimethyl-2,2'-bipyridine by action of palladium on charcoal. In an attempt here to couple the more complex monomer 3-ethyl nicotinate, the reaction ran into problems. Rather than giving the expected bipyridyl product the reaction yielded an intractable black tar which was largely composed of unreacted starting material (9.2 g). This may be accounted for by various reasons. Firstly, the ester group may have been involved in contamination of the catalyst. This may be done by hydrolysis of the ester followed by coordination of the carboxylate onto the Pd metal. Secondly, the diacid itself is known to have solubility problems and so again hydrolysis of the coupled ester or coupling of the hydrolysed ester would result in material that is difficult to extract from the catalyst. This method was abandoned without further investigation.

A further attempt at Pd catalysed coupling was run by the method of Bamfield and Quan.²² This method relies on the reduction of aryl halides and so leads to regiospecific

coupling through the positions left by the halogen leaving group. Coupling of 6-chloro-3-ethylnicotinate by this method gave the desired product **6** in 2.6 % yield. The low yield combined with the need for a substantial quantity of the product for following stages led to this method being abandoned.

The next approach to pyridyl coupling used a homogenous nickel catalyst with zinc as the reducing agent.^{24,35} Here again a small quantity (0.57 g 7.4 %) of **6** was isolated. However, the need for time consuming extraction of the product from a complex reaction mixture was a major drawback. The attempt was successful in isolating a small amount of pure material without the need for column chromatography but in order to achieve significant yields it became evident that chromatography would be required. It was decided to try alternative methods that would better survive scaling up.

Commercial Raney nickel was employed as a coupling agent with interesting results. As described in the introduction this catalyst is highly pyrophoric and although proven to be effective when degassed, the less risky methods dealt with above were attempted first. Since degassing of the freshly prepared catalyst is the stage where most explosions occur it was decided to attempt coupling with commercial material supplied as a slurry in water. The water was exchanged for organic solvents which would be miscible with the reagents and expected products. This was done by decantation and at this stage the need for flame retardant gloves became evident as any minute spillages of the metal quickly dried and burst into flame. The first attempt at coupling 3-ethylnicotinate used ethanol as a solvent which was chosen for its common use with the catalyst during hydrogenations. A fire and subsequent loss of reaction products during workup led to ethanol being replaced with chloroform in a subsequent attempt. This was successful in producing **6** in low yield (0.88 g, 2.2 %).

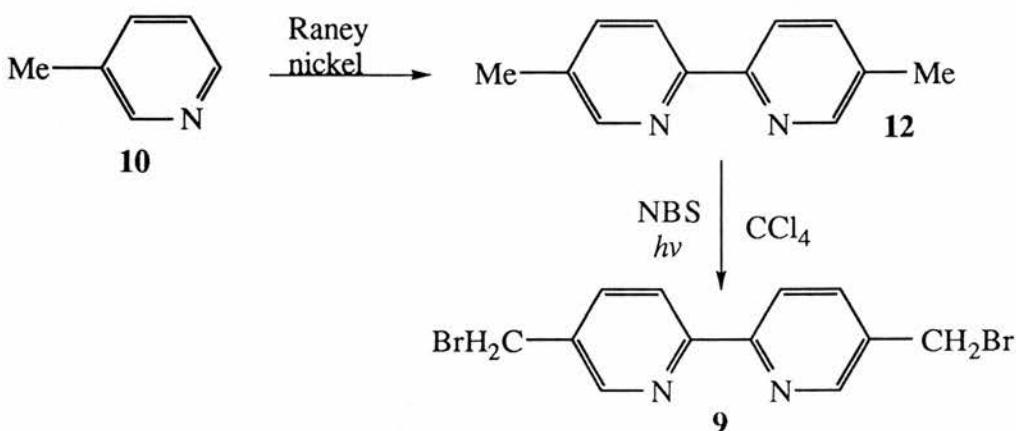
Following on communications with Prof P. Moore³⁷ of the University of Warwick it was found that the best methods to couple pyridines was determined by the nature and

positions of the substituents. The Moore group found that 4- and 2-methylpyridines were best coupled to give the corresponding 4,4'- and 6,6'-bipyridyls by Pd catalyst. The 5,5'-dimethyl-2,2'-bipyridyl was best prepared by the use of freshly prepared degassed Raney nickel. The experience of the Moore group had been that commercial Raney nickel was ineffective as a coupling catalyst for this reaction.

Provided that sufficient 5,5'-dimethyl-2,2'-bipyridyl could be prepared it would serve as a building block for poly(bipyridinevinylene) *via* a number of stages starting with oxidation of the methyl groups to the carboxylic acid, a reaction with which we have had some experience in this laboratory.²⁸ Further communications with Prof. Moore revealed that his group had found that free radical halogenation of **12** can result in monohalogenation of each of the methyl groups. Ebmeyer and Vogtle³⁸ had found this important result on photolysing *N*-bromosuccinimide with **12** and achieved bis(5,5'-bromomethyl)-2,2'-bipyridyl **9** in good yield without contamination by partly reacted or overreacted (non-halogenated to trihalomethyl) products. This was a surprising finding, given the problems associated with such reactions using the more readily available 4,4- and 6,6-dimethylbipridines (mentioned in the Introduction to this chapter) where a considerable mixture of products are reported. A possible reason for the success of this reaction lies in the lower relative reactivity of the *meta* site compared to the *ortho* and *para* derivatives. The latter can stabilise through resonance to provide the pyridine N radical, an intermediate that is unavailable to the *meta* substituted compound. A subsequent lowering of reactivity on monohalogenation on the 5,5'-sites of **12** makes further halogenation unlikely thus providing the desired isomer **9** as the major product.

The newly found possibility of producing **9** in only two steps from 3-picoline **10** was seized upon. Degassed W7-J Raney nickel was prepared using great caution and this was found to effectively couple **10** to **12** in multigram quantities. Subsequent dibromination using NBS was successful in providing **9** in high yield. The process was

successfully scaled up to provide this key intermediate in sufficient quantities for polymerisation studies and for further steps to provide other novel monomers.

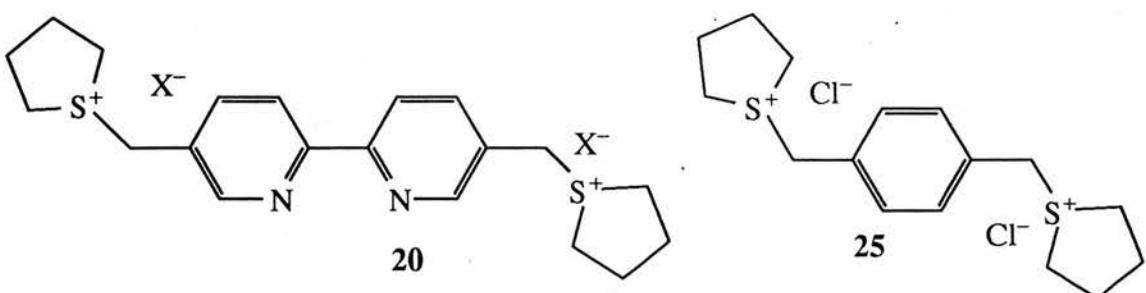


3.3.2 Gilsch route to poly(bipyridinvinylenes)

A Gilsch type polymerisation of **9** was attempted firstly using THF as solvent. This solvent failed to fully dissolve the bipyridine and so a subsequent attempt using dry 1,4-dioxane was run. Although this solvent completely dissolved the reagents, no reaction was observed. This important observation will be discussed in comparison with the other monomers prepared.

3.3.3 Direct Wessling route to poly(bipyridinvinylenes)

A Wessling³³ type monomer was prepared by the action of two equivalents of tetrahydrothiophene on **9**. The xylene equivalent of this salt with chloride counterions **25** was found to be easily isolated in pure crystalline form. This was not the case with the initial dibromide salt for the bipyridine **20** and the resulting oil was difficult to purify. The tetrahydrothienyl groups are designed to be thermally labile so distillation would risk loss. Also chromatography would require polar solvents; evaporation of these may also provide

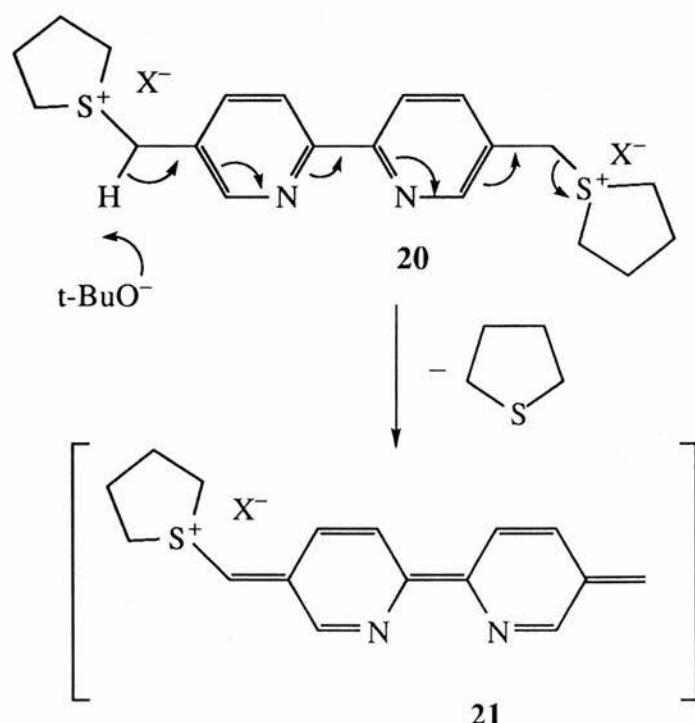


conditions for the loss of the tetrahydrothienyl groups. It was decided to exchange the counter ion in order to reduce solubility. After an initial attempt to isolate the perchlorate salt failed the experiment was repeated and addition of potassium hexafluorophosphate to a solution of the crude dibromide salt of **20** resulted in the formation of crystals of the dihexafluorophosphate salt.

Once isolated, the monomer **20** was used for polymerisation studies. The Wessling route to polymerisation is commonly run using water as this has been found to be an excellent solvent for the preservation of the chemical and conformational integrity of the monomer salts and polycationic precursor polymers for PPV.⁴³ Unfortunately **25** was found to be only sparingly soluble in aqueous base and polymerisation in this medium was unsuccessful. Polymerisation was then attempted in DMF using firstly NaOH then the stronger base potassium-*t*-butoxide. The monomer readily dissolved in DMF; however, no reaction was observed with NaOH base. With K⁺Bu^tO⁻, however, a deep red colouration resulted immediately on base addition. This colouration is believed to be due to the formation of the highly coloured quinoid intermediate **21** formed as a result of the base abstraction of a benzylic proton from **20** and subsequent rearrangement involving the loss of a tetrahydrothienyl group. The reactive intermediate **21** may then polymerise or oligomerise.

Precipitation of the polymerisation products by addition of the reaction mixture to methanol gave a small quantity of a bright yellow solid (7 mg). The solid was insoluble in most organic solvents but expanded to form a highly fluorescent gel that partially dissolved

in DMSO on sonication. NMR of the material was run in d⁶-DMSO but so little material was soluble that the ¹H NMR was only attainable after a 4 h run on a 300 MHz instrument. This spectrum is discussed with comparison to that of the more soluble materials later.



3.3.4 Wessling route with methanol work-up

The remaining products were worked up by evaporation of the solvents down to 5 ml and flooding the remainder with methanol. This reduced the concentration of DMF and consequently precipitated out a further small quantity of pale yellow precipitate A. This material was more soluble in DMSO and ¹H NMR revealed more detail. On comparison to the spectrum of the starting material Figure 3.1 the major bipyridyl peaks are shifted downfield from TMS and also show shoulders in the same positions of those of the starting materials. The relation to the starting material is clear from the IR spectrum which shows many identical absorptions. The cationic nature of the material maintained as displayed by the characteristic PF₆⁻ counter ion absorptions (ν_{\max} 818 and 562).

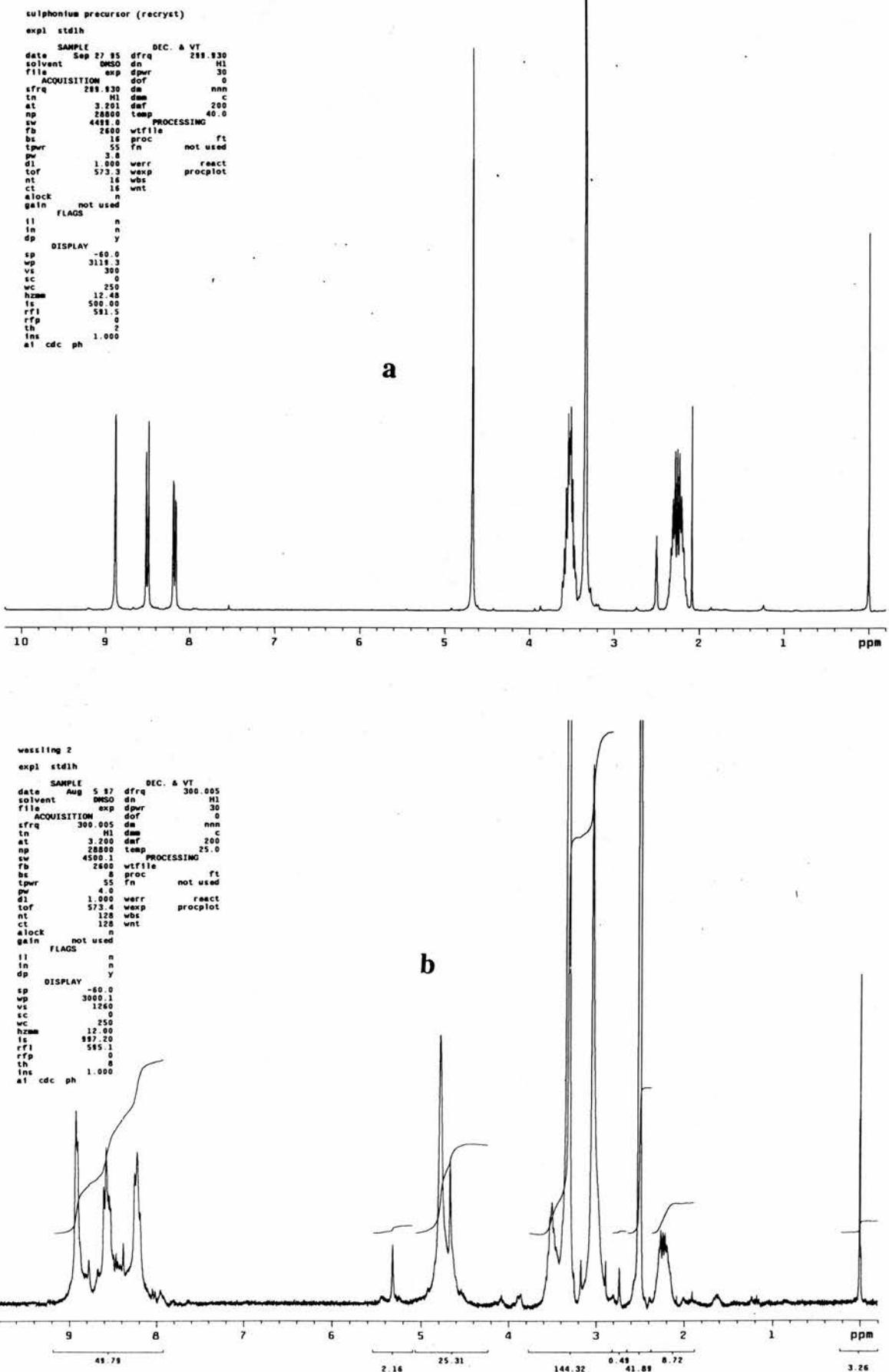
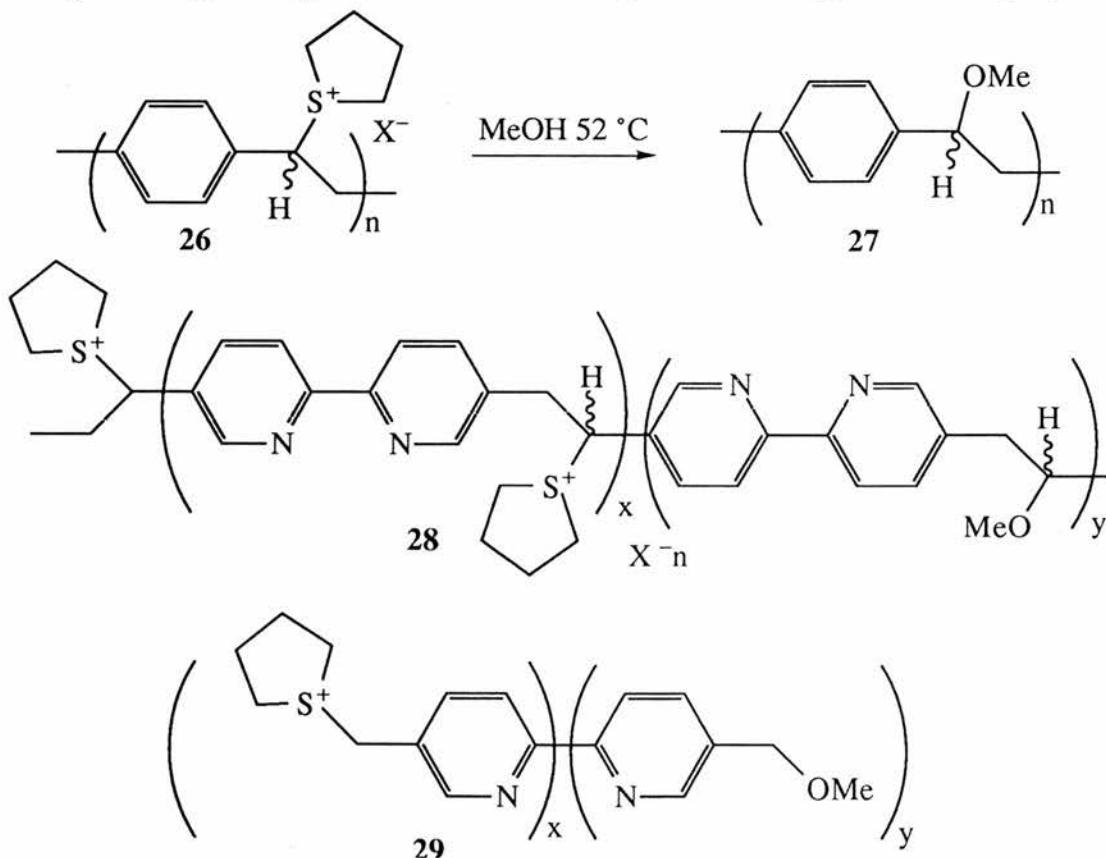


