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Synthesis of Novel Polymers for Light Emitting and Metal Ion Sensing Applications

A thesis presented by Joanne Ritchie to the University of
St. Andrews in application for the degree of Doctor of
Philosophy

Supervisor: Dr. J. A. Crayston

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Contents

Abbreviations

Acac	Acetylacetonoate
Alq_3	Aluminium Trisquinolate
DBM	Dibenzoylmethane
DCM	Dichloromethane
DMF	Dimethyl formamide
EL	Electroluminescence
HOMO	Highest Occupied Molecular Orbital
IR	Infrared
ITO	Indium Tin Oxide
LCD	Liquid Crystal Display
LEP	Light Emitting Polymer
LUMO	Lowest Unoccupied Molecular Orbital
OLED	Organic Light Emitting Diode
PL	Photoluminescence
PLED	Polymer Light Emitting Diode
PLQY	Photoluminescent Quantum Yield
PPP	Poly(*p*-phenylene)
PPV	Poly(*p*-phenylene vinylene)
NMR	Nuclear Magnetic Resonance
THF	Tetrahydrofuran

Acknowledgements

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Finally, I would like to thank my family and boyfriend Steven, who were always there to pick me up both physically and mentally. I couldn't have asked for more.

Abstract

Polyfluorenes are an important class of light emitting polymers due to their excellent quantum yields and thermal stabilities. One drawback that polyfluorenes exhibit is poor colour stability. In this work we report the synthesis of a bench mark polymer poly(1,4-phenylene-9,9-dihexylfluorene) which emits blue light with a solution photoluminescence emission maximum of 409 nm. A series of seven copolymers of fluorene were prepared by substituting *para* phenylenes with increasing amounts of *meta* linkages. By incorporating *meta* linkages the colour stability of the blue polymer were improved and the long wavelength emission attributed to either excimer or fluorenone can be suppressed.

An alternating copolymer poly(3,8-phenanthroline)-2,7-(9,9-dihexylfluorene) was also prepared. This polymer emitted blue light at 410 nm with a small solvatochromic effect. This polymer also displayed strong ionochromism to a selection of transition and main group metal ions and would therefore be a sensitive metal ion detector. Colour tuning of this polymer was also achieved through coordination of a europium complex to the phenanthroline repeat units to achieve red light emission. Attempts were also made to prepare a green light emitter by coordinating a terbium complex.

Several different synthetic strategies were explored for the covalent attachment of an aluminium trisquinolate (Alq_3) type complex onto a fluorene based

polymer. Despite progress being made in this area, the aluminium complex was not covalently attached to the polyfluorene. However, aluminium quinolate was successfully attached to polystyrene. This was achieved by functionalising polystyrene to form an acetyl acetonate type ligand which could coordinate to aluminium. This polymer had an emission maximum of 520 nm corresponding to the green emission associated with aluminium trisquinolate.

Chapter 1

Introduction

The discovery in 1977 that polyacetylene, when doped, showed conductivities of the same magnitude as some metals[1] sparked an interest into conjugated polymers that resulted in an enormous array of uses and applications for organic semiconductors including artificial muscles[2], stealth paint[3], biosensors and electrochromic (smart) windows.[4] But it was not until 1990 that conjugated polymers were shown to emit light.[5] Since then the area of light-emitting polymers has become one of the fastest growing domains in terms of numbers of scientific papers published in recent times. This is due to the potential applications that these materials have for flat panel displays such as laptops and mobile phone displays. Since devices can be synthesized from polymers, cheap solution based technology such as screen printing or inkjet printing[6] can be used to fabricate devices instead of vacuum deposition required in the traditional inorganic light-emitting diode (LED) fabrication. The mechanical properties of polymers also allow for the design of flexible displays; electronic newspapers and roll up road signs have been envisaged. Additionally light emitting polymer displays have low power consumption and greater viewing angles than rival liquid crystal displays (LCDs).

It is less than fifteen years since light emitting polymers were discovered however the technology has rapidly improved to the extent that several products with light emitting polymer displays have entered the market. These include electric razors, car stereos with polymer backlights and a Kodak digital camera with full colour OLED display (Fig. 1.1).[7]

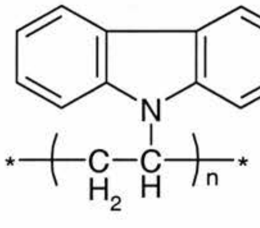
Figure 1.1:Kodak digital camera comprising an OLED display

Science is constantly moving forward and there still remain improvements and new discoveries that can be made in the field of light-emitting polymers.

1.1 Organic Light Emitting Diodes

Electroluminescence is the non-thermal emission of light from a material when an electric current is applied. For several decades the phenomenon of electroluminescence has been exploited for use in light emitting diodes (LEDs) formed solely from various inorganic materials such as gallium arsenide. Despite electroluminescence being observed in anthracene crystals in the 1960s it was thought that organic light emitting diodes (OLEDs) were not feasible due to very poor efficiencies.[8]

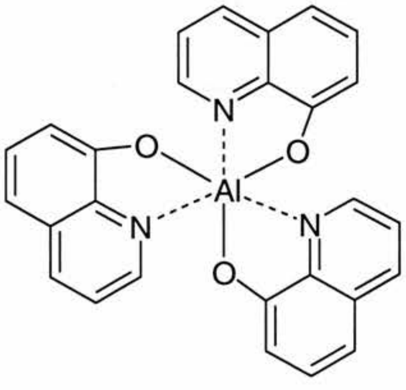
The first light-emitting polymer, though not a conjugated polymer, was polyvinylcarbazole, **1,** which was made into devices in 1983 by R. H. Partridge.[9]



1

Partridge carried out an extensive study of this material and produced a series of detailed papers on this topic. Fluorescent additives such as perylene or triphenylbutadiene were added to the polyvinylcarbazole to improve the fluorescence output. Surprisingly, this paper did not have the scientific impact it deserved and remained largely uncited.

In 1986 Van Slyke and Tang showed that 8-hydroxyquinoline aluminium (Alq_3) **2** could be made into an LED[10] and although efficiencies were extremely low in comparision to traditional inorganic LEDs there was enough promise demonstrated in this paper to prompt more research and interest in this area.



2

Organic LEDs have many advantages over their inorganic counterparts primarily because the synthesis involves fewer stages and consequently they are cheaper to prepare. In comparison to inorganic displays, OLEDs would comprise of lightweight components and could potentially be made flexible.

1.2 Polymer Light-Emitting Diodes (PLEDs)

In 1990 Holmes et al. reported a conjugated polymer that really sparked the frenzy of interest into this area of research.[5] The potential of polymer light emitting diodes (PLEDs) was enormous, not only could flexible displays be made as in the case of the OLEDs but the PLEDs would combine light emission with the mechanical properties of polymers. Small molecule devices suffer from the thin films recrystallising during their use whereas LEPs are much more capable of withstanding the harsh operating conditions found in an LED device. The need for expensive microfabrication equipment is a drawback in both traditional inorganic LEDs and the small molecule organic LEDs, as it is both costly and time consuming. Polymer LEDs can be fabricated using the relatively simple technique of spin coating and in future the use of high vacuums in processing may be eradicated completely. It is also possible to produce large area displays with polymer devices as they can be easily fabricated using solution processable techniques such as spin coating, screen printing or even through conventional inkjet printing techniques. Since the initial discovery in 1990 by Holmes a large number of families of light emitting polymer have been reported which are discussed in more detail in sections 1.4 – 1.7.

1.3 Light Emission

Light is emitted from conjugated polymers following excitation of electrons from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) by ultraviolet light or an applied voltage. The excited polymer then returns to the ground state by either a non-radiative process or by the emission of light. Emission occurs from the lowest energy band gap and therefore energy is transferred from high energy states to lower energy states This means that for a device containing two different polymers emission will generally be observed from the long wavelength emitter. Similarly for a polymer with a range of conjugation lengths (i.e. segments of coplanar rings) emission will occur from the longest conjugated segment. This gives a larger Stokes shift to the emission and prevents reabsorption of the emitted light by the polymer (Fig 1.2). Also the emission often displays vibrational structure characteristic of a well defined single emitting segment. Two kinds of energy transfer are known to exist for conjugated polymers. Firstly energy can be transferred along a polymer chain over relatively short distances, referred to as Dexter transfer. The second type of energy transfer is between different chains (interchain energy transfer) or different chain segments. This can occur over larger distances than for Dexter transfer and is referred to as Förster transfer.[12] Both of these processes have different selection rules which are discussed in more detail in Chapter 3.

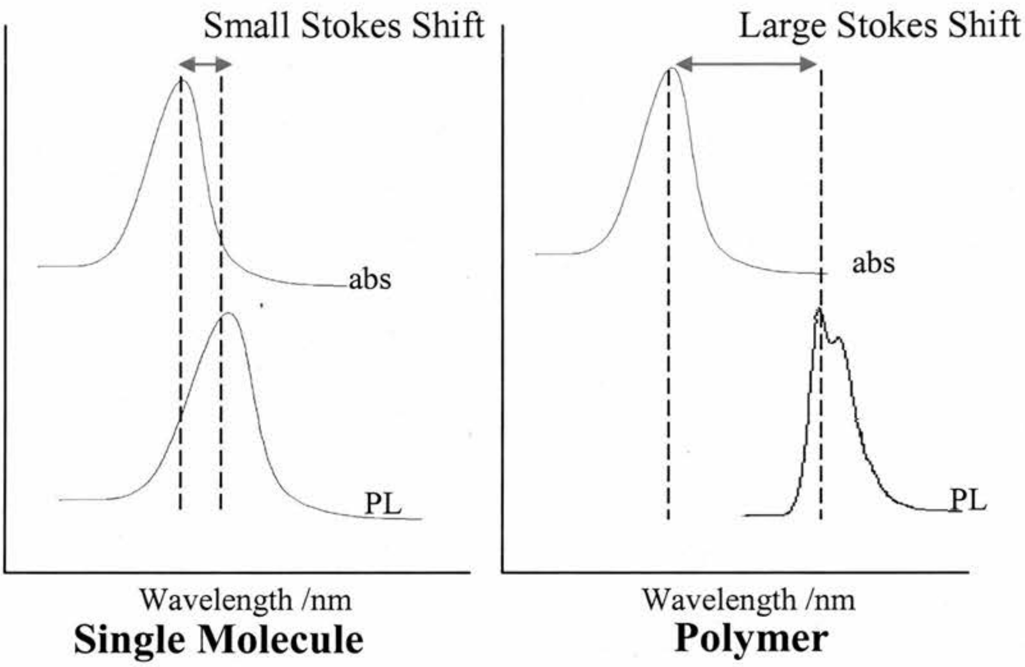


Figure 1.2: Relative Stokes shift for small molecules and polymers

1.3.1 Electroluminescence From Single Layer Devices

In order to produce electroluminescent light, the organic light emitting material is sandwiched between two electrodes and a voltage is then applied. This forms the basis of a single layer device the structure of which is shown in Figure 1.3. To allow for the emission of light one of the electrodes must be transparent as well as conducting. Indium-tin oxide (ITO) is commonly used since it is transparent and has a relatively high work function making it a suitable anode.