Figure 3.1: ^1H NMR Spectra of **20** (a) and precipitate (b).

The majority of the benzylic protons are also shifted downfield again with evidence of residual starting material in a 1:4 ratio. The tetrahydrothienyl multiplets again appear in the 1:4 ratio with the new product and a further new singlet peak is evident at δ_H 3.02 that has a ratio of 3:2 vs the benzylic carbon peak of the new product. The large peaks at δ_H 3.30 and 2.50 are attributed to DMSO and absorbed water.

The key to characterising the new product lies in the 2:3 integration ratio of the shifted benzylic protons to the new peak at δ_H 3.02. Considering this peak to be due to an isolated methyl group the first assumption was that this could be a picoline methyl; however, the methyl singlet for 5,5'-dimethyl-2,2'-bipyridyl is found at δ_H 2.35. The best suggestion (if not the solution) for the structure of the new product was found on examining the work of Holmes *et al*⁴⁴ on similar PPVs. Heating the tetrahydrothienyl substituted precursor polymer **26** with methanol led to exchange of the groups to give the methoxy substituted precursor polymer **27**. Similar heating with methanol was done during the workup of the reaction products for the bipyridines. The methoxy substituent in this case gave a singlet at δ_H 3.19 which is reasonably close to the δ_H 3.02 for our polymer.



Reaction of the monomer **20**, oligomers or polymer with methanol may be expected to provide similar products. A polymer such as **28** may be formed but the lack of any measurable signal for the chiral benzylic CH (observed at δ_H 4.28 for the PPV precursor **27**) lends problems to this analysis. However, the chiral nature of this proton would give a broad signal that would not be detectable in low concentrations and small signals at δ_H 4.08 and 3.09 could possibly be indicative of its presence.

A more likely explanation for the structure of the new product may be the mixed monomer **29**. This may be comprised of a mixture of pure starting material and fully converted methoxy substituted monomer, partly converted monomer, or a mixture of the three products. Provided the integration ratio is satisfied for the combination of methoxy substituted (x) and tetrahydrothienyl substituted (y) components in a 4:1 ratio a combination of these molecules can account for the products.

For the less soluble precipitate **B** the NMR spectrum Figure 3.2 has less detail. The lower solubility and gel formation on dissolving the precipitate suggests that polymeric material may be present. This is supported by the broadness of the signals in the 1H spectrum. Comparison to the spectrum in Figure 1 shows that the tetrahydrothienyl group (δ_H 2.37 - 2.00, the other peak is lost under the DMSO/water signal) is still present on some fraction of the material. Some methoxy substituted material (δ_H 3.12 - 2.90) may also be present, and the benzylic region is broadened again, suggestive of the presence of a polymer or large oligomer. A further interesting detail is the presence of a small signal at δ_H 5.12 which may be due to vinyl protons, suggesting some full conversion to the conjugated polymer, but this assignment is uncertain. Further characterisation would be required to elucidate the structure of this material however this is hampered by solubility and the small quantity obtained. A copolymer of the form **29** is probably the best representation of the structure of the material that can be devised with the information obtained.

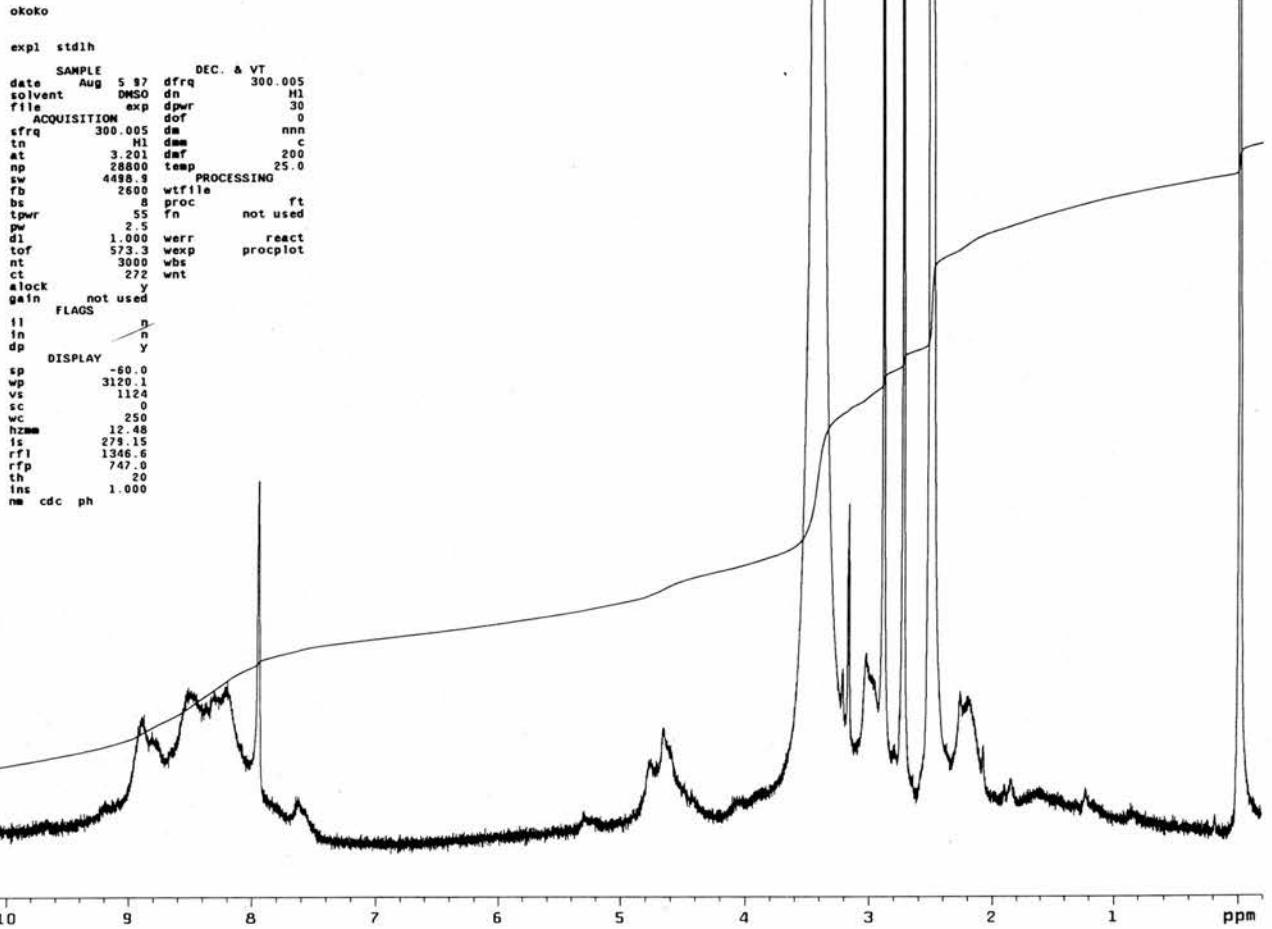
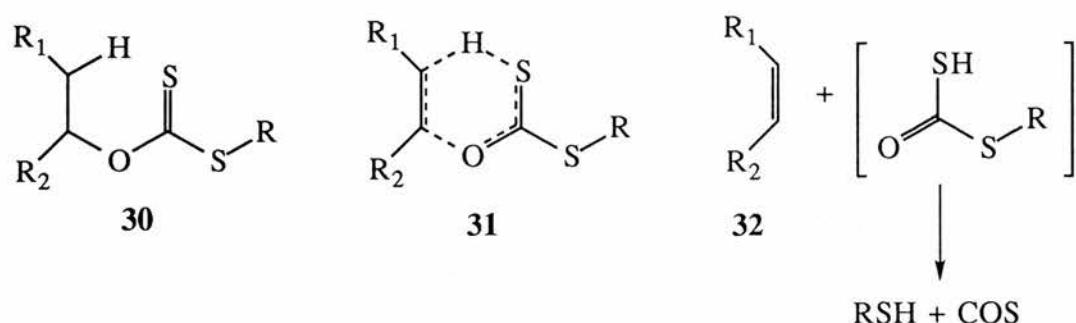


Figure 3.2: ^1H NMR Spectra of precipitate B

3.3.5 Son Route to poly(bipyridinevinylenes)

During the progress of this work, many advances have been made to increase the luminescence efficiency of PPV. Evidence from Yan et al⁴⁵ suggests that PL efficiency in PPV may be increased by separating the polymer chains which will reduce the tendency of PPV to pack into a crystalline like state. Inspired by this Son *et al*⁴⁰ has been aimed at providing amorphous PPV by engineering the introduction of *cis* double bonds into PPV. This is done by a variation of the Chugaev reaction reviewed by DePuy and King⁴⁶

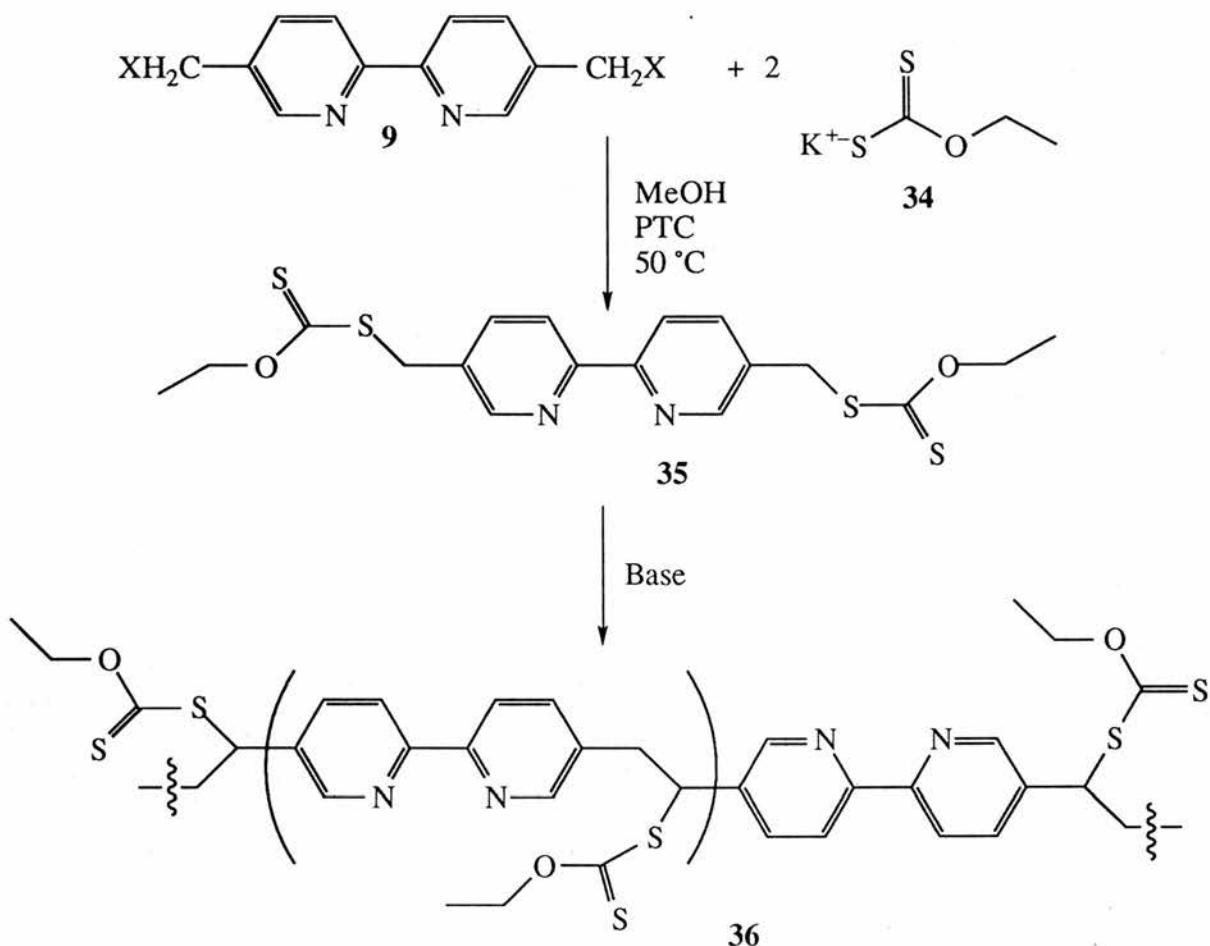
The Wessling route discussed above relies on pyrolytic extrusion of the thermally labile tetrahydrothienyl group to provide almost purely *trans* linkages between the aryl groups. The Chugaev reaction involves the pyrolytic decomposition of a xanthate **30** to provide *cis* linkages. On pyrolysis, the reaction proceeds through a six membered transition state **31** to give decomposition products⁴⁷ comprised of the mainly *cis* alkene **32** and an unstable dithiocarbonate derivative which subsequently decomposes to give carbon oxysulphide and a mercaptan.



To apply this reaction to the synthesis of PPV, Son *et al*⁴⁰ reacted potassium ethyl xanthate **33** with 1,4-dibromomethyl benzene. In our work we substituted this for the bipyridine equivalent **9**. This reaction was very successful and provided a 'Son' type bipyridine monomer substituted with ethoxythiocarbonylthiomethyl groups **35** in high purity and yield. The great potential advantage of this material over the Wessling precursor to poly(bipyridinevinylene) lies in its solubility in common solvents. Unlike the Wessling monomer **20** which was isolated as the dihexafluorophosphate salt, the Son monomer **35** is highly soluble in THF which is a good solvent for base polymerisation.

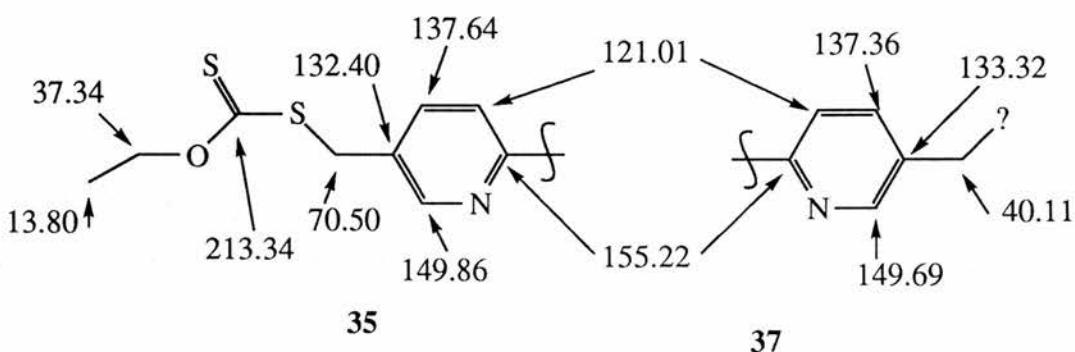
Polymerisation towards the Son precursor to PPV apparently takes place by the same mechanism as the Wessling route. This was displayed by an intense red colouration on addition of potassium-t-butoxide to 1,4-bis-(ethoxythiocarbonylthiomethyl)benzene which is indicative of quinoid formation. Using the same reaction with **35** we expected to obtain the bipyridyl variant of the Son precursor polymer **35**. In practice we observed the

deep red colouration on addition of the base. However, on work up and analysis it became evident that the sought precursor polymer was not the reaction product.



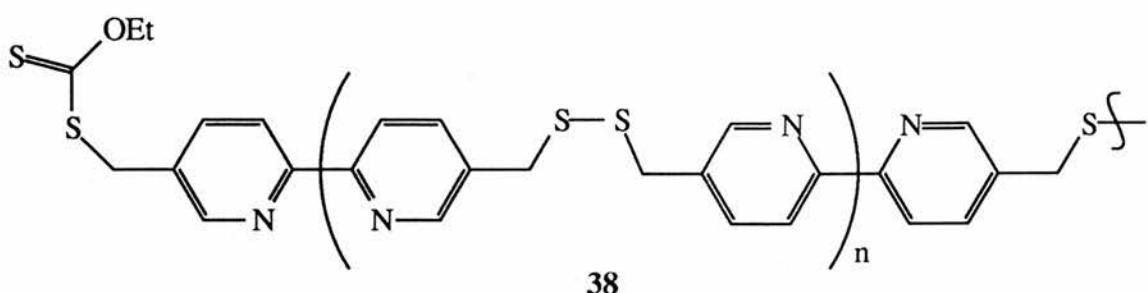
The polymerisation reactions yielded small quantities of a yellow precipitate that was soluble in chloroform. Analysis by NMR showed that a mixture of starting material and further components was present with each in different concentrations between runs. This difference in concentrations was a valuable aid to characterising the products since the integrals on the ^1H spectra could be used to discriminate between the components and this showed that only two products were present. From the aromatic signals it was evident that the unknown product was a related bipyridyl with the signals shifted upfield. Integration of the aliphatic peaks showed that the unknown was not a xanthate and it only gave rise to one aliphatic signal, a singlet at $\delta_{\text{H}} 3.65$ in a 2:1 ratio vs an aromatic proton. This in turn suggested a bipyridyl with two symmetrical methylene groups. This evidence was

supported by the ^{13}C spectra which again showed the starting material and new signals generated by the unknown. Two aromatic carbons (δ_{C} 155.22, q and 121.01, CH) had identical shifts to the starting material whilst the remaining three had moved by different frequencies upfield. A benzylic carbon was present at δ_{C} 40.11, again upfield from the xanthate. So the pattern of a bipyridyl with a methylene group coordinated to a less electron withdrawing substituent than the xanthate emerged. The ^{13}C spectra of **35** and the unknown **37** can hence be assigned and from this we can see that the δ_{C} for C2 and C3 are the same for both components so they may well belong to the same unsymmetrical molecule.

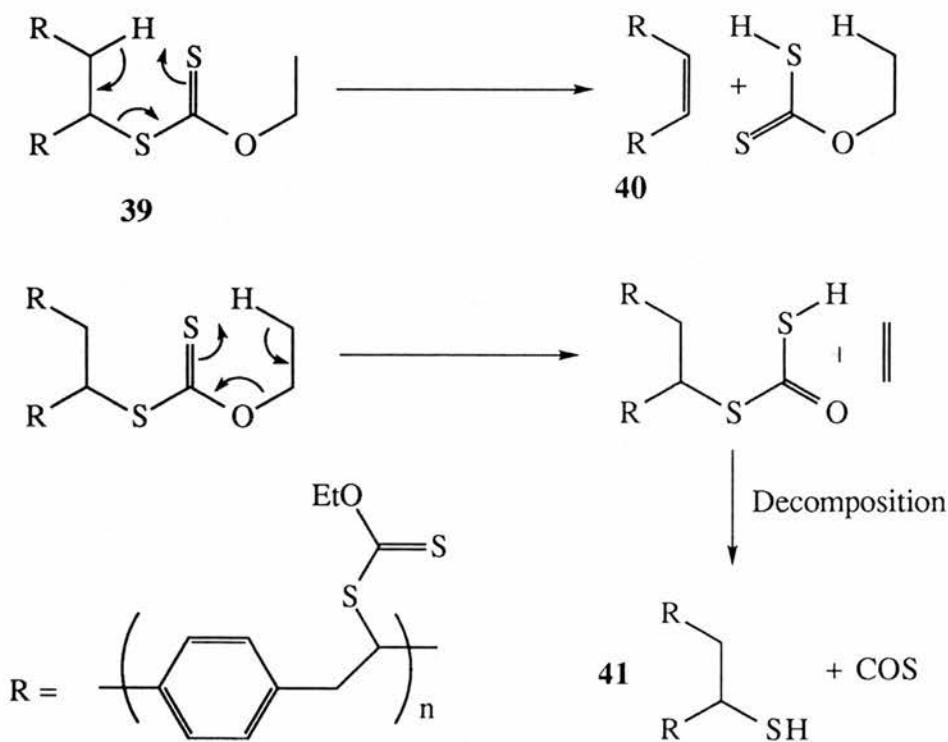


The nature of the substituent on the benzylic carbon of **37** was believed to be related to the decomposition of the xanthate. Wardell⁴⁸ has reviewed the use of this modification of the Chugayev reaction for the conversion of halide to thiol by hydrolysis under basic conditions. Further to this, the thiols may readily undergo aerial oxidation to form disulphides. Comparison of the NMR spectra of two models, benzyl mercaptan⁴⁹ and benzyl disulphide⁵⁰ was informative. Firstly the benzylic methylene for the mercaptan (δ_{H} 3.7, δ_{C} 29) showed strong coupling to the thiol proton when run in the same CDCl_3 solvent as **37**. Since neither this coupling nor any signal for the thiol proton (δ_{H} 2.7, t) was present in the spectrum of the polymerisation products this model was discarded. Secondly, benzyl disulphide turned out to be a very good model with the benzylic methylenes shifts at δ_{H} 3.6, δ_{C} 43 comparing very favourably with those for **37** (δ_{H} 3.65, δ_{C} 40.11). Thus the expected structure for the unknown product is of the form **38** with the

ratios of xanthate end groups to disulphide coupling groups being satisfied by the inclusion of a quantity of unreacted starting material.



This result and review of the Chugayev mechanism does raise questions concerning the versatility of the Son route to conjugated polymers. In our case the addition of base to **35**, although apparently successful in generating a highly coloured quinoid, did not do so in any measurable quantity indicated by the products. The apparent production of disulphides is intriguing since Son⁴⁰ reports that on polymerisation to the precursor polymer **39** an inseparable component with a low molecular weight of less than 2000 is found. This may be due to the inclusion of disulphides and we have found no reports to date that have an alternative explanation for this inclusion.



Of further interest, the proposed pyrolytic elimination of the xanthate can go by two reasonable routes to give either the conjugated polymer **40** or the thiol **41**. The latter reaction has considerable precedent in the literature^{46,47} and so it may well turn out that close analysis of the Son polymer's structure will reveal the presence of alternate conjugated and thiol units. Subsequent oxidation of these thiols may result in disulphides which would provide a cross linked polymer. It is interesting to consider that such cross linking, if it exists, may have unusual effects upon the luminescence properties of the polymer. Son et al⁴⁰ claim that the polymer has superior luminescence properties and can carry higher current densities than PPV by the Wessling route. Perhaps this is not simply by the engineering of *cis* conjugated units.

3.4 Conclusions

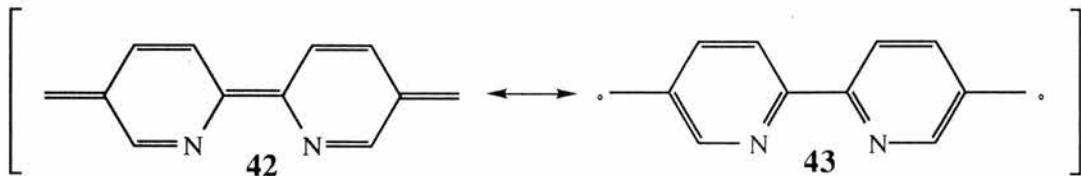
5,5'-dibromomethyl-2,2'-bipyridine was conveniently prepared by coupling 3-picoline with W-7 Raney nickel followed by bromination with NBS. Attempts at a Gilsch type polymerisation with this monomer failed. It is suggested that this may be due to solubility problems in suitable solvents.

The corresponding Wessling type monomer was prepared by the reaction of 5,5'-bisbromomethyl-2,2'-bipyridyl with tetrahydrothiophene. The dibromide salt of the monomer was found to be non-crystalline and thus difficult to purify. Exchange of the counter ion to hexafluorophosphate produced a pure crystalline salt; however, this was insoluble in most solvents. Solubility problems with this monomer led to difficulties for polymerisation but the use of DMF solvent and potassium t-butoxide base has provided a small quantity of a polymer with a ^1H NMR resembling the expected alkyl linked precursor polymer. The small quantity obtained and sparingly soluble nature of this polymer hindered further characterisation. Evidence for substitution of the tetrahydrothienyl groups by methoxy groups was found; this is a precedented process for the analogous PPV type precursor.

5,5'-Bis(ethoxycarbonylthiomethyl)-2,2'-bipyridyl was prepared by the reaction of potassium ethyl xanthate with the bromomethyl bipyridyl. The use of the xanthate leaving group aided solubility of the monomer, however attempted polymerisation led to unexpected products. The presence of disulphide linkages between bipyridyls in these products is suggested and supported by precedented processes and NMR of model compounds. It is also suggested that the Son route to PPV may give rise to contamination by disulphides in both the precursor step and perhaps on the thermal elimination step. This would give rise to the possibility of cross linkages of the polymer chain through disulphides.

The base polymerisation reaction common to the Wessling route for the synthesis of PPV does not work so efficiently in the bipyridyl system. A deep red colouration is obtained by the action of base on the Wessling and Son route bipyridyl monomers. This may be the formation of the expected quinoid intermediate. However, only in the case of the Wessling monomers does this give rise to products that may be related to the sought precursor polymer. The deep red colouration may be explained by the formation of a very small, constant concentration of the quinoid. Since the bipyridyl system offers greater delocalisation of the intermediate in comparison to the xlenyl intermediate for PPV, this may give rise to a stronger absorption and deeper colouration even in minute concentration. Such an extremely low concentration may lead to quenching of any polymerisation and this would account for the low yields of products obtained.

It is suggested that the lower polymerisation yields may be due to the presence of the nitrogen heteroatoms. These electronegative centres may have the effect of stabilising any quinoid **42** formed. The electronegativity of the nitrogens combined with the delocalisation available in the bipyridine may lower the diradical character **43** of the intermediate thus decreasing its reactivity and tendency to polymerise.



Further reasons for the inefficiency of the polymerisation reactions may be suggested. The presence of coloured species other than the quinoid may not be ruled out. Perhaps the formation of the anion by base abstraction may give a coloured species that is stabilised by the electron deficient rings. Such an intermediate would not require loss of either the tetrahydrothienyl or xanthate group. This is supported by the appearance of only very small quantities of products which have lost their leaving groups.

3.5 References

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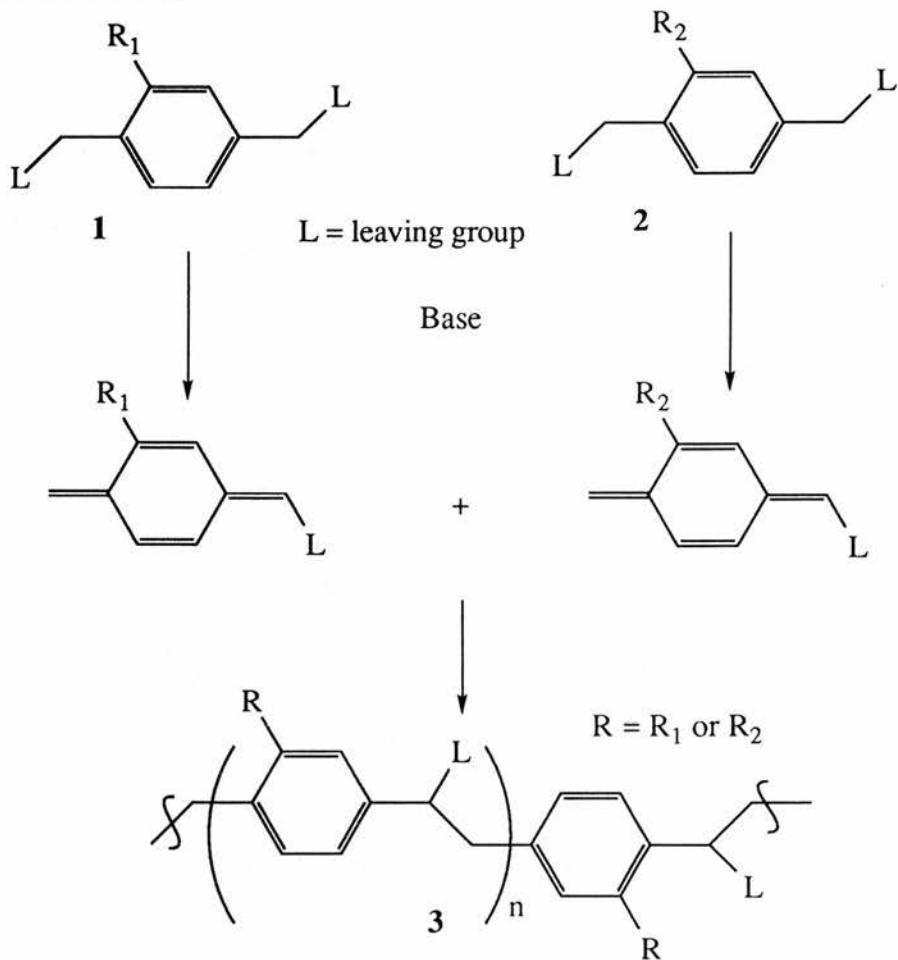
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Chapter 4

Synthesis of Wittig Monomers for Co-Polymers of Poly(bipyridinevinylene) and their Polymerisation Behaviour

4.1 Introduction.

In the previous Chapter, we investigated synthetic routes towards poly(bipyridinevinylene) which relied on precursor polymer methods such as that of Wessling¹. These reactions are all driven by the base abstraction of benzylic hydrogens followed by the formation of reactive intermediates. The intermediates then polymerise in a random fashion to give precursor polymers which are then processed prior to thermal conversion to give the conjugated polymer. This type of polymerisation can cause problems if a non homogenous system is employed. For example, co-polymerisation of **1** and **2** will lead to a co-polymer **3** consisting of the monomer units of **1** and **2** in an orderless random fashion .