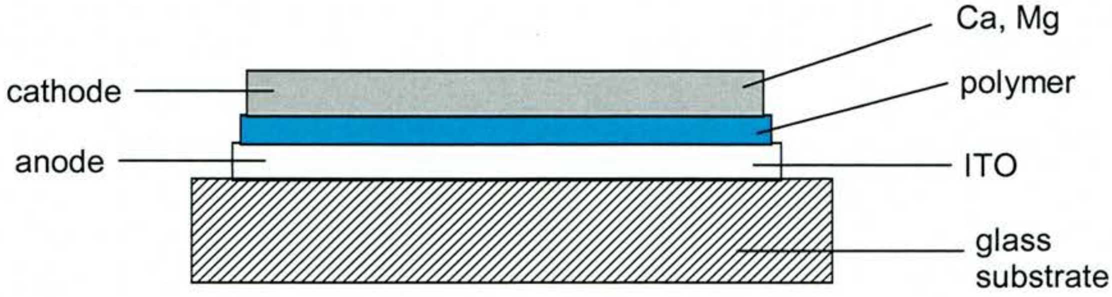


Figure 1.3: Structure of an OLED

A number of different metals have been used successfully as the cathode in LEDs. Calcium and magnesium are frequently used due to their low work function, which results in a lower energy barrier to electron injection than for other metals. Unfortunately calcium metal is extremely air sensitive and it is necessary to apply another conducting layer to protect the calcium from the atmosphere. Typically aluminium is used for this purpose due to its inertness in air and suitable work function. The cathode injects electrons into the LUMO whilst the anode creates holes in the HOMO creating a radical anion and radical cation respectively (Fig 1.4a). The applied electric field then causes these charges to migrate through the polymer until two opposite charges meet. When this occurs the radicals combine to form either a singlet or triplet excited state (Fig 1.4b). Simple spin statistics predict that one singlet for every three triplets will form. The singlet states can then decay back to the ground state by emitting a photon of light; however, this is spin forbidden for triplets. This creates a maximum internal quantum efficiency for a fluorescent material of 25%.[13]

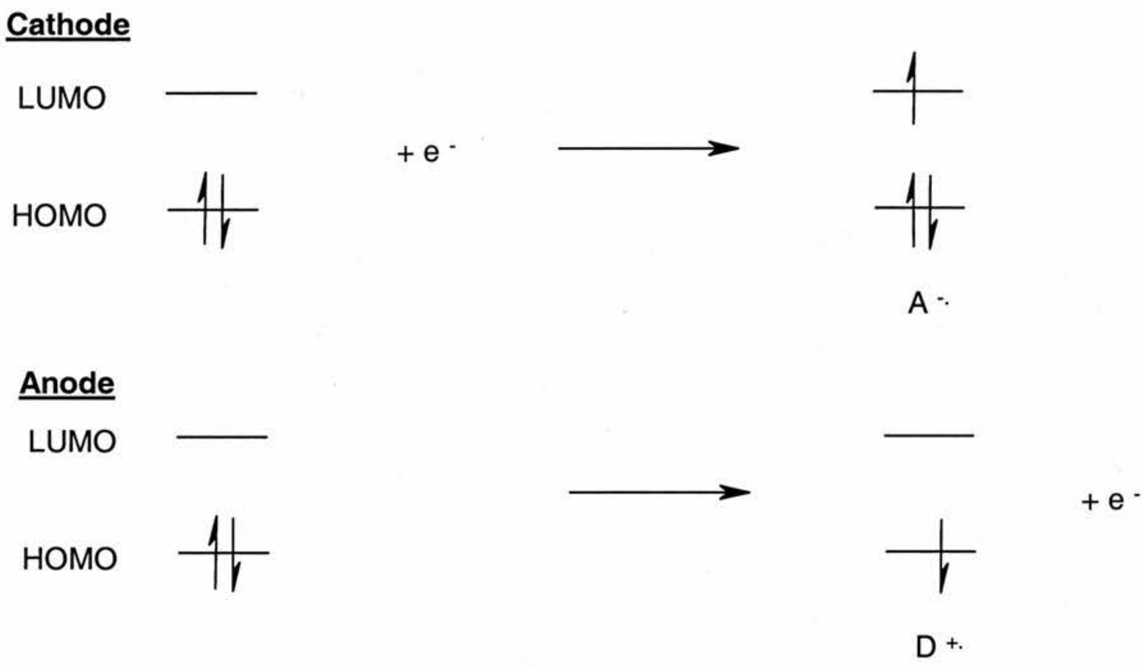


Figure 1.4a: Generation of radical species generated during device operation. D denotes the energy donating species, A denotes the energy acceptor and the emissive species.

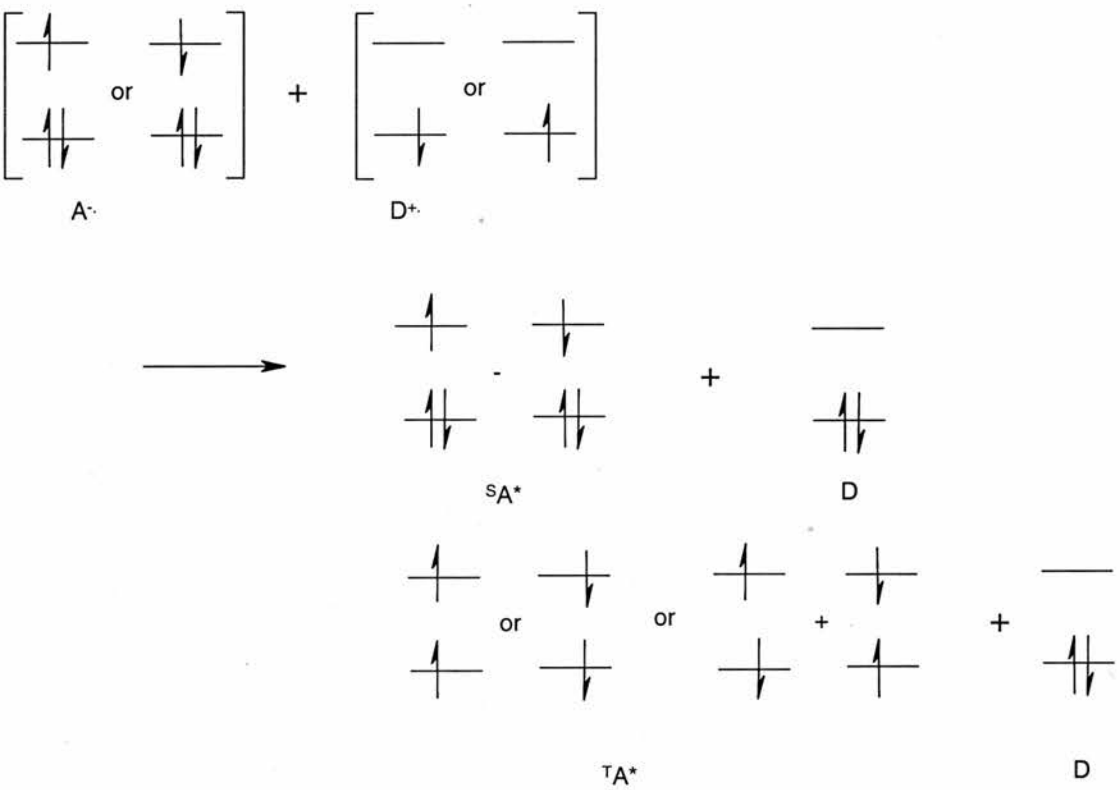


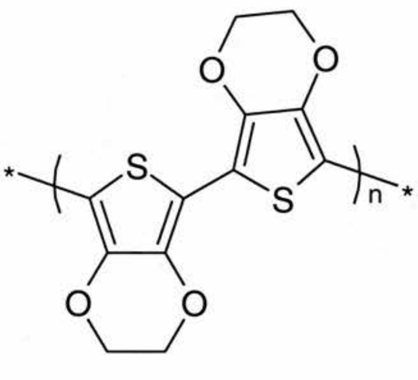
Figure 1.4b: Combination of A and D leads to 1 singlet and 3 triplet excited states.

Quantum chemical calculations have recently shown that chain length is a factor in the ratio of singlet to triplet excited states that are formed. The probability of singlet exciton formation is increased with increasing chain length. Thus the spin statistical limit of 25% may only apply to small molecule devices.[14] This theoretical calculation is substantiated by experiment by Heeger in which an alkoxy derivative of PPV where a ratio of the electroluminescence efficiency to photoluminescence efficiency was approximately 50%. This could only be achieved if the spin statistical limit of 25% was exceeded.[15]

The efficiency of a device can be measured by either the internal or external efficiency. The internal efficiency is the number of photons emitted per electron injected. This assumes that all the light generated is received by the viewer. The external efficiency takes into account that the viewer does not receive all of the light. It has been shown that the external efficiency is a factor of $2n^2$ smaller than the internal efficiency, where n is the refractive index of the polymer.[11]

1.3.2 Multilayer Devices

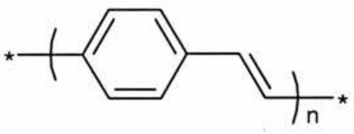
Unfortunately, the energy levels of a light emitting polymer are frequently mismatched to the energy levels of the contact electrodes giving rise to an energy barrier for either hole or electron injection into the organic layer. In order to optimise the device efficiency it is desirable to have balanced charge injection. Electron injection can be improved in some cases through the use of a low work function cathode such as calcium. For most polymers however a need exists to form a bilayer or even multilayer device to improve charge injection. For those polymers with low HOMO levels a hole transporting layer is required. This can take the form of a layer of polyethylenedioxythiophene (PEDOT) **3** which can be spin coated directly on top of the ITO from water. Since PEDOT is insoluble in common organic solvents the light emitting polymer can then be spin coated on top of this layer. Some polymers also require electron transporting layers. The Alq_3 compex is commonly used, however due to the insolubility of this material it has to be vacuum deposited onto the light-emitting polymer layer.[16] Since a hole-transporting layer also blocks electron transport these layers are sometimes referred to as charge confinement layers. See section 1.7.3 for a discussion of the energy levels in a multilayer polyfluorene device.



3

1.4 Polyphenylene vinylene (PPV)

The first conjugated LEP discovered by Holmes et al. in 1990 was poly(p-phenylene vinylene) or PPV **4.** PPV type polymers still remain one of the most widely studied family's of light emitting polymers.



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This polymer has emission maxima of 2.25 eV and 2.4 eV, emitting light of wavelength 551 and 520 nm respectively which falls in the green-yellow part of the electromagnetic spectrum. The photoluminescence quantum yield of this polymer was 8%. Unfortunately PPV is an insoluble polymer making it very difficult to be processed and made into devices. Several methods have been used in order to overcome this problem. Frequently, a soluble precursor polymer is spin coated onto a substrate, which is then converted into PPV by heating in a vacuum for 10 hours (Fig. 1.5).