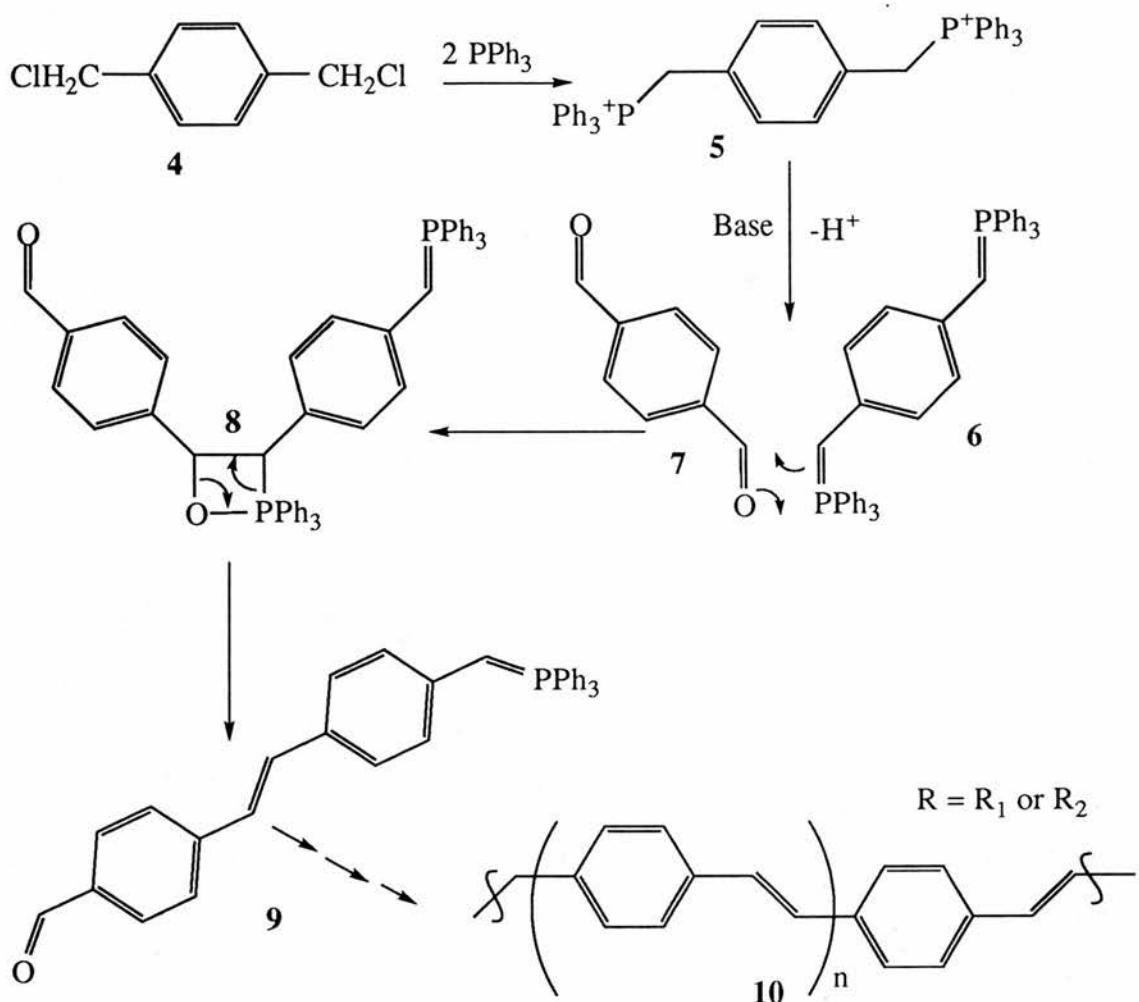


To provide better defined poly(arylenevinylene) co-polymers, other routes may be employed and these have been reviewed by Roncali² and by Horhold.³ Of the alternative routes, the most popular methods are the Knoevenagel condensation and the Wittig

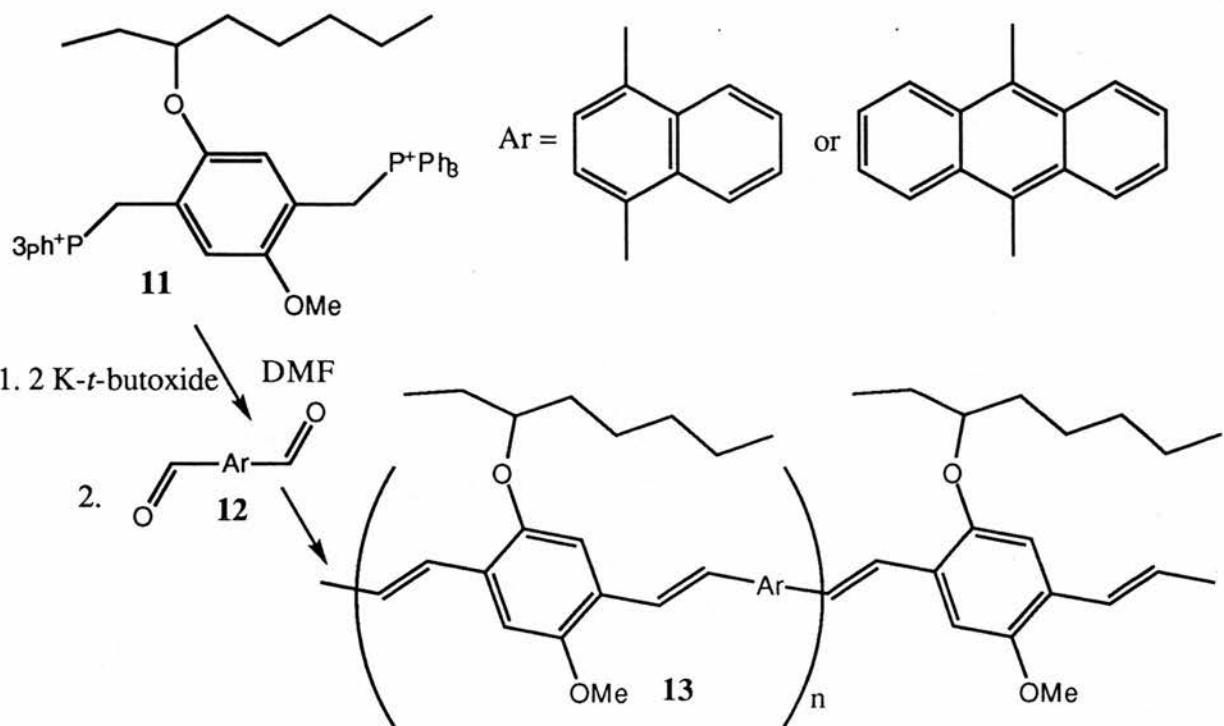
olefination reactions. An example of the use of the Knoevenagel condensation by Holmes *et al*⁴ has been given in Chapter 1 and a main feature of this reaction is the engineering of a cyano group on the vinylene linkage. This type of reaction demands careful control of reaction conditions to avoid side products from Michael additions and so if incorporation of an electron withdrawing group is unnecessary, other methods may be preferable. Turning to the Wittig reaction⁵, two methods have been commonly used in the formation of poly(arylenevinylenes). The first relies on phosphines and the other is the Wadsworth Emmons modification⁶ which relies on phosphonates. Both effectively convert aldehydes or ketones into olefins by similar routes.

Kossmehl⁷ has done much work in the synthesis of polyarylene vinylenes using the Wittig reaction. For example, reflux of 1,4-dichloromethyl benzene **4** with triphenylphosphine in toluene gives the bis-phosphonium salt **5**. Action of base on the salt gives the ylide **6** which reacts with benzene-1,4-dicarboxaldehyde **7** through the oxaphosphetane **8** to give the olefin **9**. Further oligomerisation gives fully conjugated PPV **10**.

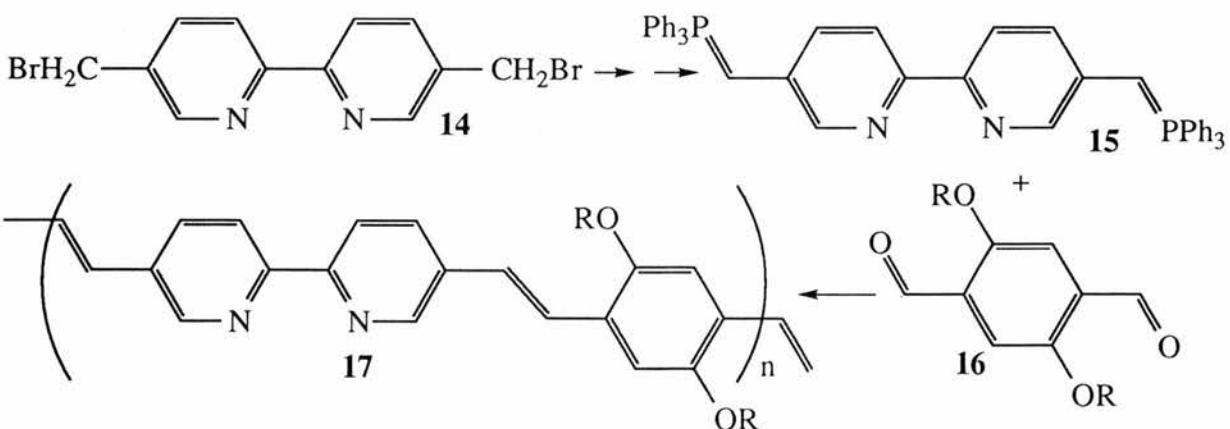
Although the PPV obtained from this reaction is an insoluble rigid rod polymer there is great scope for synthetic modification of the aryl groups to include solubilising alkyl or alkoxy substituents. Further to this, the reaction provides the polymer in a precise order and so 1:1 co-polymers can be made simply by synthetic alteration of either the diphosphonium salt or the dialdehyde. These factors have been recently exploited by Ferraris *et al*⁸ to produce co-polymers incorporating monomer units such as naphthalenes



that are insoluble as homopolymers. For these polymers 2-methoxy-5-(2'-ethylhexyloxy)-1,4-xylenebis(triphenyl-phosphonium bromide) **11** was used to provide a solubilising group. The dialdehyde of the less soluble aromatic compound **12** was synthesised and the two were polymerised by the Wittig reaction to give a co-polymer that was soluble in chloroform **13**. The molecular weights of these polymers were of the order of 8000 to 25000. This is considerably smaller than those commonly reported for PPV prepared by the Wessling route⁹ (M_w 5.6×10^5) and this shows a limitation of the Wittig polymerisation which may be partly explained by the lower solubility of the polymers. However the precise engineering available with the Wittig procedure makes it a very interesting synthetic route to novel polymers.



Continuing our work towards poly(bipyridinevinylenes), we can see a role for Wittig polymerisation. In Chapter 3 we discovered that base driven polymerisations such as the Wessling route to PPV were not so effective with our bipyridyl analogues. The synthetic work, however, did furnish 5,5'-dibromomethyl-2,2'-bipyridine **14**. Preparation of its diphosphonium salt may furnish ylide **15** which can be co-polymerised with a dialdehyde. For example, co-polymerisation with an aryl dialdehyde with alkoxy solubilising groups **16** may lead to a bipyridinevinylene co-polymer **17** with enhanced processing properties.



4.2 Experimental

General experimental techniques remain the same as for Chapter 2 save for the following exceptions. UV-visible spectra were run on a Perkin-Elmer Lambda 14 spectrophotometer or a Philips PU8720 spectrophotometer. Steady-state photoluminescence and excitation spectra were recorded on a PTI (Photon Technology International Inc.) QM-1 fluorimeter which is of a modular but conventional layout.¹⁹ The measurements were carried out at the Department of Chemistry, Edinburgh University, by Dr Zoe Pikramenou. The excitation wavelength was chosen to be close to, or on the low wavelength side of the maximum of the main absorption band of the polymer sample.

Preparation of 1,4-Dihexyloxybenzene and 4-hexyloxyphenol

This was supplied by P. Madden¹⁰ by the method of Swatos and Gordon.¹¹ To a solution of hydroquinone (20 g, 0.18 mol) in methanol (100 cm³) was added a solution of potassium hydroxide (21.06 g, 0.36 mol) in methanol (120 cm³) at RT. After 5 min stirring, a mixture of *n*-hexyl bromide (118 g, 0.72 mol) in acetone (200 cm³) was added slowly to the reaction mixture. This mixture was refluxed for 9 hours. It was then concentrated by evaporation of solvents, diluted with water and extracted into dichloromethane (500 cm³). The dichloromethane extracts were dried over magnesium sulphate and evaporated to dryness under reduced pressure to yield a dark brown viscous liquid which on cooling solidified to form dark brown slightly translucent crystals which had an oily residue trapped between the crystal layers. *n*-Hexyl bromide was distilled off under reduced pressure and the product was recrystallised from light petroleum, yielding a dark brown solid (yield 33.66 g, 76.16%) δ_H 6.8 (4H, s, ArH), 3.85 (4H, t, *J* 7, ArCH₂), 1.90 - 1.25 (17H, m, methylenes) and 0.85 (6H, m, Me). This spectrum indicated that the product formed was a mixture of both mono and dialkylated species. This represented itself as shoulder peaks on the singlet and the triplet. This preparation was repeated several times to obtain sufficient monosubstituted phenol.

Purification (separation of mono and disubstituted species)

A solution of the above products in sodium hydroxide (2 M, 200 cm³) was stirred for 30 min in order to ensure complete conversion of the monosubstituted phenol into the salt form. Separation of the disubstituted product was accomplished by extraction into dichloromethane. The dichloromethane extracts were dried over magnesium sulphate and the solvent was removed under reduced pressure and then under a rotary pump to afford cream/yellow coloured crystals (25.96 g); δ_H 6.85 (4H, s, ArH), 3.85 (4H, t, *J* 7, OCH₂), 1.65-1.90 (4H, m, methylene), 1.20-1.55 (12H, m, methylenes) and 0.85 (6H, m, Me). The monosubstituted phenol was released from solution by addition of HCl (2 M, 200 cm³) followed by extraction into dichloromethane. The extracts were dried over magnesium sulphate and the solvent evaporated under reduced pressure and then under a rotary pump to afford a dark brown solid (4.40 g). δ_H 6.80 (4H, s, ArH), 3.85 (2H, t, *J* 7, OCH₂), 1.70 (2H, m, methylene), 1.20-1.50 (6H, m, methylenes) and 0.85 (3H, m, Me).

2,5-Bis(chloromethyl)-1,4-hexyloxybenzene

This was supplied by P. Madden¹⁰ and was prepared by the following method.

To a solution of 1,4 dihexyloxybenzene (25.96 g, 0.092 mol) in dioxane (180 cm³) was added conc. HCl (20.5 cm³) at room temperature. HCl gas was bubbled through the solution for 15 mins after which formaldehyde (3 x 10 cm³ portions) were added slowly over 30 min for one and a half hours. HCl gas was bubbled through the mixture continuously for three and a half hours. After that time the HCl gas flow was stopped and conc. HCl (95 cm³) was added to the reaction mixture. The resulting solution was cooled whereupon the product was obtained.(yield 6.03 g, 17.5%); δ_H 6.91 (2H, s, ArH), 4.64 (4H, s, ArCH₂Cl), 3.97 (4H, t, *J* 7, OCH₂), 1.78 (4H, m, methylene), 1.25 (4H, m, methylene), 1.33 (8H, m, methylenes) and 0.89 (6H, t, *J* 7, Me); δ_C 150.79 (ArC), 127.24, (ArC) 114.49 (ArC), 69.22 (ArOCH₂), 41.43 (ArCH₂Cl), 31.59 (CH₂), 25.78 (CH₂), 22.64 (CH₂) and 14.05 (CH₃).

This product was also prepared by the method of Phol and Espenson.¹² 1,4 dihexyloxybenzene (22.24 g, 80 mmol) and paraformaldehyde were added to a mixture of concentrated phosphoric (49 cm³) hydrochloric (54 cm³) and acetic (66 cm³) acids and the mixture was stirred briskly at RT. HCl gas was generated by the controlled addition of concentrated sulphuric acid to sodium chloride and bubbled through the mixture for 5 h. The organics were then extracted with ether (3 x 200 cm³). The solvent was evaporated off and the residues recrystallised from hexane to give two crops (9.8 g and 5.7 g) of 2,5-bis(chloromethyl)-1,4-hexyloxybenzene (41.3 mmol, 52%) with spectroscopy identical to the above.

Preparation of potassium benzene selenite

This was done by modification of the method of Syper and Meochowski.¹³

a. *Preparation of benzene selenic acid*

Diphenyl diselenide (5.0 g, 16.6 mmol) was stirred at 0 °C in dichloromethane. Hydrogen peroxide (7 cm³, 30 %) was added dropwise over 2.5 h. then the mixture was allowed to stir for a further 30 min. White crystals developed which were filtered cold and washed with cold water (10 cm³) and cold dichloromethane (10 cm³) then dried in air. This gave benzene selenic acid (4.74 g, 76 %).

b. *Preparation of potassium benzene selenite*

Potassium-t-butoxide (2.81 g, 25 mmol) was dissolved in dry ethanol (25 cm³) and stirred at RT. Benzene selenic acid (4.74 g, 25 mmol) was added portionwise to the stirred solution over 30 min. The solvent was evaporated off and the residues treated with ether (20 cm³). The products were then filtered off, washed with ether and dried in vacuo to yield potassium benzene selenite (5.21 g, 92 %).

Several repeats of the above procedure using recycled diphenyl diselenide gave similar yields.

Preparation of 1,4-dihexyloxy-2,5-benzenedicarboxaldehyde

This was done by modification of the method of Syper and Meochowski.¹³

2,5-Bis(chloromethyl)-1,4-hexyloxybenzene (3.0 g, 8 mmol), potassium benzene selenite (3.85 g, 17 mmol) and potassium hydrogen phosphate (2.96 g, 17 mmol) were refluxed in acetonitrile (75 cm³) for 22 h. After cooling the mixture was diluted with water (50 cm³) and extracted with dichloromethane (3 x 30 cm³). The extract was dried and evaporated then the residues were separated on a silica gel (0.2 mm) column (3 x 15 cm). Diphenyl diselenide was eluted with 40-60 bp petroleum ether and recrystallised from ethanol for re-use. The dialdehyde was then eluted with chloroform, the solvent evaporated and the product recrystallised from hexane to give 1,4-dihexyloxy-2,5-benzenedicarboxaldehyde (2.38 g, 89 %); m.p. 74 - 75.5 °C (lit¹⁴; 75-76.5 °C) δ_H 10.51 (2H, s, ArCHO), 7.44 (2H, s, ArH), 4.09 (4H, t, J 7, OCH₂), 1.83 (4H, m, methylene), 1.29 (4H, m, methylene), 1.33 (8H, m, methylenes) and 0.89 (6H, m, Me); δ_C 189.75 (ArCHO), 155.46 (ArC), 129.46 (ArC), 111.77 (ArC), 69.35 (ArOCH₂), 31.53 (CH₂), 29.06 (CH₂), 25.73 (CH₂), 22.61 (CH₂) and 14.03 (CH₃).

Preparation of 5,5'-bis(triphenylphosphoniomethyl)-2,2'-bipyridyl dibromide

This was done by modification of the method of Michaelis and Gimborn¹⁵

5,5'-Dibromomethyl-2,2'-bipyridyl (1.03 g, 4 mmol) and triphenylphosphine (2.06 g, 8 mmol) were stirred in toluene (100 cm³) and heated to reflux. On heating some material precipitated out of the reaction mixture and this was redissolved by the addition of dry DMF (50 cm³). The reflux was continued for 2 h after which the solution was allowed to cool during which time a very light pink precipitate developed. The precipitate was filtered off to give a light pink powder which was washed with 40 - 60 °C bp petroleum ether and dried to give the product 5,5'-bis(triphenylphosphoniomethyl)-2,2'-bipyridyl dibromide (2.06 g, 67 %); dec 240 °C; δ_H (d⁶-DMSO) 8.26 (1H, s, ArH), 8.13 (1H, d, ArH), 7.98-7.84 (3H, m, ArH) 7.80-7.64 (12H, m, ArH), 7.46 (1H, d, ArH) and 5.37 (2H, d, J 16, ArCH₂P); δ_P +21.90 and 29.0 (trace). Traces of DMF (δ_H 2.88 and 2.72) and many very small signals in the aromatic region remained in spectrum after thorough washing.

The above reaction was repeated with 1.58 g (6 mmol) of the bipyridine and 3.09 g (12 mmol) of triphenylphosphine refluxed in DMF (100 cm³) overnight. The DMF was evaporated off and the products washed with water then dried in vacuo. The product was a yellow powder (3.2 g, 78 %) sparingly soluble in chloroform. δ_H 8.60-8.00 (5H, m, ArH), 8.00-7.20 (40H, m, ArH) and 5.37 (1H, d, J16, ArCH₂P); δ_P +21.90 and 29.0

Preparation of 2,2'-bipyridyl-5,5'-dicarboxaldehyde

This was done by modification of the method of Syper and Meochowski.¹³ 5,5'-Dibromomethyl-2,2'-bipyridyl (3.1 g, 12 mmol), potassium benzene selenite (5.64 g, 24 mmol) and potassium hydrogen phosphate (4.18 g, 24 mmol) were refluxed in dry THF (70 cm³) for 24 h. After cooling the mixture was diluted with water (50 cm³) and extracted with dichloromethane (3 x 30 cm³). During the extractions a cloudy yellow precipitate was observed in the aqueous layer so the extractions were continued (3 x 100 cm³). The organics were then dried and evaporated then treated with ether (100 cm³) and filtered. This treatment was repeated twice then the ether was dried and evaporated to recover diphenyl diselenide. The filtrate was recrystallised from acetonitrile to give 2,2'-bipyridyl-5,5'-dicarboxaldehyde (0.7 g, 27 %), m.p. 215.5-217.5 °C; Found C 66.92, H 3.74, N 13.20, C₁₂H₈N₂O₂ requires C 67.92, H 3.80, N 13.20; δ_H (d⁶-benzene) 10.22 (2H, s, ArCHO), 9.19 (2H, s, ArH), 8.73 (2H, d, ArH) and 8.35 (2H, d, ArH); δ_C 191.47 (ArCHO), 153.30 (ArC), 151.98 (ArC), 137.62 (ArC), 132.50 (ArC) and 122.66 (ArC).

The above reaction was repeated substituting acetonitrile for THF. This gave the product in 62 % yield.

Preparation of 1,4-dihexyloxy-2,5-bis(triphenylphosphoniomethyl)benzene

This was done by modification of the method of Michaelis and Gimborn.¹⁵ 2,5-Bis(chloromethyl)-1,4-hexyloxybenzene (6.0 g, 16 mmol) and triphenylphosphine (8.4 g, 32 mmol) were refluxed in dry toluene (80 cm³). After 1.5 h considerable material had precipitated out of the solution so dry DMF (80 cm³) was added and the reflux

continued for a further 2 h. The solution was cooled to give a white precipitate which was filtered and washed with 40 - 60 °C bp petroleum ether and dried to give the product 1,4-dihexyloxy-2,5-bis(triphenylphosphoniomethyl)benzene (11.35 g, 79 %); m.p. 242-244 °C; Found C 74.30, H 6.97, C₅₈H₆₆Cl₂O₂P₂ requires C 75.07, H 7.17; δ_H 7.92 (12H, m, ArH), 7.71 (18H, m, ArH), 6.63 (2H, s, ArH), 5.00 (4H, d, J 16, ArCH₂P), 3.90 (4H, m, ArOCH₂), 1.25 (4H, m, methylene) 1.09 (12H, m, methylenes) and 0.88 (6H, t, Me); δ_C 150.19 (ArC), 135.13 (ArC), 134.03 (d, J 10) (ArC), 130.20 (ArC), 130.04 (d, J 11) (ArC), 118.05 (d, J 95) (ArC), 116.23 (d, J 89) (ArC), 67.79 (OCH₂), 30.8 (CH₂), 27.82 (CH₂), 24.67 (CH₂), 23.5 (d, J 56) (ArCH₂P), 21.89 (CH₂) and 13.84 (CH₃); δ_P +22.09.

Wittig condensation polymerisation of 1,4-dihexyloxy-2,5-benzenedicarboxaldehyde and 5,5'-bis(triphenylphosphoniomethyl)-2,2'-bipyridyl dibromide.

This was done by modification of the method of Bestmann and Arnason.¹⁶

5,5'-Bis(triphenylphosphoniomethyl)-2,2'-bipyridyl dibromide (0.50 g, 0.58 mmol) was suspended in dry THF (30 cm³) under nitrogen at 0 °C. A solution of n-butyl lithium in hexanes (0.5 cm³, 2.4 M) was added *via* syringe. On addition of the base the suspension rapidly developed a dark metallic blue colouration which was maintained for 30 min. A solution of 1,4-dihexyloxy-2,5-benzenedicarboxaldehyde (0.20 g, 0.6 mmol) in dry THF (5 cm³) was then added *via* syringe and the mixture turned to a bright red colouration. A great deal of solid material was still evident in the suspension which was only noticed on the colour change. The mixture was left to stir for 1.5 h by which time it had turned a dull yellow colouration, then refluxed for a further 1 h. The products were then cooled and poured into methanol and a precipitate was filtered off (0.32 g). Much of the precipitate was a yellow powder reminiscent of the bipyridyl starting material and was insoluble in chloroform. Further filtration to remove this material gave a yellow solution and ¹H NMR showed that this comprised mainly of the starting material 1,4-dihexyloxy-2,5-benzenedicarboxaldehyde with impurities in the aromatic region (δ_H 7.80-7.40, m)

presumed to be traces of triphenylphosphine oxide. No polymeric material was isolated although it is possible that small quantities may have been present in the insoluble filtrate.

Repeat of the above reaction with extra care over the dryness of materials and glassware gave the same colour changes and products.

Wittig condensation polymerisation of 1,4-dihexyloxy-2,5-bis(triphenylphosphoniomethyl)benzene and 2,2'-bipyridyl-5,5'-dicarboxaldehyde

Using the same procedure as above, 1,4-dihexyloxy-2,5-bis(triphenylphosphoniomethyl)benzene (1.34 g, 1.5 mmol) was suspended and stirred in dry THF. A solution of n-butyl lithium in hexanes (1.25 cm³, 2.4 M) was added and the suspension immediately turned blue - black. On warming the suspension to 50 °C the colour lightened and turned red and only a trace of solid was visible. The solution was then cooled to RT and a solution of 2,2'-bipyridyl-5,5'-dicarboxaldehyde in dry dioxane (0.3 g, 1.5 mmol) was added. The red colour immediately deepened and a red precipitate developed. The mixture was then stirred under reflux for a further hour then the products were poured into methanol. A dark red fine precipitate resulted and attempts to filter off this material failed due to clogging of the sinter. The solvents were evaporated off to leave a bright red solid. The solid was subjected to Soxhlet extraction with ethyl acetate for three days until the solvent covering the thimble was clear. Evaporation of the solvent left a red solid (1.33 g); δ_H 7.73-7.32 (80H, m, ArH), 4.02-3.62 (4H, m,), 3.60-3.41 (4H, m), 1.90-1.60 (8H, m) 1.60-1.01 (24H, m) and 0.88 (6H, m). Comparison with authentic spectra shows that this is consistent with a mixture of triphenylphosphine oxide, residual ethyl acetate and a small quantity of a product bearing the hexyloxy side chain. A dark red solid (0.49 g) remained in the thimble. Assuming this is the polymeric product this gives a 68 % yield (1.02 mmol). ν_{max}.2920, 2856, 1589, 1510, 1450, 1413, 1204, 1028, 864, 781 and 513. This product was not completely soluble in any of the many organic solvents tried but a red colouration was obtained by sonication of the solid in chloroform (λ_{max} 400.8 nm) and a lighter red colouration was obtained by sonication in acetone. Sonication in DMSO caused

swelling of the product but the swollen polymer failed to dissolve. Heating the polymer to boiling in DMSO dissolved the swollen polymer but it quickly reprecipitated at temperatures around 100 °C. ^1H NMR (d^6 -DMSO) of hot filtered polymer and a suspension of the polymer failed to resolve any signals at 50 °C. Trifluoroacetic acid was added to a suspension of the polymer in acetone. The colouration of the dissolved fraction changed to red-green (λ_{max} 444.8 nm) and the solid turned dark brown. Neutralisation with aqueous NaOH returned firstly the solution to its original colour (λ_{max} 399.2 nm) immediately on addition of the base and the solid changed back to a red colouration over a period of 10 min. To a further solution of the polymer, a solution of zinc acetate in chloroform was added. The solution turned to a pale yellow green colouration (λ_{max} 438.4 nm). On addition of ammonia the solution returned to its original colouration and absorption maximum.

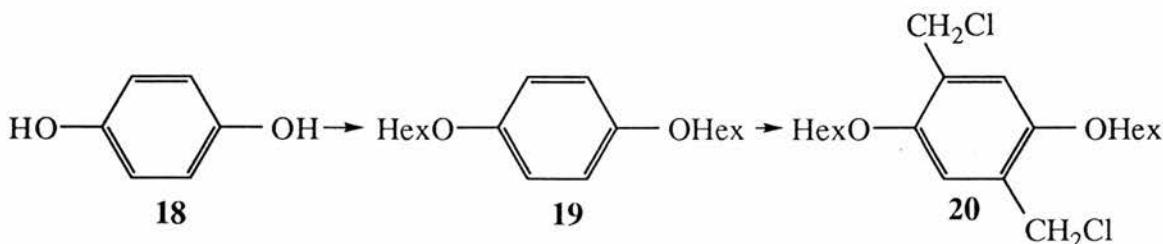
Both the solid polymer and very dilute solutions of the polymer exhibit strong fluorescence under UV light. Due to interest in these characteristics a sample of the material was sent to the University of Edinburgh for analysis by photoluminescence and excitation spectroscopy. Results of this analysis are presented in the discussion.

4.3 Discussion

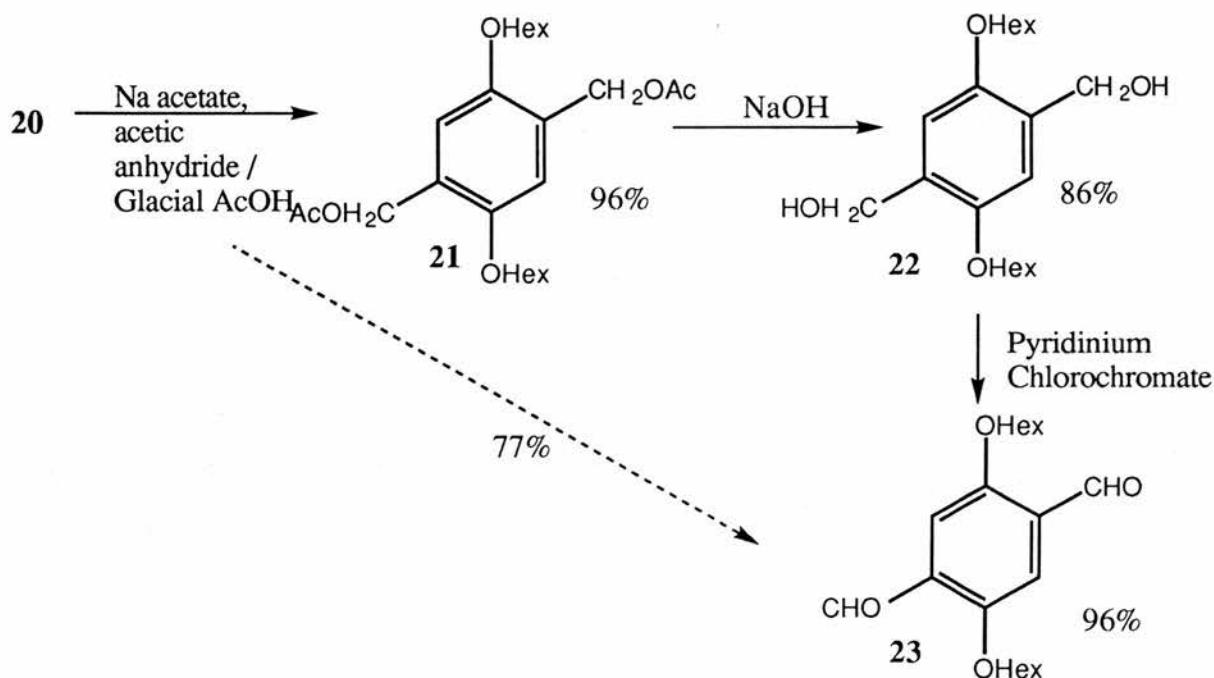
4.3.1 Preparation of the Wittig route monomers.