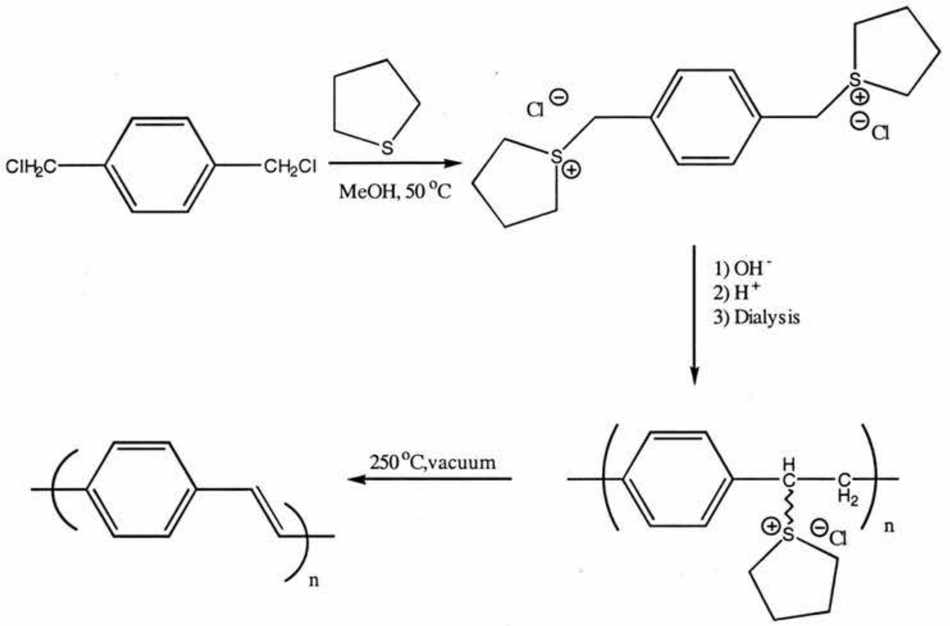
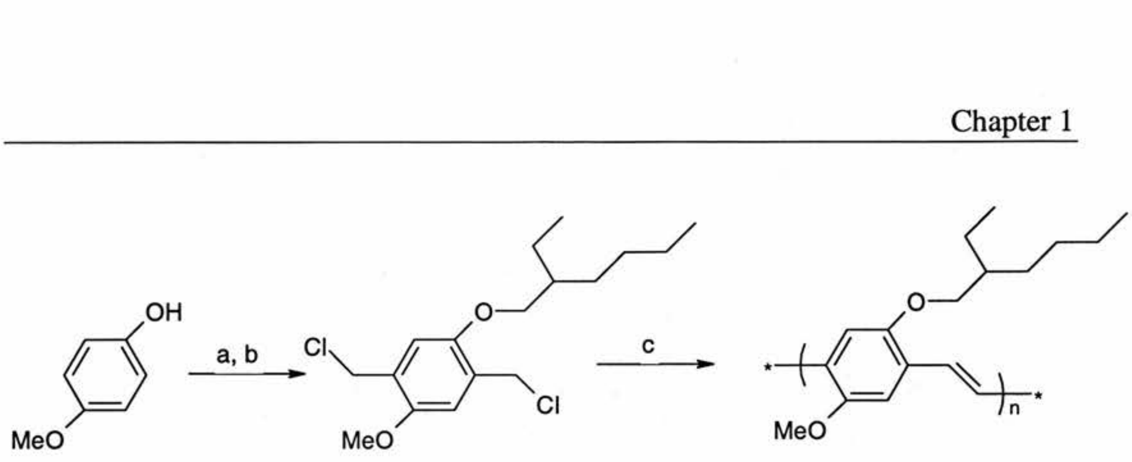


Figure 1.5: Synthesis of PPV

Although this represents a solution to the solubility problem incomplete conversion of the precursor polymer leads to defects along the polymer chain. Such defects are saturated groups and therefore disrupt the conjugation of the polymer.[17]

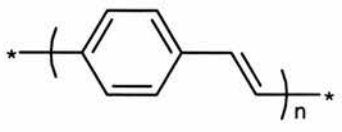
Another method of overcoming the solubility hurdle is to attach alkyl groups on the benzene ring. These chains mimic the action of a solvent making the polymer more soluble, which can then be spin coated directly from solution without the need for any further treatment. Although these alkoxy substituted PPVs can also be prepared using the sulfonium precursor route shown in Figure 1.5 the preferred route was developed by Gilch (Fig. 1.6) since this method affords less defect formation.[18]



a) 3-bromomethyl)heptane, KOH, EtOH
b) HCHO, HCl, dioxane
c) KOt-Bu

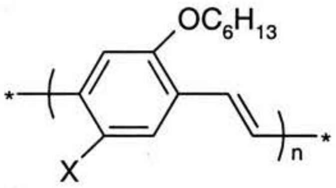
Figure 1.6: Gilch synthesis

By varying the substituents along the polymer the emission colour from the PPV polymer can also be tuned to the extent that a range of soluble PPV derivatives can now be prepared in a variety of different colours.[19]



green-yellow

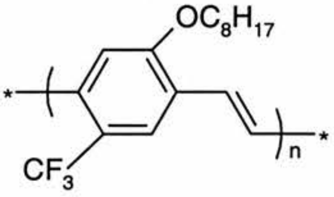
5



X=Br, Cl

red

6

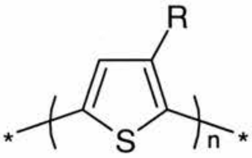


yellow-orange

7

1.5 Polythiophenes

Another family of conjugated polymers that emits light is the polyalkylthiophenes. These polymers are relatively simple to prepare from the corresponding dibromothiophene monomer in the presence of excess ferric chloride.[20] They can also be prepared in a slightly more controlled fashion by the coupling of suitable monomers.[21]



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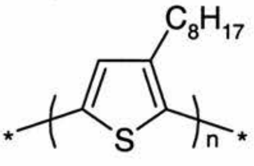
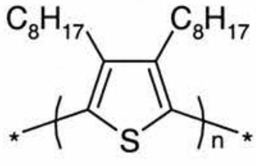
Initially the efficiency of the polyalkylthiophenes was disappointing although they did display very good red colour purity. A vast amount of research has since been carried out and the photoluminescence quantum efficiency has been improved through the use of charge carrier confinement layers or doping with fluorescent dyes.[22]

Polyalkylthiophenes are generally utilised for their red emission. However, like PPVs, polyalkylthiophenes have been shown to emit light in a range of different wavelengths including all three primary colours. This is achieved through attaching different R groups and by controlling the polymer regioregularity. If the polymer is synthesized in a controlled head to tail manner the conjugation length of the polymer is increased relative to a regiorandom polymer due to a reduction in steric hindrance between the two alkyl groups. This increase in conjugation length leads to a red shift in the photoluminescence emission spectrum.[23]



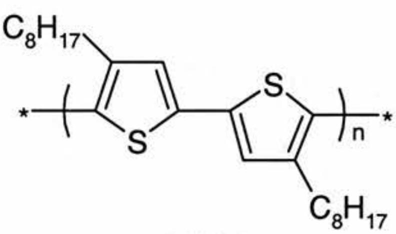
red

9



blue

10



green

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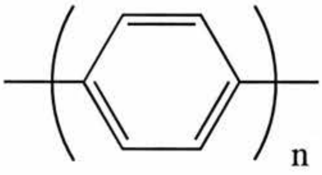
1.6 Poly(*p*-phenylene) (PPP)

In order to make a full colour display light emitters of all three primary colours i.e. red, blue and green are required. Synthesis of a blue emitter is difficult to achieve both in organic and inorganic LEDS, due to the wide HOMO-LUMO band gap intrinsic in blue emitters. A higher electric field must be applied relative to red and green emitters and as a result blue emitters must display higher thermal and oxidative stabilities than is necessary for other colours. This has been demonstrated in a study by I.S.Millard on the lifetimes of some Cambridge Display Technology light emitting polymers at elevated temperatures.[24] The results of the study indicate that the green polymer had an average lifetime of 2700 h and the red polymer had an average 3600 h. The blue polymer on the other hand had a significantly lower lifetime of only 1000 h. Since this study was carried out improvements have been made in the lifetimes of polymers emitting all three colours however it is only very recently that a blue polymer has been found with a lifetime of 10000 h required for use in displays.



12

The first blue LEP discovered was poly(p-phenylene) or PPP **12.**[25] With an emission maximum of 459 nm PPP is a blue emitter with a high PL efficiency. It also boasts high mechanical strength, excellent thermal stability and chemical resistance. However PPP displays poor EL efficiencies in the range of 0.01% to 0.5% photons per electron.[26] Furthermore difficulties have been encountered in synthesizing and processing high molecular weight PPP since like PPV, PPP is an insoluble polymer. Soluble precursor polymers have been used to form PPP films (Fig. 1.7), however the polymers produced contained many defects including about 10% of 1,2 coupling over the desired 1,4 coupling.[27]

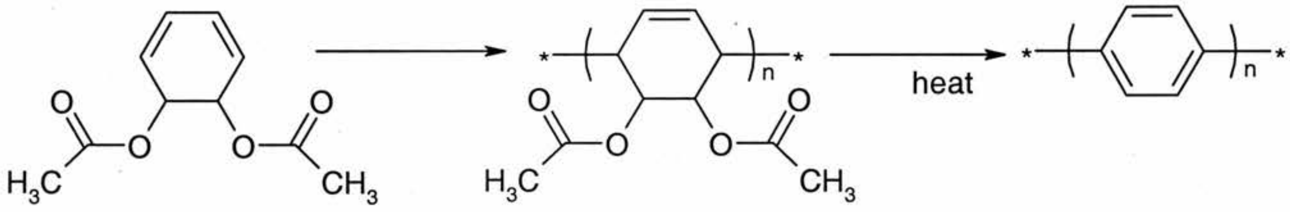
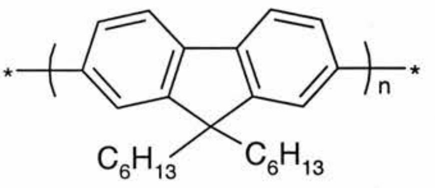


Figure 1.7: PPP precursor route synthesis

Various groups have had some success in preparing soluble derivatives of PPP by attaching alkyl groups in the same way as for PPV. Whilst this solves the insolubility problem, steric interactions between side chains alter the phenylene-phenylene torsional angle from 23° to over 60° with deleterious effects on the π orbital overlap. This results in a loss of conjugation in the polymer backbone leading to a decrease in efficiency and a blue shift in the emission spectrum.[28]

1.7 Polyfluorenes

Polyfluorenes are sometimes referred to as step ladder PPP's since they have a PPP backbone with a planar ladder like structure. The first polyfluorene LED was made by Yoshino et al. using poly(9,9-dihexylfluorene) **13**.[29]



13

Polyfluorenes represent a promising family of LEPs for blue emission for several reasons. Firstly, they display good thermal and oxidative stability with good quantum conversion. This class of polymers are also rigid rod polymers suffering from poor solubility. In the case of polyfluorenes however solubility can be readily improved by the introduction of alkyl side chains at the C9 position. Since the aromatic rings are held at the C9 position the phenylene-phenylene remains virtually planar. The alkyl side chains lie perpendicular to the aromatic rings and therefore do not cause any steric hindrance, preserving the conjugation of the backbone.[30]

Polyfluorenes have also been shown to display liquid crystalline properties.[31] This is an important quality for use in displays as the light can be polarized and hence greater contrast between light and dark pixels can be achieved.

1.7.1 Polyfluorene Synthesis

The Yamamoto method, Figure 1.8A can be used to synthesize homopolymers as well as random alternating copolymers.[32] Alternating copolymers can be synthesised through Suzuki coupling B) which tolerates a wide variety of different functional groups.[33]

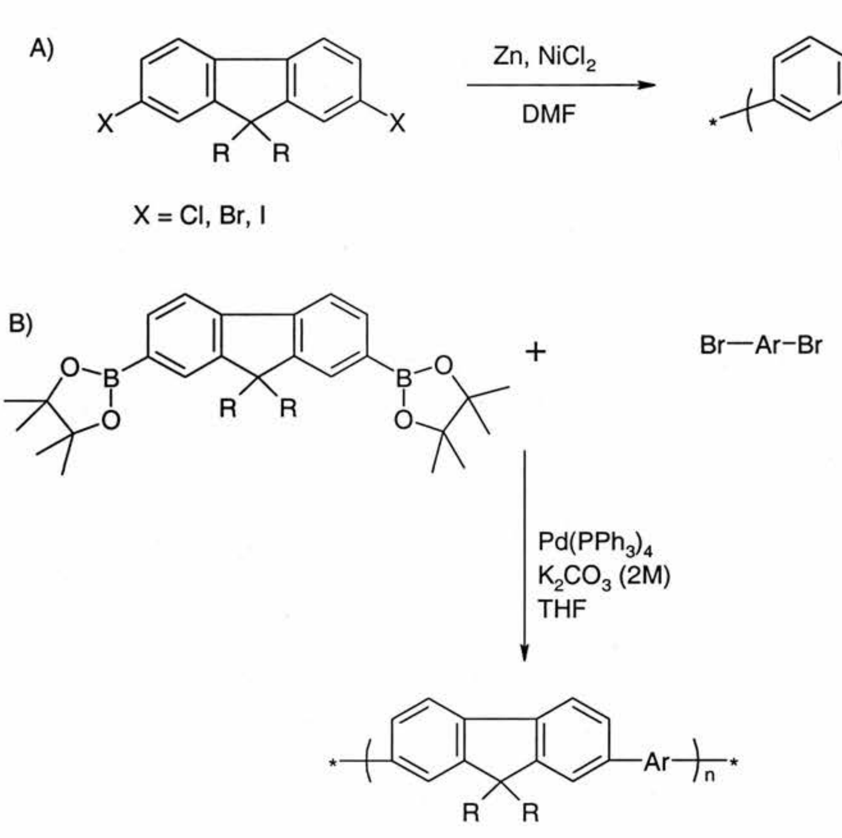


Figure 1.8: Synthesis of polyfluorenes

The Suzuki coupling is particularly powerful as the polymer properties can be easily tuned by varying the structure of the monomers and indeed a large number of different polyfluorene copolymers have been made in this way as shown in Figure 1.9.[34]

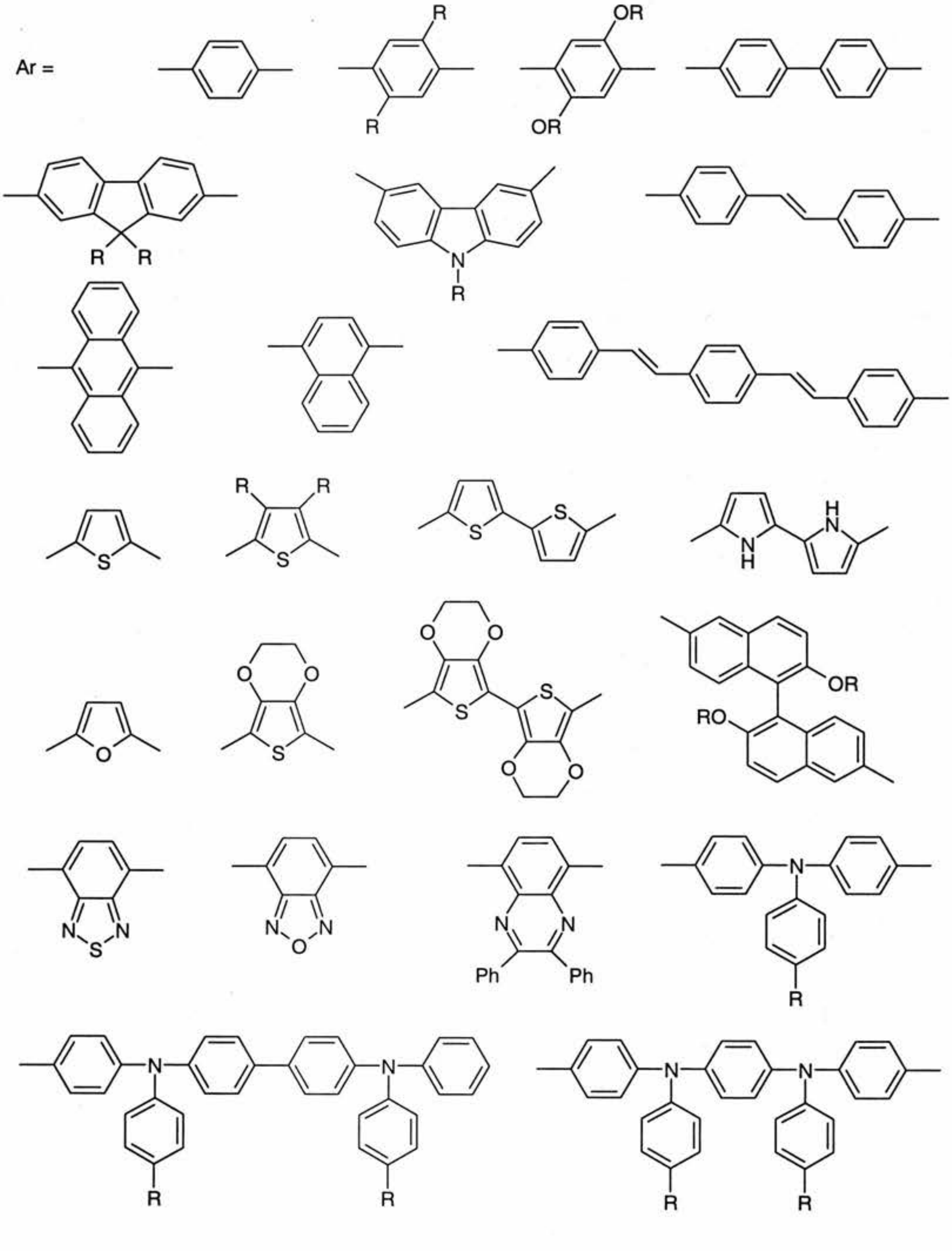
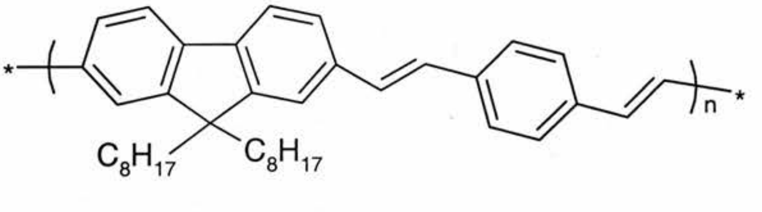


Figure 1.9: Polyfluorene Copolymers

1.7.2 Colour Tuning of Polyfluorenes

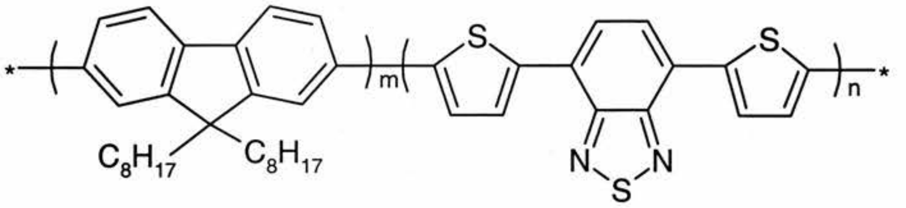
Polyfluorenes are the only class of polymers that to date have been shown to emit light from a full spectrum of colours. For example, blue is obtained for polymer **13,** green has been obtained from **14.**[35] Cambridge Display Technology have also demonstrated a red light-emitting polyfluorene the structure of which, however, is an industrial secret.[24]



green

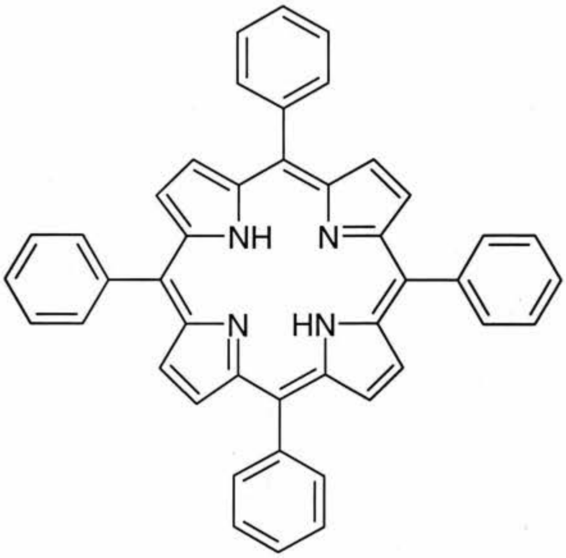
14

Block copolymers as well as alternating copolymers are another method of tuning the emission properties. In the case of polymer **15** a polyfluorene has been synthesised and another lower band gap polymer attached to produce a red light emitting polymer. In the solid state as little as 1% of the DBT unit is required in order that emission occurs solely from the DBT unit. This is due to the DBT sites having a narrow band gap and therefore energy is transferred from the polyfluorene to the DBT units where the excitons are trapped.[36]



15

Varying the structure of the monomers is perhaps the most reliable and simplest way of tuning the emission colour, however, it is not the only method. Red emission can be obtained by doping poly(9,9-dioctylfluorene) (PFO) a blue emitter with tetraphenylporphyrin **16.**[37]



16

The porphyrin has a high oscillator strength Soret band absorption in the blue. A Förster energy transfer then occurs to the Q band which results in a characteristic red emission.

1.7.3 Improving Polyfluorene Devices

Although these polymers exhibit high photoluminescence quantum efficiencies as well as good thermal and chemical stability, there are some areas that could be improved. The first problem with polyfluorenes is that there exists a large energy barrier between the work function of ITO and polyfluorene's HOMO level (Fig. 1.10). Consequently there is an energy barrier to the injection of holes from the ITO into the polyfluorene. Hole injection can be improved through the use of a hole transporting layer such as PEDOT discussed in 1.3.2. There is a good match in energy between the LUMO and the work function of calcium. In order to use a cheaper, less reactive cathode, such as magnesium or aluminium, electron transporting layers are required.[38]