The first synthetic target in this section was 1,4-dihexyloxy-2,5-benzene dicarboxaldehyde. This was chosen as a possible solubilising group for a Wittig co-polymer due to its aryl ring which would provide a continuous conjugated backbone. The hexyloxy groups give a favourable ratio of alkyl to aryl carbons and this should aid the processability of a co-polymer. A further reason for this choice was that another member of the group¹² was involved in the synthesis of a precursor to this molecule and so a supply of starting material was readily available.

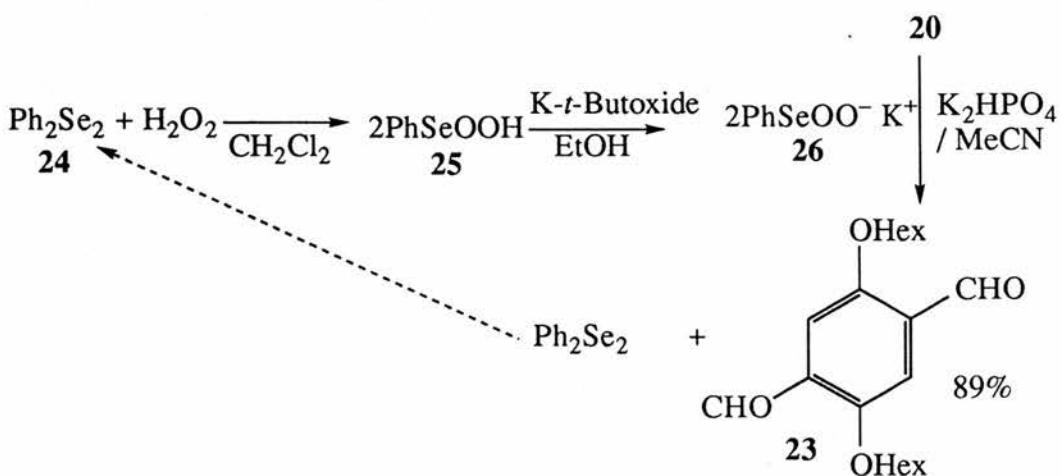
Starting with hydroquinone **18**, alkylation was achieved *via* the Williamson reaction. Conversion of the phenol to phenoxide was accomplished using potassium hydroxide and on addition of bromohexene the phenoxide attacked the alkyl halide to give the ethers. Conversion to the diether was found to be incomplete so purification was done by adding the mixture to aqueous sodium hydroxide. The monoether was converted to the water soluble sodium salt and so separation was conveniently achieved by extraction with dichloromethane to give 1,4-dihexyloxybenzene **19**. Chloromethylation to give 2,5-bis(chloromethyl)-1,4-hexyloxybenzene **20** was run by two methods with a far greater yield being achieved using the more acidic medium.¹² This improvement may be associated with an increase in the concentration of HOCH₂⁺ ion from formaldehyde due to the more acidic conditions.¹⁷



Oxidation of **20** to 1,4-dihexyloxy-2,5-benzene dicarboxaldehyde was done by Holmes *et al*¹⁴ in three steps. Conversion of the dichloride **20** to the diol **22** by hydroxide cannot be done directly owing to the likelihood of polymerisation. It was thus done through the acetate **21** which could be safely hydrolysed. Oxidation of **22** with pyridinium chlorochromate gave the dialdehyde **23** with an overall yield of 77%.

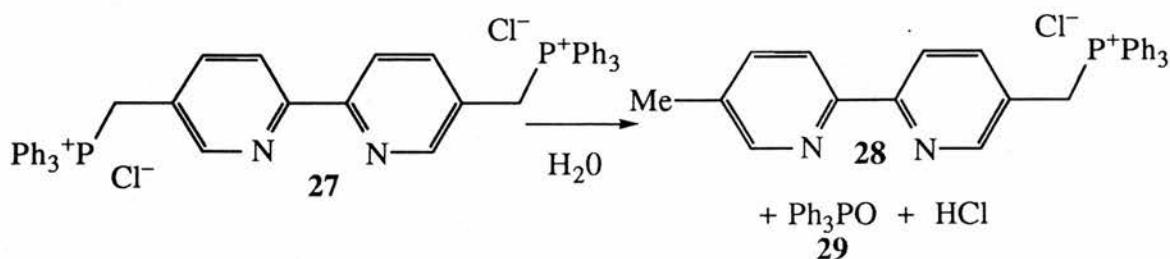


On studying the literature¹³ we found that oxidation of bis(chloromethyl)-1,4-methoxybenzene to the corresponding dialdehyde may be done in one step by the use of potassium benzene selenate **26**. This was prepared by the oxidation of diphenyl diselenide with peroxide to give benzeneselenic acid **25**, followed by salt formation by adding the acid to potassium ethoxide. Rather than using potassium ethoxide as the base we repeated method using potassium-t-butoxide. The salt **26** was used to oxidise **20** in a single step to **23** in 89 % yield. One of the main attractions of this reaction is the convenient recovery of the starting material in pure form ready for re-use.

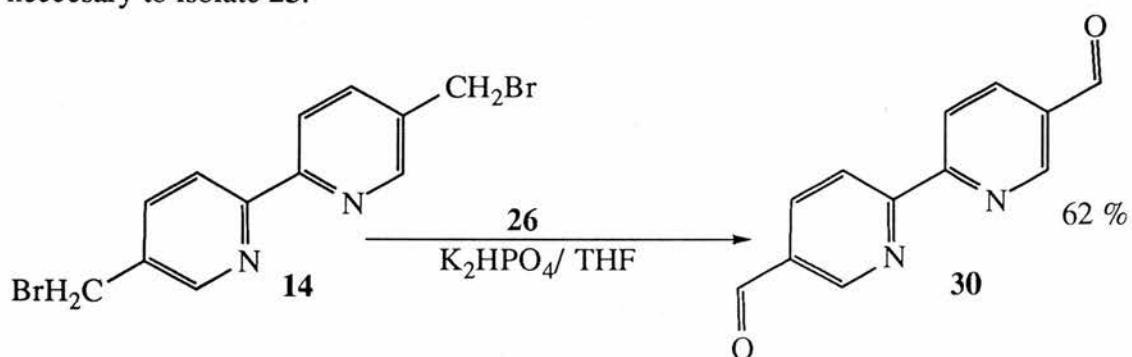


With the dialdehyde prepared, attention now turned to the synthesis of 5,5'-bis(triphenylphosphoniomethyl)-2,2'-bipyridyl dibromide **27**. 5,5'-Dibromomethyl-2,2'-bipyridyl **14** was reacted with two equivalents of triphenylphosphine in toluene/DMF solvent to give **27** as a powder sparingly soluble in DMSO. ^1H NMR of this compound showed some minor impurities that were difficult to remove.

The reaction was repeated using DMF as the solvent and on this occasion more impurities were found. ^1H NMR of the products showed that the expected phosphonium salt **27** was present due to the characteristic splitting of the benzylic protons α to phosphorus ($\delta_{\text{H}} 5.37$ (d, $J_{\text{PH}} 16$)). However the integration in the aromatic region showed that a great deal of impurities were present along with a further peak at $\delta_{\text{H}} 2.35$ which corresponds to the methyl group of 5,5'-dimethylbipyridyl. It is suggested that the bulk of the material may be the monophosphonium salt **28** and triphenylphosphine oxide **29**. These are hydrolysis products of the salt and so it is expected that the product sought was made then hydrolysed by the absorption of a small quantity of water during reflux overnight. This material was discarded and the product from the first attempt was used for subsequent reactions.



Given the success of the oxidation of the dichloride **20** to the dialdehyde **23** it was decided to try to synthesise the bipyridyl equivalent. Syper and Meochowski¹³ do not include any pyridyls in their examples of this reaction so the choice of solvent and workup were devised by experiment. The use of THF as a solvent for **14** was successful but repeat of the reaction with acetonitrile proved this to be the better choice. The workup devised was very satisfactory. Due to insolubility of the dialdehyde product **30** in ether, the diphenyl diselenide side product can be conveniently removed by washing. This avoids the more time consuming removal of this material by elution through a column which was necessary to isolate **23**.



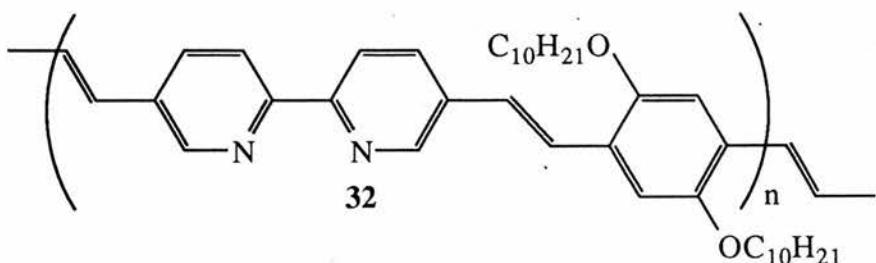
Preparation of 1,4-dihexyloxy-2,5-bis(triphenylphosphoniomethyl)benzene was straightforward save for the necessity of the addition of dry DMF to ensure that the products would stay in solution until the reaction was completed. This manoeuvre proved effective.

4.3.2 Polymerisation of the Wittig route monomers.

The Wittig condensation polymerisation of 1,4-dihydroxy-2,5-benzenedicarboxaldehyde **23** and 5,5'-bis(triphenylphosphoniomethyl)-2,2'-bipyridyl dibromide **27** was unsuccessful in providing the sought co-polymer. The main reason for this failure is believed to be due to solubility problems with the diphosphonium salt. The bulk of the products isolated comprised of unreacted **23** and phosphine oxide with an insoluble powder believed to be partially hydrolysed **27**. The striking colour change to blue black on addition of the base may have been due to formation of the ylide and its fast hydrolysis with traces of water in the solvent. Once the dialdehyde was added and the colour changed to a more transparent red it became evident that formation of the ylides was incomplete due to the amount of solids in the mixture. Over time the red colouration faded to be replaced with a dull yellow. It is expected that all the ylides formed had reacted by this point but the mixture was refluxed to aid solubility of any unreacted materials. No further red colouration was observed during reflux so the reaction was discontinued.

On repeat of the above with great care over dryness of glassware and reagents the same results were found. Due to the insoluble nature of **27** and difficulties in purifying this reagent this reaction was abandoned.

After the experimental part of this work was completed, Wasielewski et al¹⁸ published details of very closely related work towards bipyridinevinylene co-polymers which provides valuable comparative information. As with this investigation, problems were found in the synthesis of **27** and this compound was dropped from their synthetic route. As an alternative the monophosphonium salt **33** was prepared and used to construct oligomers as building blocks. Polymerisation of these gave **32**. Some parts of the synthetic route are somewhat ambiguous and these, along with further comparisons to our own study, will be discussed in Chapter 5.



The Wittig condensation polymerisation of 1,4-dihexyloxy-2,5-bis (triphenylphosphoniomethyl) benzene and 2,2'-bipyridyl-5,5'-dicarboxaldehyde gave rise to the expected triphenylphosphine oxide by-product and a red solid (polymer **31**) that was insoluble in most solvents in 68 % yield. The insoluble nature of this product made NMR unobtainable even on overnight runs at 300 MHz for ^1H . Alternative methods of characterisation are discussed below.

4.3.3 Electronic Absorption, Photoluminescence (PL) and Excitation spectroscopy of **31**

Solution spectra

The UV-visible spectrum (absorption spectrum) of orange polymer **31** dissolved in chloroform displayed one major band with $\lambda_{\text{max}} = 401 \text{ nm}$. The assignment of this band may be studied using solvatochromic effects. The band position did not depend particularly on the solvent polarity as is usual for a $\pi-\pi^*$ transition which is expected to shift slightly to longer wavelength as the solvent polarity increases (bathochromic shift). (The energy of the π^* orbital is slightly decreased by hydrogen bonding). If the band were a $n-\pi^*$ transition (i.e. from an orbital based on the nitrogen such as the lone pair) then the absorption band would shift markedly to higher energy as the polarity of the solvent increased (hypsochromic effect).

Trifluoroacetic acid was added to a suspension of the polymer in acetone. The colouration of the dissolved fraction changed to red-green ($\lambda_{\text{max}} 444.8 \text{ nm}$) and the solid

turned dark brown. Neutralisation with aqueous NaOH returned firstly the solution to its original colour (λ_{max} 399.2 nm) immediately on addition of the base and the solid changed back to a red colouration over a period of 10 min. We expect this change in the chromophore is due to reversible protonation / deprotonation of bipyridyl groups on the polymer backbone. To a further solution of the polymer, a solution of zinc acetate in chloroform was added. The solution turned to a pale yellow green colouration (λ_{max} 438.4 nm). On addition of ammonia the solution returned to its original colouration and absorption maximum. This behavior may be due to chelation of the zinc ion to the bipyridyl segments followed by release on addition of ammonia.

Photoluminescence (PL) spectra (i.e. fluorescence or emission spectra) and excitation spectra of the polymers were obtained in acetone solution (Figure 4.1). The PL emission is centred at $\lambda_{\text{em}} = 515$ nm. This occurs at much lower energy than the green light emitted by conjugated polybipyridine in formic acid solution ($\lambda_{\text{em}} = 440$ nm).²⁰ However it is very close to the value for polymer **32** ($\lambda_{\text{em}} = 507$ nm).

Figure 4.1 (b) shows the excitation spectrum, in which the intensity of the light emitted at a single wavelength (here chosen to be 515 nm, the emission maximum) is monitored as a function of excitation wavelength. Usually, the excitation spectrum has the same form as the absorption spectrum, since the more light that is absorbed by the molecule the greater the number of photons that will be emitted. This can be very useful, for example, if as in this case the absorption spectrum is difficult to measure as it is so absorbing, or if it is in the solid state. Notice that the excitation spectrum displays vibrational fine structure (sometimes termed vibronic, or phonon sidebands) due to the excitation from the lower $v=0$ level to the various $v=0,1,2,\dots$ etc upper levels (see Figure 4.2). The frequency separation between these peaks cannot be determined from the spectrum with great certainty, but the values ($760, 600, 1080, 1443 \text{ cm}^{-1}$, all $\pm 200 \text{ cm}^{-1}$) are in the region of skeletal vibrations of the molecule. The presence of several different frequencies means that more than one fundamental vibration is involved.