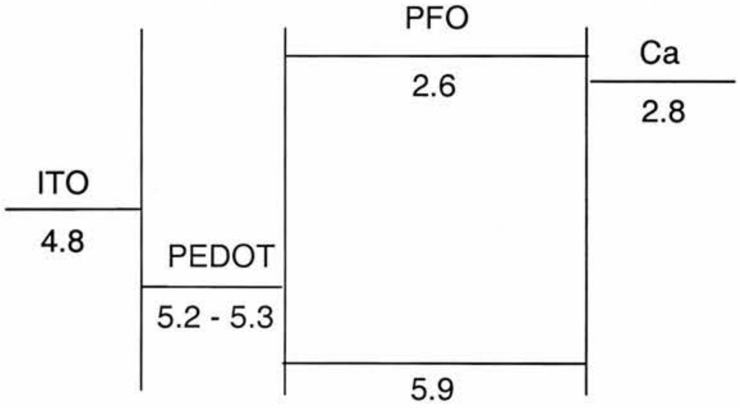
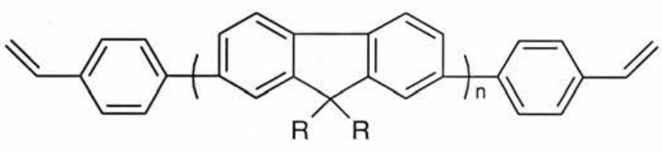
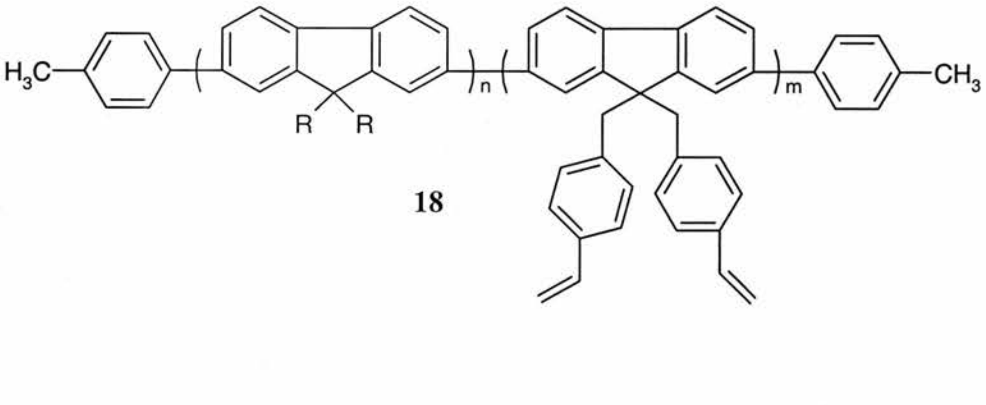


Figure 1.10: Energy levels in PFO EL devices

One disadvantage to multilayer devices is that the individual layers are frequently soluble in the same solvents making it very difficult to produce several individual uniform layers. In this respect it is desirable to have the soluble precursor polymers, which become insoluble on curing as in PPV. One method of overcoming this barrier is to synthesise cross-linking polymers. For example, a polyfluorene derivative such as **17** and **18** can be made which is soluble and spin-coated onto the device under construction. The substrate is then heated to 200 °C for 10 to 60 minutes depending on the polymers molecular weight to cross link the polymer which is then insoluble in common organic solvents.[39]

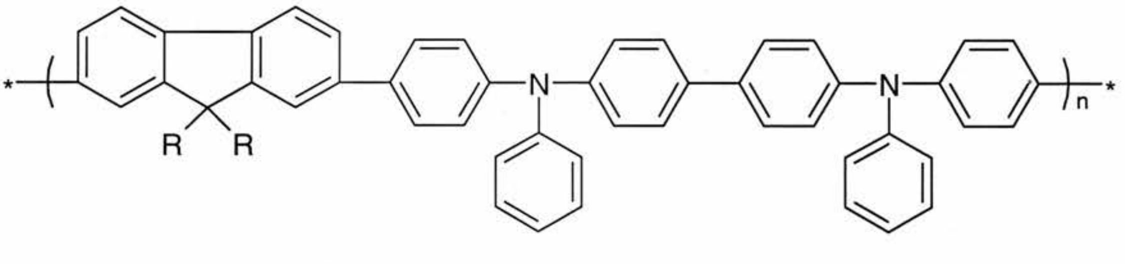


17



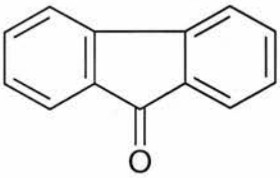
18

Another method of improving the hole transport properties is to synthesize a copolymer which already contains hole transporting units such as triarylamine units.[40] However such methods can disrupt the liquid crystalline properties observed in polyfluorenes. Simply attaching triarylamine end groups to the polyfluorene provides the necessary hole transporting properties whilst preserving the chain stiffness and therefore the liquid crystalline properties.[41]



19

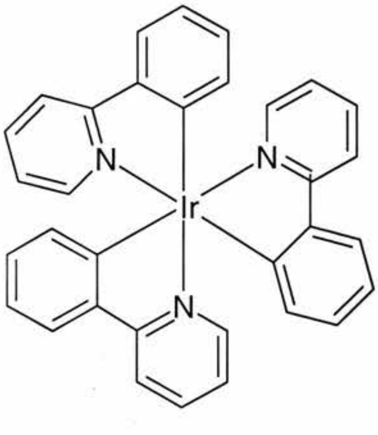
The maximum wavelength emission for polyfluorene type polymer is in the region of 420 nm making the polymer a good blue. Unfortunately, over a period of time an additional peak forms at approximately 540 nm.[42] This peak is in the green section of the electromagnetic spectrum and increases in intensity over time, to the extent that the original blue device turns green. This is obviously a big shortcoming to the use of polyfluorenes in LEDs and a considerable amount of research has been focussed at discovering what causes this additional long wavelength peak and how it can be prevented. To date, two explanations for this peak have been proposed however neither argument has been shown to be indisputably correct. The first theory proposed involves chain alignment during operation of the device allowing an excited chain to couple to a non-excited chain (excimer) and emit light at lower energy. The second proposal is that the polymer is thermally oxidised to form carbonyl moieties (fluorenone) **20** along the backbone, which are also lower in energy. Both of these theories and the methods used to try and prevent the long wavelength emission are discussed in detail in Chapter 2.



20

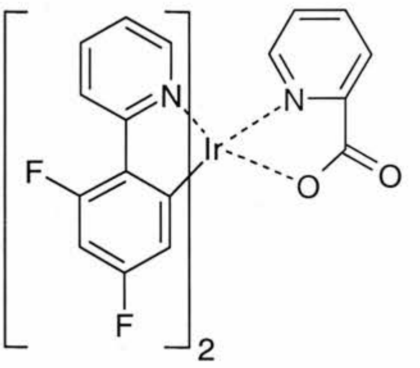
1.8 Phosphorescent Devices

Whilst significant advances have been made in both OLEDs and PLEDs there is an intrinsic limit of 25% internal efficiency for OLEDs due to these materials being purely fluorescent (light is emitted from the singlet excited state). For polymers any triplet states formed will reduce the quantum efficiency as these states undergo non-radiatve processes to return to the ground state. Using one of the many phosphorescent metal complexes that have radiative triplet excited states would make internal efficiencies of 100% a realistic target. Several different phosphorescent metal complexes exist, for example, those of platinum and iridium. For optimum device efficiency a metal with a short triplet lifetime is desired so that the excited state does not become quenched, which in turn would reduce the quantum efficiency of the device. The triplet lifetimes of several iridium complexes are suitable and therefore iridium complexes are the preferred choice for use in phosphorescent devices.[43] One of the most frequently used iridium complexes is $Ir(ppy)_3$ **21** which emits green light.



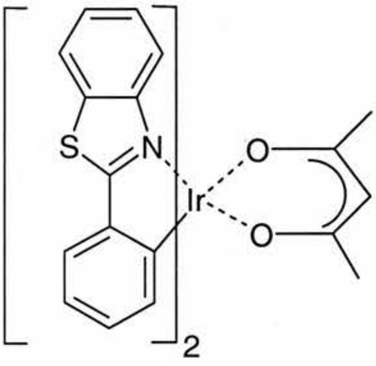
21

By altering the structure of the ligand attached to the iridium the colour of the emission can be tuned and red, green and blue phosphorescent devices have been prepared.[44]



FIrpic Blue

22

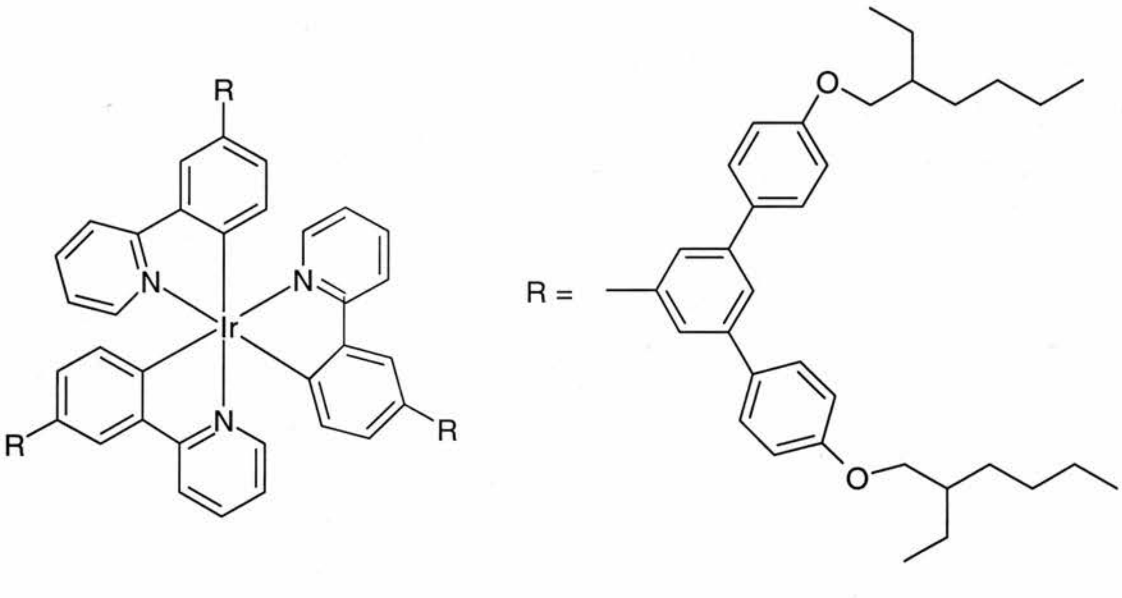


$Bt_2Ir(acac)$ Red

23

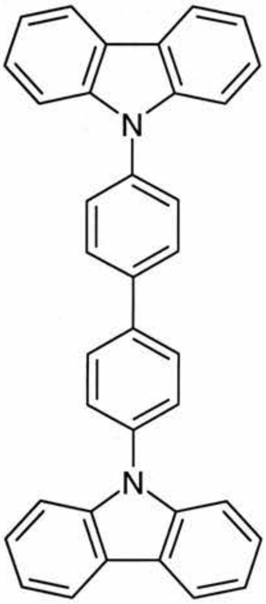
Triplet-triplet annihilation is prevented by doping the iridium complexes into polymers such as polyvinylcarbazole (PVK). PVK is a conducting polymer and acts as a spacer to separate the iridium chromophores. This also has the dual advantage of allowing the iridium complexes to be solution processable.[45] Light emission occurs by an exothermic or Förster transfer of energy from the host (often a polymer) to the dopant (the phosphorescent material). The relative energies of the two materials ensures that this energy transfer is not reversible and therefore a large external quantum efficiency can be obtained for a relatively small amount of iridium complex.[46] However, devices may suffer from phase separation of the individual components which is detrimental to device performance.

In order to prevent triplet-triplet annihilation (which would greatly reduce the device efficiency) it is desirable to protect the core of the molecule from other triplet emitters. As already stated this can be achieved with some success by doping into a conjugated polymer. Another very effective method of achieving this was reported by Burn et al. using dendrimer ligands to surround and protect the iridium core. The colour of emission can be tuned by altering the core of the molecule and the properties of the material controlled by variation of the dendritic structure.[47]



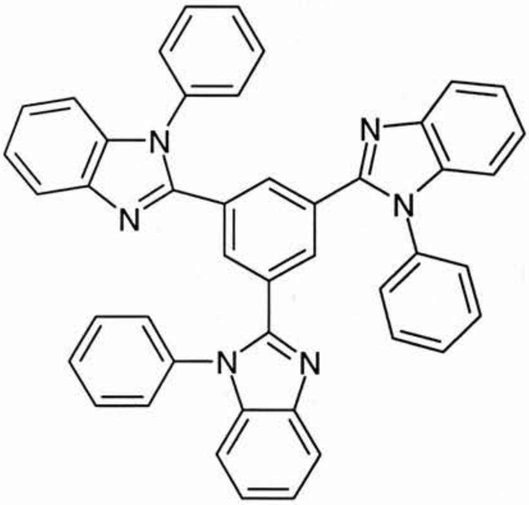
24

For example, the iridium dendrimer **24** has an external quantum efficiency of 10.4 % in a single layer device. These phosphorescent dendrimers also have the additional advantage that they are sufficiently soluble and massive enough to be spin coated from solution. These high efficiencies can be achieved by forming bilayer devices with electron transporting / hole blocking layers or through blending of the dendrimers with a host such as 4,4,'bis(n-carbazolyl)biphenyl (CBP) **25** and an electron transporter such as 1,3,5-tris(2-N-phenylbenzimidazolyl)benzene (TBPI) **26**



CBP

25

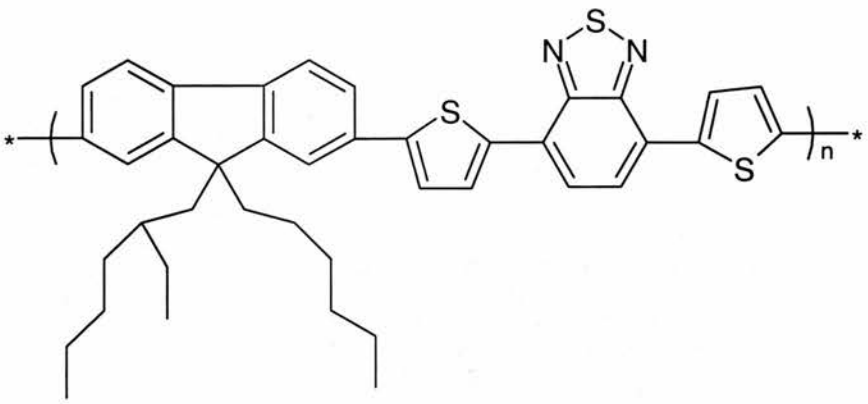


TPBI

26

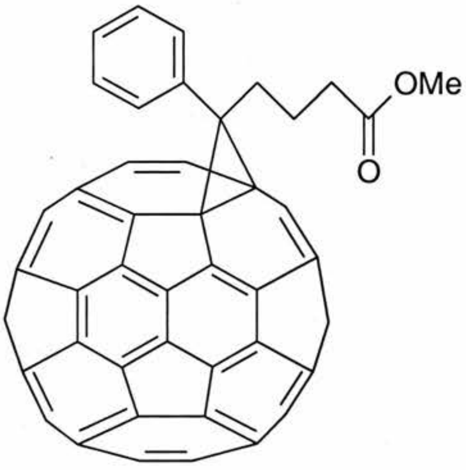
1.9 Other Applications of Light-Emitting Polymers

The majority of research into light-emitting polymers has been focussed on improving the optical properties for use in organic light-emitting diodes for use in a display of some sort. A small number of research groups have focussed their attention on exploiting the properties of these polymers for different applications. In the main these polymers are excited in order to produce light, however these polymers can also work in the reverse whereby light is used to excite the polymer forming excitons, which dissociate and the resulting charges produced migrate to the appropriate electrode. In effect, the PLED can also operate as an organic solar cell. Conjugated polymers make good organic solar cells due to their excellent charge transport properties but also because of their strong absorption in the uv-vis spectrum. In order to optimise the solar cell, as much light as possible must be harvested and, in particular the polymer must absorb as much of the solar spectrum as possible. Frequently, copolymers are prepared to lower the band gap and therefore enhance red light absorption as typical conjugated polymers absorb very poorly in the red region of the electromagnetic spectrum. This has been achieved for polyfluorenes by synthesis of an alternating copolymer poly(2,7-(9-(2'-ethylhexyl)-9-hexyl-fluorene)-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole) (PFDTBT) **27.** This polymer has a maximum absorption of 550 nm, which helps to generate large photocurrents. [48]



27

Another method of improving these solar cells is to dope the material with a fullerene derivative such as [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) **28**, which acts as an electron acceptor and improves the charge carrier mobilities of the solar cell. To date, the most efficient polymer solar cell is prepared from poly(3-hexylthiophene) and PCBM and produces and energy conversion efficiency of around 3%.[49]



28

Conjugated polymers emit different colours of light on exposure to a variety of different conditions such as temperature, solvent, exposure to ions, uv radiation, chemical and biological moieties.[50] Investigations into the viability of these materials as chemical and biochemical sensors are now being carried out.

Recently, Molecular Vision, a spinout company from Imperial College has been set up to produce medical tests utilising light emitting polymer technology.[51] The proposed test would be disposable, credit card sized devices (Fig. 1.11), allowing general practitioners (GPs) to obtain a patients sample, run the test and obtain the results in a matter of minutes. The device would consist of a sample injector, light source supplied by a light emitting polymer and a detector. Light-emitting polymers are ideal for this type of application since they are cheap and relatively easy to manufacture. Moreover the wavelength of emission can be tailored to an appropriate wavelength through chemical tuning to the desired wavelength for a particular test.

Figure 1.11: Medical test device incorporating light-emitting polymer technology

1.10 Aims

Polyfluorenes are a class of blue light emitting polymer which have shown excellent quantum yields and stabilities, however, they do suffer from poor colour stability over time. The first aim of this dissertation was to address the issue of colour stability in alternating copolymers of fluorene. It was anticipated that the colour stability could be improved through interruption of the conjugation along the polymer backbone, thus preventing excimer formation and/or energy transfer to the fluorenone sites. The interruption will be introduced by incorporating a kink in the chain or a *meta* phenylene linkage. This would disrupt the formation of excimers and hopefully suppress the long wavelength peak in the emission spectrum.

The second aim of this project was to design an alternating copolymer of fluorene capable of binding metals such that the emission colour could be tuned or the polymer used as a metal ion sensor by coordination of different metals. The phenanthroline group was chosen as a suitable metal binding ligand because it is a well known bidentate ligand to a variety of different metals.

It was also desirable to synthesize a polymeric analogue of aluminium trisquinolate that would hopefully combine the light emission properties of the aluminium trisquinolate and the solution processibility of the polymer. This was investigated with the aim of coordinating the aluminium quinolate to a polyfluorene type of polymer and also a more readily available polystyrene derivative. Although not conjugated this polymer would have a very high density of chromophores as in the successful light-emitting polymer poly(vinyl carbazole) and non-conjugated dendrimers. Nevertheless its was anticipated that additives such as tetraphenyl-biphenyl-4,4'-diamine TPD would have to be added to improve the charge transport properties of the polymer.

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Chapter 2

Synthesis and Optical Properties of *Meta*-Linked Polyfluorenes

2.1 Introduction

Polyfluorenes are a promising class of blue light-emitting polymers due to their high oxidative and thermal stability[1]. One disadvantage that this class of polymer has is the formation of an additional emission peak in the green region of the spectrum.[2] This band detrimentally alters the emission colour from blue to green or even white. There has been much debate in the literature as to the origin of this additional emission band. The two most common explanations are that it arises from: (i) the formation of carbonyl moieties along the chain or (ii) the formation of excimer or aggregates.

2.1.1 Carbonyl Groups

Carbonyl groups, termed fluorenones, are formed where the C9 of the fluorene has only been singly alkylated (the mono alkylated fluorene cannot be completed removed during synthesis) and is thermally oxidised upon annealing or during device operation to a carbonyl moiety.[3]

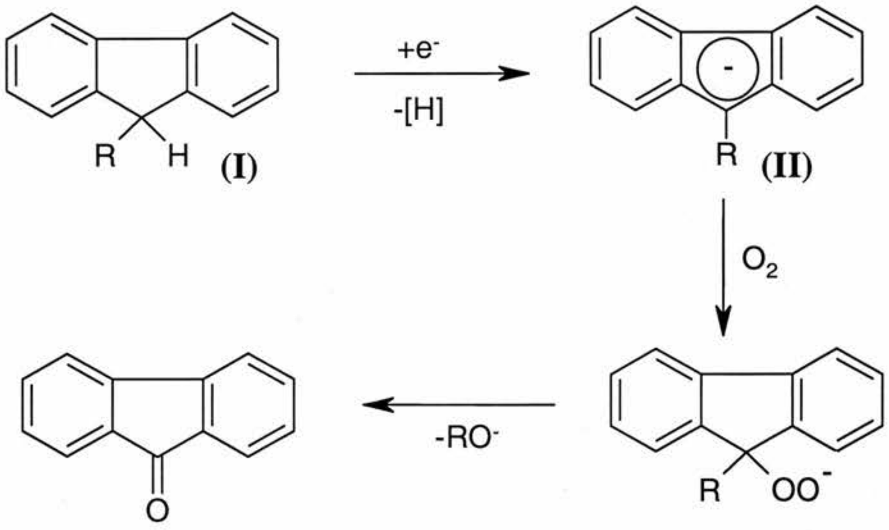


Figure 2.1: Formation of fluorenone

Quantitatively the amount of mono alkylated species is negligible and poses no problem in absorption and photoluminescence spectra. However, in a device under EL conditions the charges migrate across the device and will emit at the lowest energy. Fluorenone has a lower excited state energy than polyfluorene. Therefore, even if the amount of fluorenone in the sample is very small there will be a dominant long wavelength peak in an EL spectrum due to emission from the fluorenone. This emission swamps the desired blue emission.

A copolymer consisting of varying equivalencies of dinonylfluorene and fluorenone has been reported by S. Panozzo et al. When excited at 390 nm this polymer exhibits an emission band at 460 nm and 600 nm corresponding to the fluorene and fluorenone repeat units, respectively. In the solid state emission (PL or EL conditions) emission occurs solely from the fluorenone moieties, presumably by energy transfer from the fluorene to fluorenone facilitated by smaller interchain distances.[4]

2.1.2 Definition of an Excimer

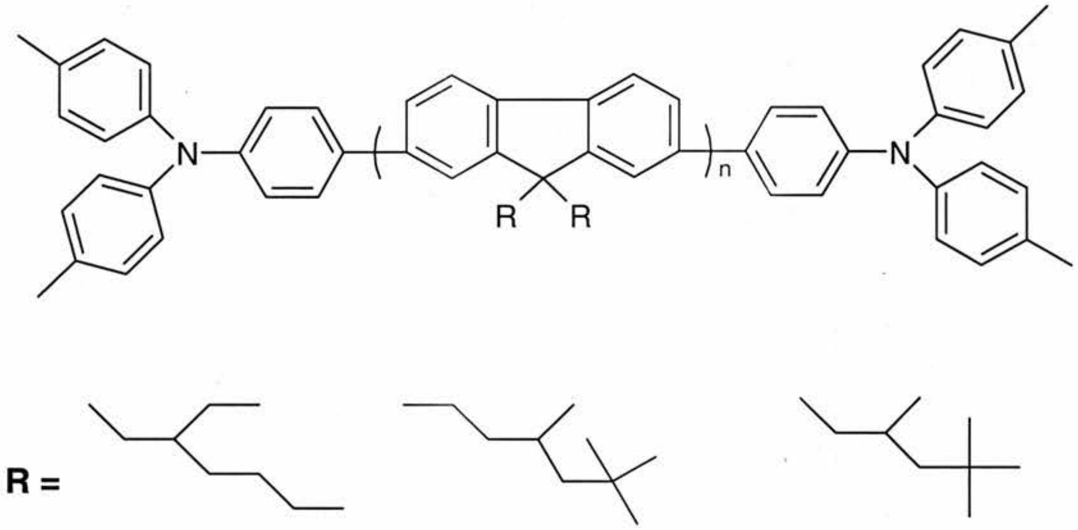
Excimers arise where polymer chains are closely packed giving rise to chromophores that lie to within 3 or 4 Å of one another. An excited state chromophore then interacts with a non-excited chromophore to create an excimer. If the two chromophores are different then the term exciplex is used. Evidence for excimers in the solid state appears when an additional band in the emission spectra is observed. Since the chains of the polymer must be closely packed the excimer emission is naturally not seen in solution spectroscopy. In a dilute solution values of 50% for the photoluminescence quantum yield (PLQY) have been reported which decreases dramatically to 7% for a thin film.[5] A study by J.Teetsov et al. reveals that higher PLQY values can also be obtained by attaching bulky side groups to the polymer. This increases the intrachain distance and helps to prevent the formation of excimers.[6]