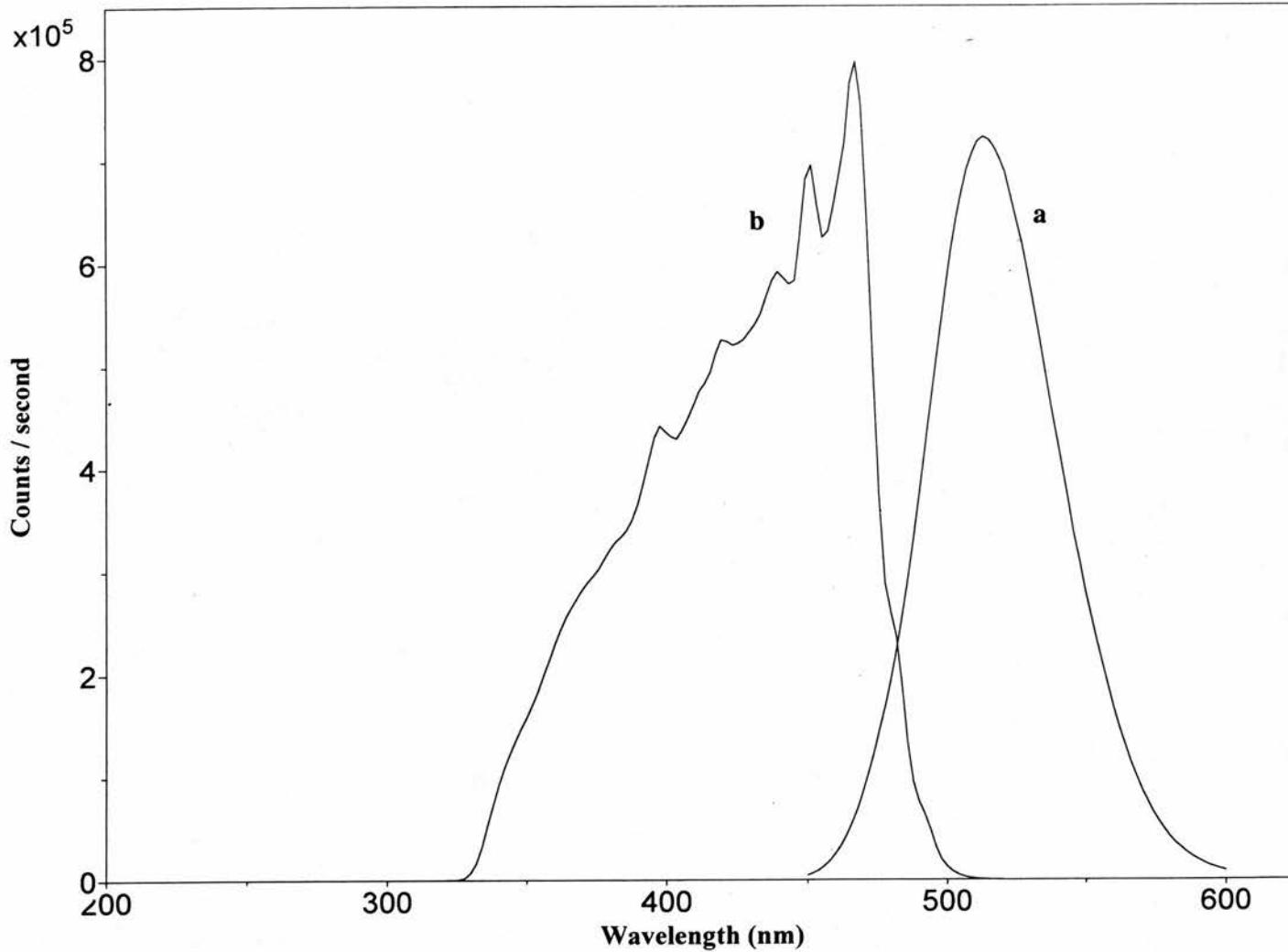


Figure 4.1: (a) (Right hand peak centred at 515 nm) PL spectrum of polymer 31 in acetone with a constant excitation wavelength $\lambda_{ex} = 350$ nm. (b) Excitation spectrum showing the variation in emission intensity at $\lambda_{em} = 515$ nm as the excitation wavelength is varied in the range 300-550 nm.

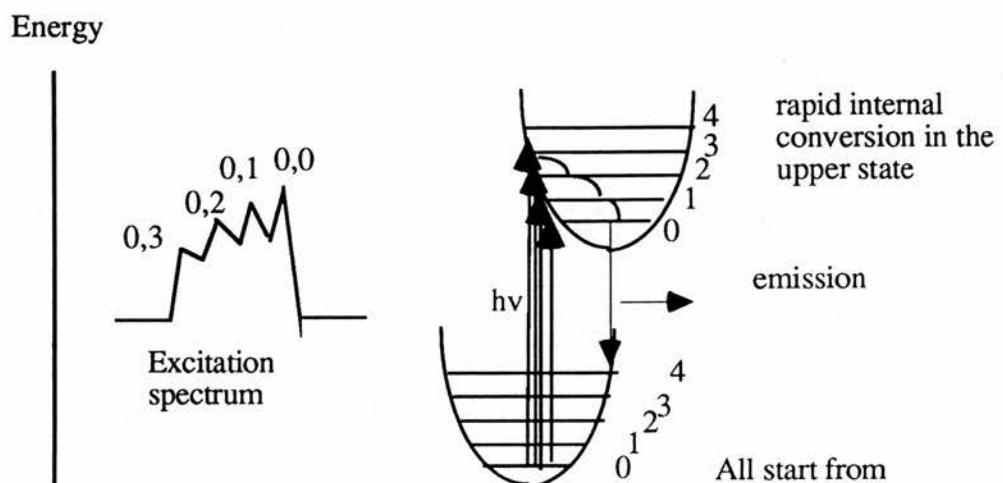


Figure 4.2: Diagram showing how vibronic structure arises in the excitation spectrum from absorption to different levels in the upper excited state.

Solid-state spectra

The spectrum of **31** in the solid state (cast from solution of CHCl₃ onto a glass slide) shows $\lambda_{\text{max}} = 445$ nm. The corresponding solid-state emission and excitation spectra are shown in Fig. 3. These are most relevant from the point of view of fabrication of thin film devices using these materials. Emission Figure 4.3 (a) is centred at 600 nm, a bathochromic shift of 85 nm. Such large shifts are normal for PPV-like materials. The excitation spectrum has a most unusual form Figure 4.3 (b). A sharp peak at 468 nm is superimposed upon a very broad band. The position of this peak is very close to the strongest peak in the polymer's excitation spectrum in acetone. Thus, one possible assignment of this peak is to a segregated polymer segment which is not interacting with other polymer chains, but is trapped in a solvent-like micro-environment.

This compares with typical PPV values in cast thin films giving orange emission with $\lambda_{\text{em}} = 571$ nm for a yellow polymer displaying $\lambda_{\text{max}} = 454$ nm in the visible

absorption spectrum.²¹ But the closest comparison is with polypyridylvinylene (PPyV), currently in vogue because of its potential for blue emission, which in thin films has λ_{max} of 420 nm, and a broad emission centred at 590 nm (red-orange).²²

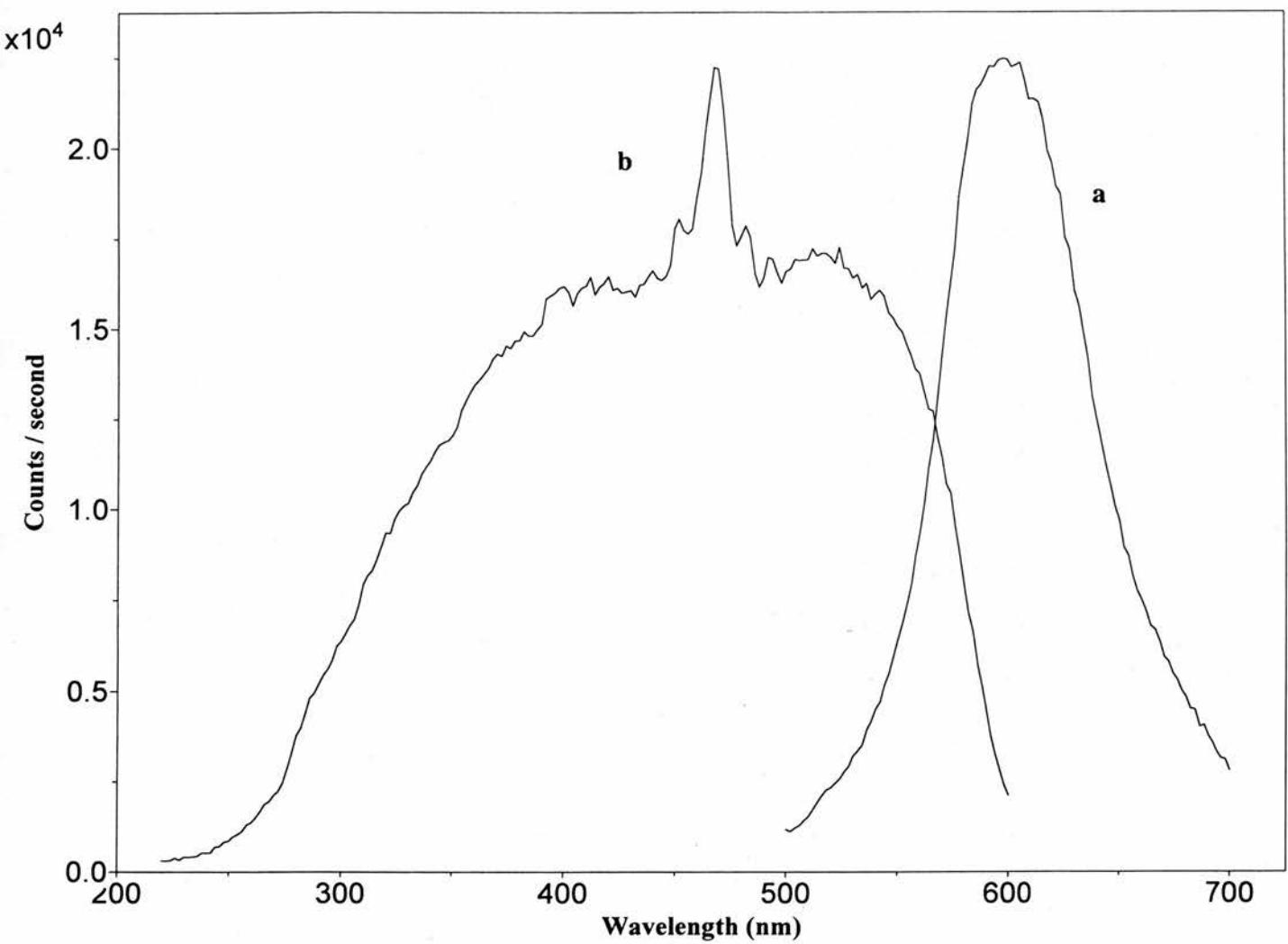


Figure 4.3: (a) (Right hand peak centred at 600 nm) PL spectrum of polymer 31 in the solid state with a constant excitation wavelength $\lambda_{ex} = 350$ nm. (b) Excitation spectrum showing the variation in emission intensity at $\lambda_{em} = 600$ nm as the excitation wavelength is varied in the range 200-600 nm.

4.4. Summary

The work has been successful in preparing a material **31** that displays many expected characteristics of a co-polymer of poly(bipyridinevinylene). Although the material is too insoluble for positive identification by NMR, evidence from electronic absorption, photoluminescence (PL) and Excitation spectroscopy in both the solid state and in solution show that the material is a conjugated polymer with absorption and emission characteristics similar to poly(pyridinevinylene).

Comparison of the copolymers **31** and **32** shows that they have much in common, such as shifts in their absorption spectra on addition of zinc acetate to their solutions and almost identical PL maxima.

Oxidation of the aryl chloromethyl group by potassium benzene selenate has been found to be a convenient and very competitive method for the production of aryl aldehydes. The reaction has also been successfully extended to provide 2,2'-bipyridyl-5,5'-dicarboxaldehyde, an important intermediate for the synthesis of poly(bipyridylvinylenes).

4.5 References

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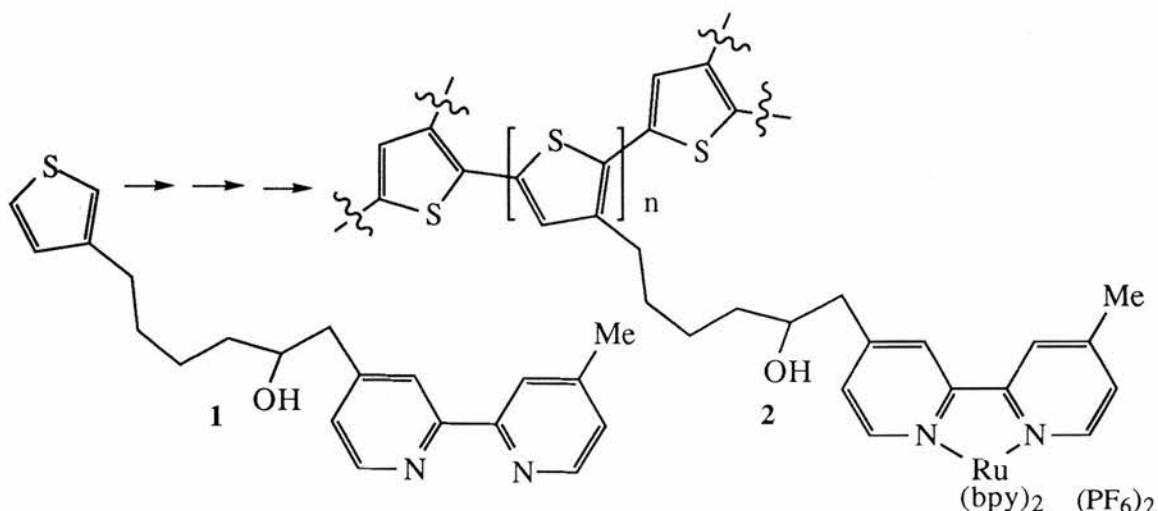
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Chapter 5

Suggestions for future work

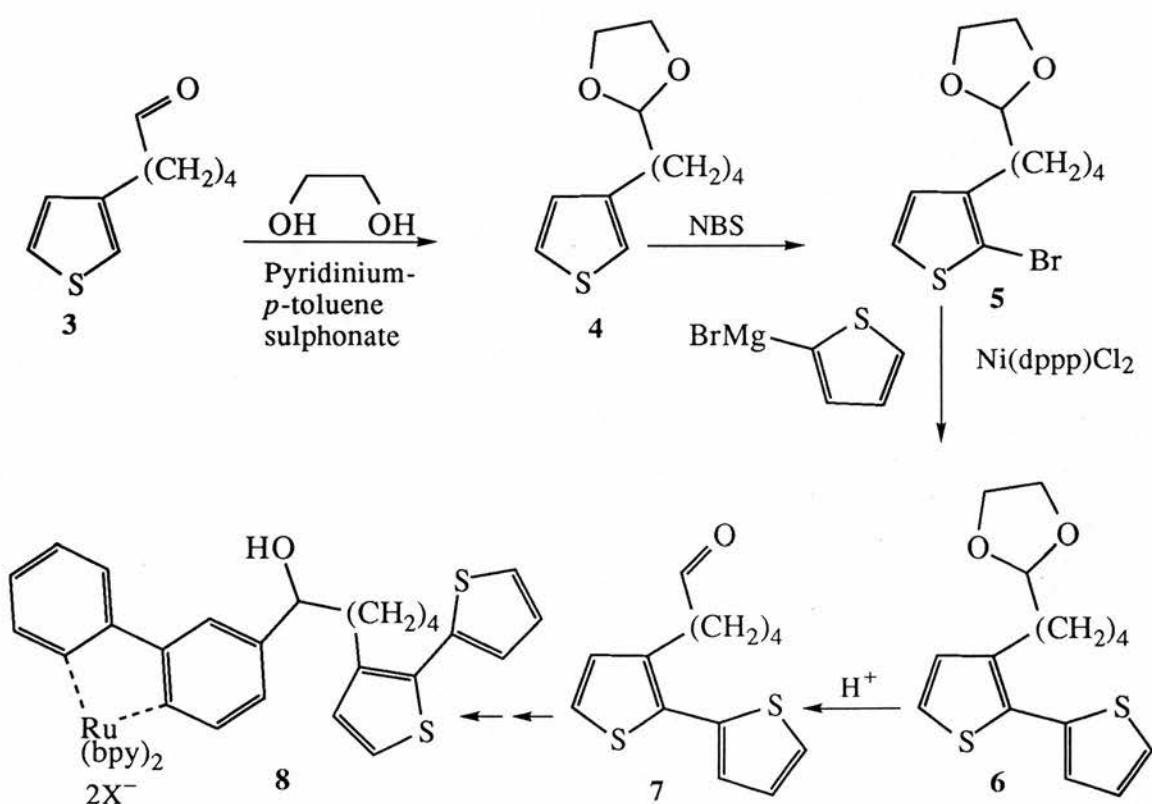
5.1. Synthesis, Chelation and Polymerisation of a Monothienyl ligand 4-[6-(3-thienyl)hexan-2-oyl]-4'methyl-2,2'-bipyridine 1

Although the synthetic target **1** and the electrochemically polymerised ruthenium complexed polymer **2** were achieved, we were unable to obtain device quality films on ITO substrates. The quality of the films obtained was found to be dependent upon the concentration of water in the electrolytic media with the best films obtained in dry media. Polymerisation usually commenced after potentiostating at +2.5 V followed by cycling. The use of this highly oxidative potential may have contributed to the production of poor films but it was found to be necessary in order start the polymerisation.



Although there are various electrochemical parameters that could yet be varied if more material were available (using CH₂Cl₂, using a cathodic depolarisor or various electrolytes), lowering the oxidation potential of the thiophene unit may be the key to producing better films. Pickup and Zhao¹ found that bithiophene acts as an excellent nucleation initiator for electrochemical polymerisation of 3-bromothiophene and deceases the minimum potential for polymerisation. We can use this principle to enhance polymerisation of the thiophene metal complex polymer **2** by modification of the synthetic route to give thiophene dimers.

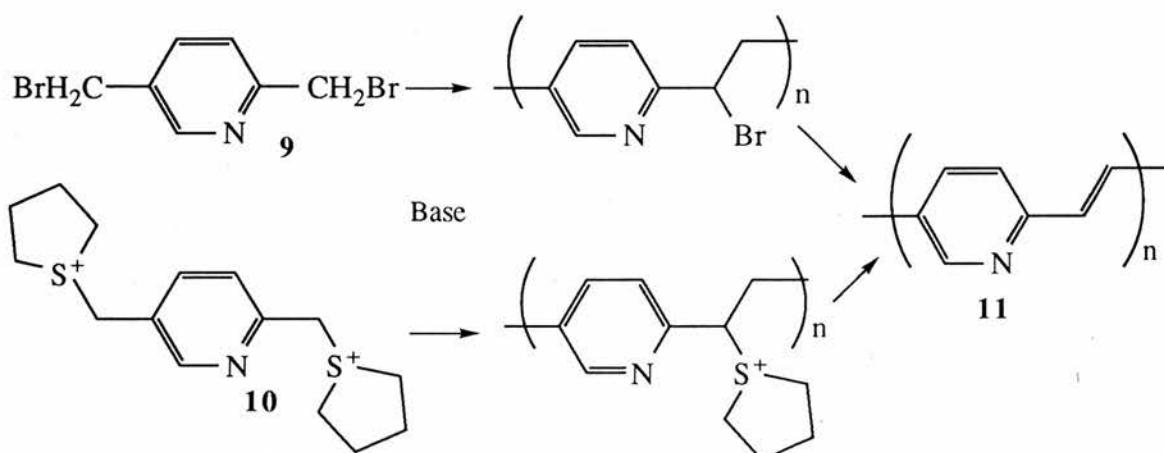
This may be done starting with the 1-(3-thienyl)pentan-5-al **3**.intermediate used in the synthesis of **1**. Protection of the aldehyde by acetal formation **4** followed by free radical bromination gives the substituted 2-bromothiophene **5**. Nickel catalysed coupling of **5** with the Grignard reagent of 2-bromothiophene gives the dimer **6** which, following deprotection to the aldehyde **7** follows the same route discussed in Chapter 2 to give the complex **8**.



Such dimerisation would obviously cut the number of metal centres to thiophene units to 1:2 and this may also have effects on the polymerisation worthy of study.

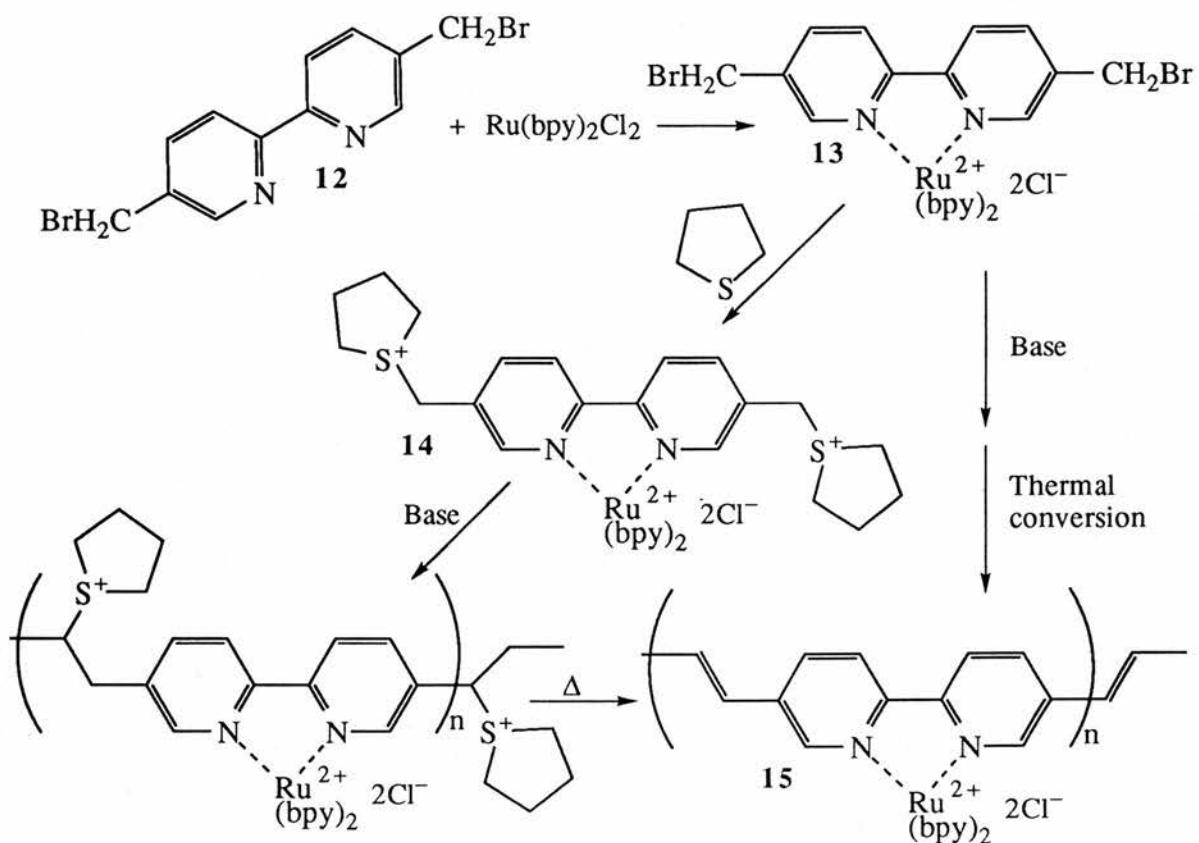
5.2 Synthesis of Monomers for Poly(bipyridinevinylene) and their Polymerisation Behaviour.

Attempts at base driven polymerisation of Gilsch, Son and Wessling type bipyridyl monomers only gave the expected precursor polymer when the Wessling style tetrahydrothienyl leaving group was employed. The Son precursor was found to give hydrolysis products by action of base and no reaction was found for the Gilsch type monomer. This is disappointing when compared to a recent report by Holmes *et al*² which shows that the Gilsch **9** and Wessling **10** pyridine analogues can be polymerised successfully to provide poly(pyridinevinylene) **11**. This shows that the polymerisation reaction can proceed using an electron deficient pyridine ring.



The lack of success for our polymerisation of the bipyridine analogues may be considered to be due to their lower solubility in comparison to **9** or **10**. Interestingly, the metal complex $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ is highly soluble in polar organic solvents. Thus polymerisation of the metal complexes may be attempted by firstly chelating 5,5'-bisbromomethyl-2,2'-bipyridine **12** to $\text{Ru}(\text{bpy})_2\text{Cl}_2$ to give the functionalised complex **13**. This complex may be regarded as a Gilsch type monomer and direct polymerisation attempted, otherwise reaction with tetrahydrothiophene could give the Wessling monomer **14**. Base polymerisation of these monomers followed by processing and thermal conversion may provide a direct route to the ruthenium complexed poly(bipyridine)

vinylenes) **15**. However, it is necessary for the ruthenium complex to be stable to base hydrolysis under these conditions.



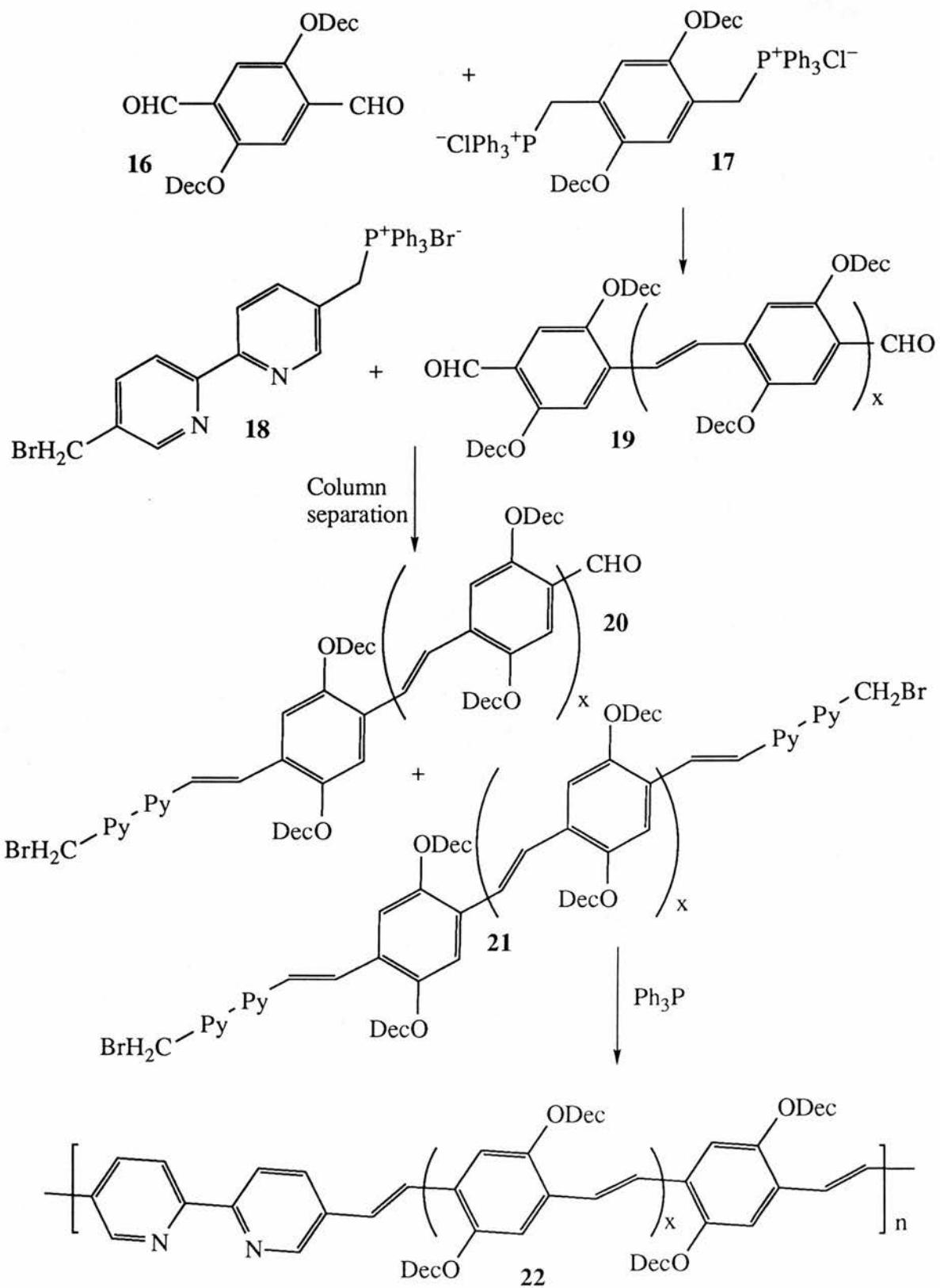
5.3 Synthesis of Wittig Monomers for Co-Polymers of Poly(bipyridine vinylene) and their Polymerisation Behaviour

Wang and Wasielewski³ recently reported upon the synthesis of two bipyridinevinylene co-polymers prepared by the Wittig reaction. Their route starts with the synthesis of a dialdehyde **16** from the corresponding dichloride in three steps by the method of Holmes *et al*⁴, a diphosphonium salt **17** and the monophosphonium salt of 5,5'-bisbromomethyl-2,2-bipyridyl **18**. Wittig olefination of **16** and **17** leads to the products **20** and **21** with $x=0$. Alternatively, Wittig olefination of **16** and **17** is reported to give **19** with $x=2$ as the product⁵. This stage is somewhat ambiguous as we might reasonably expect further oligomerisation / polymerisation products and these, along with yields and separation techniques, are not reported.

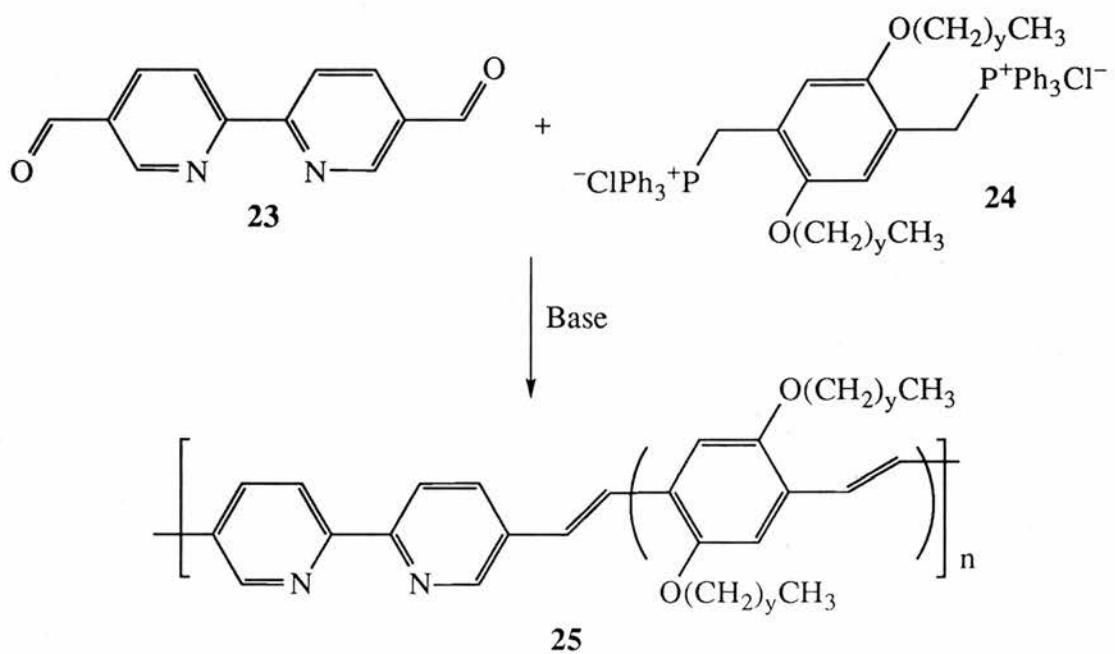
Wittig olefination of **18** and **19** gives the products **20** and **21** which were separated to show yields of 11 - 49 %. The higher yields were obtained when **19** with $x=2$ was used, probably as a result of the better solubility afforded by the higher ratio of aliphatic units.

Reaction of triphenylphosphine with **20** and **21** to give the respective mono and diphosphonium salts. Self polymerisation of monophosphonium **20** and co-polymerisation of diphosphonium **20** with **19** gave the polymer **22** in high yield.

Although this method was successful in preparing the poly(bipyridinevinylene) co-polymers it is somewhat laborious and a great deal of loss of materials occurs on the step towards the building blocks **20** and **21**. The major difference between the polymer **22** ($x=1$) and the polymer produced by our own work in chapter 5 **25** ($y=5$) is the difference in the length of the alkoxy chain. Using the oxydecyl ($y=9$) group leads to a polymer sufficiently soluble in chloroform to obtain an NMR spectrum whereas with oxyhexyl, the polymer was not soluble enough in any of the solvents tried.



Since a small difference in the alkoxy chain length is found to increase solubility so markedly then it would be sensible to try this small alteration to our polymer synthesis. This should give soluble bipyridinevinylene co-polymers by a more direct route than Wang and Wasielewski's method. Using 2,2'-bipyridine-5,5'-dicarboxaldehyde **23** (which we prepared conveniently in good yield by direct oxidation³ from the corresponding dibromide) and a diphosphonium salt **24** alkoxy groups of $y > 5$ should provide a more processable polymer than our hexyloxy example.



By using long solubilising chains it may be possible to further react the polymer with metal complexes such as $\text{Ru}(\text{bpy})_2\text{Cl}_2$ to obtain a soluble and processable conjugated metal complex polymer.

5.4 References

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