The formation of excimers has been shown to be temperature dependent. This temperature dependence is attributed to the polymer chains having sufficient mobility to move from the amorphous state that the pristine spin coated thin films have to a more aligned state at elevated temperatures. Rigid-rod polymers such as polyfluorene and poly (*para*-phenylene) have poor spectral stability during device operation since the device will operate at elevated temperatures due to the applied voltage. Temperatures as high as 86 °C have been recorded during operation of an OLED and this temperature could even be exceeded depending on the operation of the device.[7] Several methods for improving the colour stability and preventing excimer formation have been proposed and these are discussed in more detail in section 2.2.

2.1.3 Fluorenone vs Excimer

There has been a lot of debate in the literature of recent times as to the origin of the long wavelength emission peak near 540 nm in the electroluminescence spectra of polyfluorenes. Several papers have been published supporting the fluorenone theory such as the lifetime study carried out by J M Lupton.[8] Here the authors report a weak emission peak at 530 nm in the solution phase of a fluorene oligomer which would be unlikely to exist if this peak was caused by excimers. Further evidence in support of the fluorenone theory include as the polymer solution is cooled the intensity of the polyfluorene emission decreases. The intensity of the peak at 530 nm however remains constant which shows that the peak can be excited directly. As the wavelength of excitation is altered from 422 nm to 430 nm the intensity of the peak at 530 nm increases significantly which also confirms that the two peaks in the emission spectra arise from different entities. This serves to support the fluorenone argument and suggests that aggregate formation has very little effect on the solid state emission properties of polyfluorenes.

A study of the effect of the side chains on the properties of polyfluorenes has also been carried out which in direct contrast to the paper by Lupton would support the excimer forming argument. Polyfluorenes with the following side-branches attached were prepared. [9]



29a 2-ethylhexyl

29b 3,5,5-trimethylhexyl

29c 2,4,4-trimethylpentyl

Whilst the bulkier side groups help to reduce the contribution from aggregates the emission characteristics are improved considerably by the inclusion of a hole transporting layer in the device. The authors attribute this to the polyfluorene chains being more aggregated close to the anode where the bulk of the electron hole recombination takes place due to the energy barrier from PEDOT to the HOMO level of the polyfluorene being relatively large.

A comprehensive study by R.Miller et al., however, suggests that both fluorenone and excimeric phenomena can co-exist.[10] Polyfluorenes end-capped with 2-bromo fluorene were found to form an additional peak at 500 – 600 nm after very short periods of annealing. This is in accordance with the theory that the 9 position of unsubstituted polyfluorene is easily oxidisable to the fluorenone moiety. Polyfluorenes end-capped with 2-bromo-9,9-dihexylfluorene also developed undesirable green emission at 500–600 nm; however, this was much slower in forming. Polymers with higher molecular weight displayed a smaller contribution to the long wavelength peak. An explanation for this effect would be that higher molecular weight polymers have lower chain mobility and therefore these polymers cannot readily align themselves and form excimers.

2.2 Methods to Prevent Excimer Formation

2.2.1 Dendritic Side Chains

As already mentioned the attachment of bulky side chains to the C9 position improves the appearance of excimers by helping to prevent the polymer chains becoming too close. Traditionally, alkyl spacer groups of 6 – 8 carbon chain lengths have been used as this gives good solubility without introducing too much insulating material into the polymer. Unfortunately excimer emission cannot be completely suppressed by this method. Dendron side chains offer a better solution to this method of excimer suppression as the dendrimer side chains are excellent solubilisers due to their highly branched structure and can envelope and protect the polymers from aggregation and degradation.

A recent paper by Marsitzky et al. has shown mixed results for attaching the Frechet type dendrimers shown in Figure 2.2.[11]

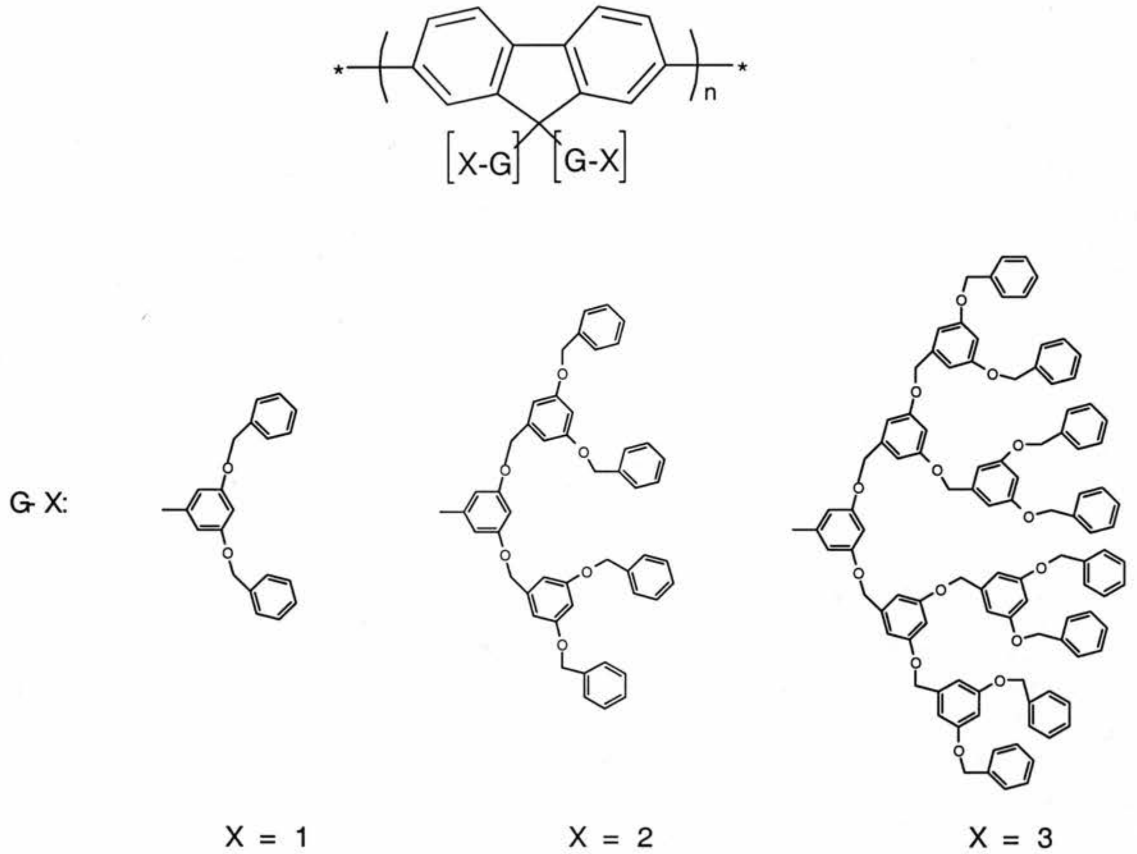
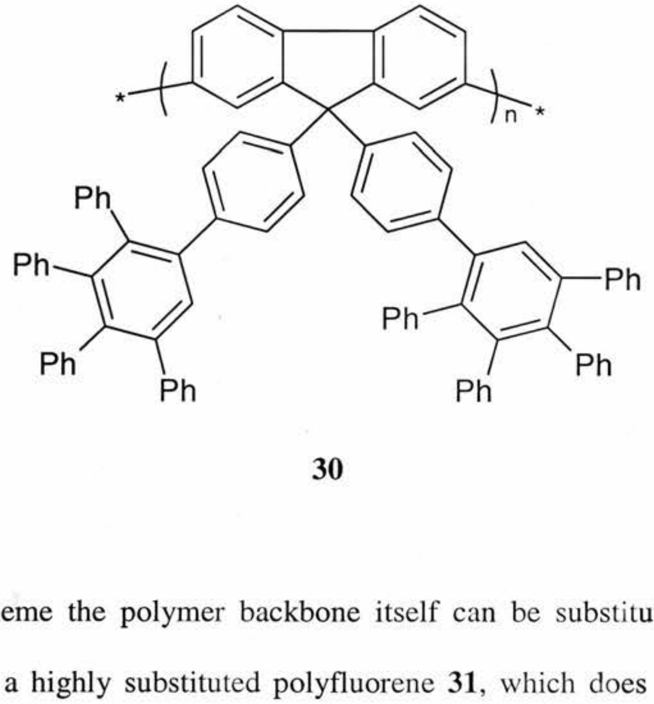


Figure 2.2: Generations of Dendrimers

It was shown that the first generation dendrimers did not fully suppress aggregate formation since the absorption spectrum of this polymer still showed a tail in the long wavelength region at around 540 nm, which has been assigned to aggregate formation. This peak was not present in the absorption spectra of the second and third generation dendrimers although these polymers suffered from low photoluminescence quantum efficiencies. This low value probably arises due to the large groups preventing formation of high molecular weight polymers and therefore crystallisation of the thin film and fluorescence quenching can occur.

Attaching dendrimers as side chains to polyfluorenes has also been explored by E.List et al.[12] These so called Mullen type dendrimers **30** are fully conjugated and consequently do not interfere with either the charge transport or emission properties of the polyfluorene. The bulky groups help to prevent aggregate formation as well as exciton migration to any fluorenone sites within the polymer and therefore good colour stability is achieved.



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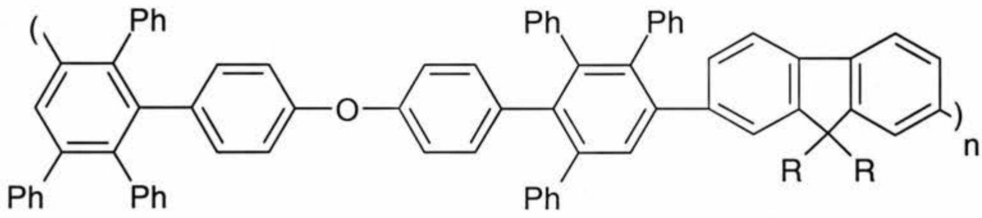
On a similar theme the polymer backbone itself can be substituted with phenyl groups to yield a highly substituted polyfluorene **31**, which does not display any excimer formation.[13]

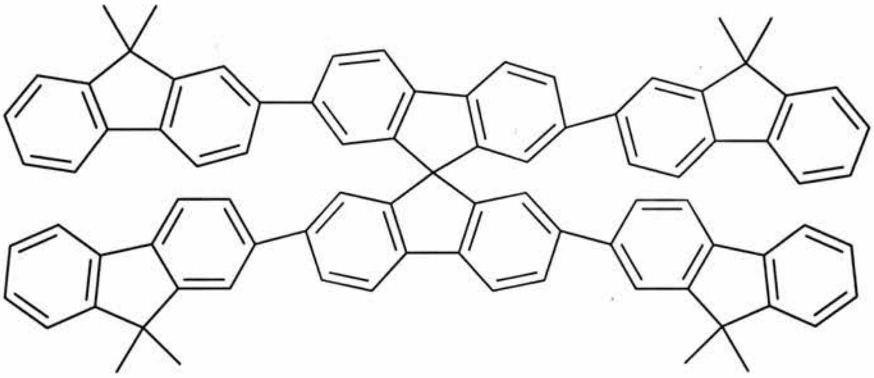


31

2.2.2 *Spiro*-functionalised polyfluorenes

Another class of polyfluorene that has been developed for stable blue emission are *spiro*-linked polyfluorenes. These polymers are based on polyfluorenes and contain two fluorene segments that are connected at the C9 position instead of having two alkyl groups. The two rings are connected through an sp^3 carbon and therefore lie at 90^{o} to one another. This prevents the polymer chains from packing closely together and reduces the probability of excimer formation. Secondly, the *spiro* centre has been shown to increase the glass transition temperature from approximately 51 °C for polydioctylfluorene[14] to 105 °C for certain spiro functionalised polymers.[15] The high glass transition temperature means polymers have a lower mobility and the probability of forming excimers is reduced.

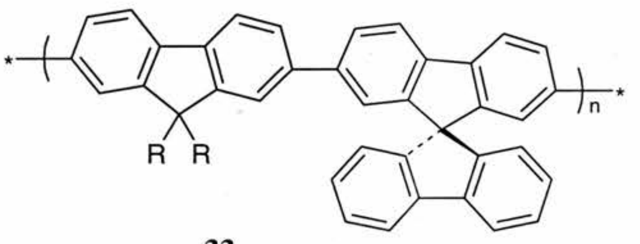
S.H.Chen et al., have synthesized spiro oligomers of the type shown in **32** with chain lengths of 3, 5 and 7 fluorenes.[16]



32

Chen chose to make oligomeric *spiro* fluorenes as they are more reproducible and have more predictable properties relative to their polymeric counterparts. The high glass transition temperature of the spiro-linked fluorene is desirable in order to form amorphous glassy films which are not prone to recrystallisation during operation of the device.

Spiro groups can be attached at regular intervals along the polymer as in **33**[17] or as a method of binding continuing the polymer chain as in **34.**[18]



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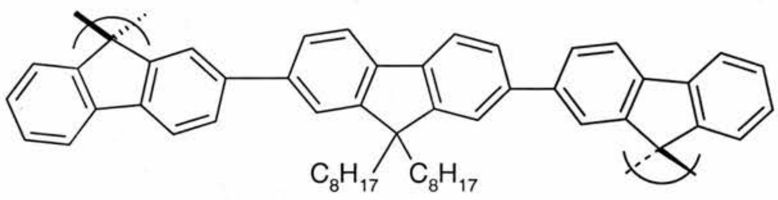
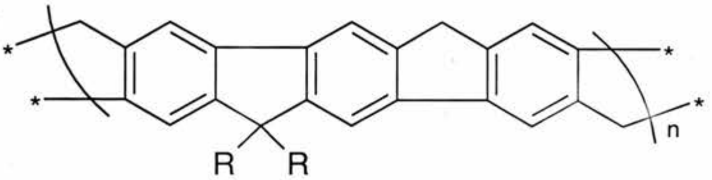


34

Whilst polymer **33** did show some improvement on the spectral stability, polymer **34** is superior and shows no long wavelength emission even after annealing under nitrogen at 150 °C for 20 hours.

2.2.3 Ladder Polyfluorenes

Ladder polymers are a class of polymer which are based on PPPs with even more bonds between the phenylene units than in polyfluorene creating a series of rings which cannot rotate with respect to one another.[19]

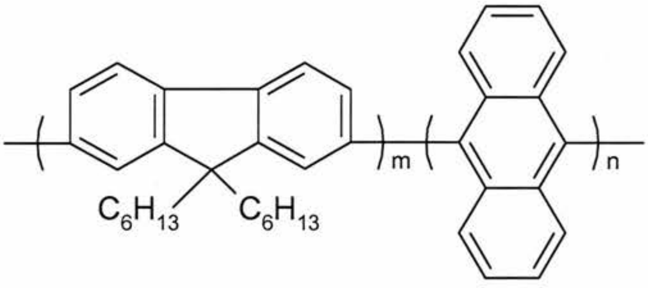


35

The structure for these ladder polymers results in high charge carrier mobilities for holes, long conjugation lengths and a low concentration of electronically active traps. These polymers are, however, even more rigid than other rigid rod polymers like PPPs and polyfluorenes for example. These polymers suffer from the same problems of solubility and aggregate formation. One method for improving the properties of ladder polymers is to prepare ladder type oligomers and attach these to polyalkylenes.[20] The shorter the alkyl spacer between the oligomeric ladders the greater the tendency for aggregate formation therefore excimer formation can be reduced by increasing the alkyl chain length. However, alkyl chains are insulating materials and as such would be detrimental to the charge transporting properties of the LED.

2.2.4 Anthracene Containing Polymers

Anthracene is a known blue light emitter and can also be incorporated into devices as a hole or electron transporter. More recently, random alternating copolymers of fluorene and anthracene have been prepared which demonstrate excellent colour stabilities. The amount of anthracene incorporated into the polymer via a nickel mediated polymerisation ranged from 15 to 50%. All of the polymers displayed blue emission at 455 nm and there was little dependence on the absorption / emission maxima with respect to the amount of anthracene incorporation.[21]



36

The formation of the long wavelength peak however is significantly improved. After annealing at 200 °C for 4 hours the 50% anthracene polymer showed no excimer emission and even after annealing for 24 hours at 250 °C the excimer emission was quite slight. Anthracene is thought to lie out of plane of the neighbouring fluorene units since in 9,10-diphenyl anthracene steric interactions cause the anthracene to strongly twist (about 60°) relative to the phenyl substituents (Fig. 2.3).[22] This twisted geometry is believed to inhibit the formation of excimers, possibly by preventing the close approach of polymer chains.

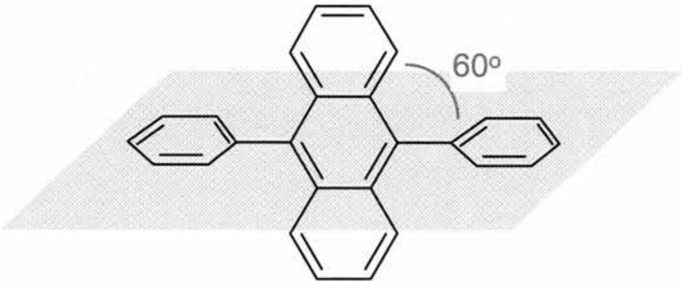
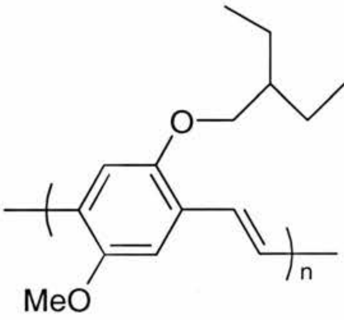


Figure 2.3: Twisting in 9,10-diphenylanthracene

Interestingly, the polymers were end capped with 2-bromofluorene, which other groups have shown to readily oxidise to the fluorenone moiety. In this case, however, the long wavelength peak is suppressed by the incorporation of the anthracene and no fluorenone emission is reported.

2.2.5 Control of Conjugation Length



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The long wavelength emission for MEH-PPV **37** has also been studied and can be attributed solely to excimer emission due to the lack of an oxidisible site. The excimer emission in this case was effectively suppressed by incorporation of saturated groups along the polymer backbone which reduces the conjugation length of the polymer. For an excimer to form there must be no interruption in the conjugation length of the pair of chains on which the excimer resides.[23] With shorter conjugation lengths two identical segments are far less likely to couple as shown in Figure 2.4.

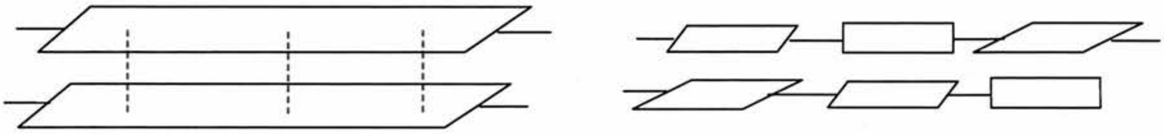


Figure 2.4 shorter conjugation lengths form fewer excimers

2.3 The Effective Conjugation Length

Conjugated polymers are often expressed as being fully conjugated with delocalized π electrons running the length of each polymer chain. In reality this is not necessarily the case. Polymers generally have broken lengths of conjugation due to defects in the polymer backbone or steric interactions causing the polymer to twist. The effective conjugation length (ECL) is a measure of the degree of conjugation a particular polymer has and may be defined as the minimum number of repeat units required to produce saturation of the optical or electronic properties. It is an important property as it defines such electronic properties as the band gap, absorption coefficients and emission quantum yields. The effective conjugation length of a polymer can be determined using a combination of experimental techniques and calculation. Oligomers of each length of repeat unit are prepared and the absorption and emission characteristics of each is recorded. The energy is determined from the absorption or emission wavelength maximum. The energy can then be plotted against $^1/n$ or n (where n is the number of repeat units) and the extrapolation of this curve gives the effective conjugation length.[24] The effective conjugation length for the alternating copolymer poly[(1,4-phenylene)-2,7-(9,9-dihexylfluorene)] has not been calculated to our knowledge. However the effective conjugation length for the similar polymer poly(9,9-dihexylfluorene) has been calculated by R.D.Miller et al.[25] Oligomers and low molecular weight polymers were prepared by end-capping with 2-bromofluorene in a nickel mediated polymerisation. These were then isolated by preparative high pressure liquid chromatography (HPLC) to yield oligomers of 3 to 10 repeat units. The absorption spectrum is then recorded for each oligomer and the maximum values are given in Table 2.1.

Table 2.1: Absorption Maxima of Fluorene Oligomers (Data from Miller et al.[25]*)*

Oligomer n^a	1/n	λmax (nm)	1/λ (cm^{-1})
3	0.3333	348	28735
4	0.2500	362	27624
5	0.2000	370	27027
6	0.1667	376	26596
7	0.1429	378	26455
8	0.1250	380	26315
9	0.1111	382	26178
10	0.1000	384	26042
PDHF	-	388	25773

^{a} *- n represents the oligomer length including the fluorene end cap.*

The absorption spectra of poly-9,9-dihexylfluorene with a degree of polymerisation of 54 is also recorded and this is used as the limiting absorption maximum at 388 nm. This is depicted as the red horizontal line in Figure 2.5. The plot is extrapolated to the point where it crosses the polymer λ_{max} line giving a value for 1/n as 0.0847 and therefore n = 11.8. The effective conjugation length for poly(9,9-

dihexylfluorene) is therefore reported as being approximately 12 repeat units or 24 aromatic rings.

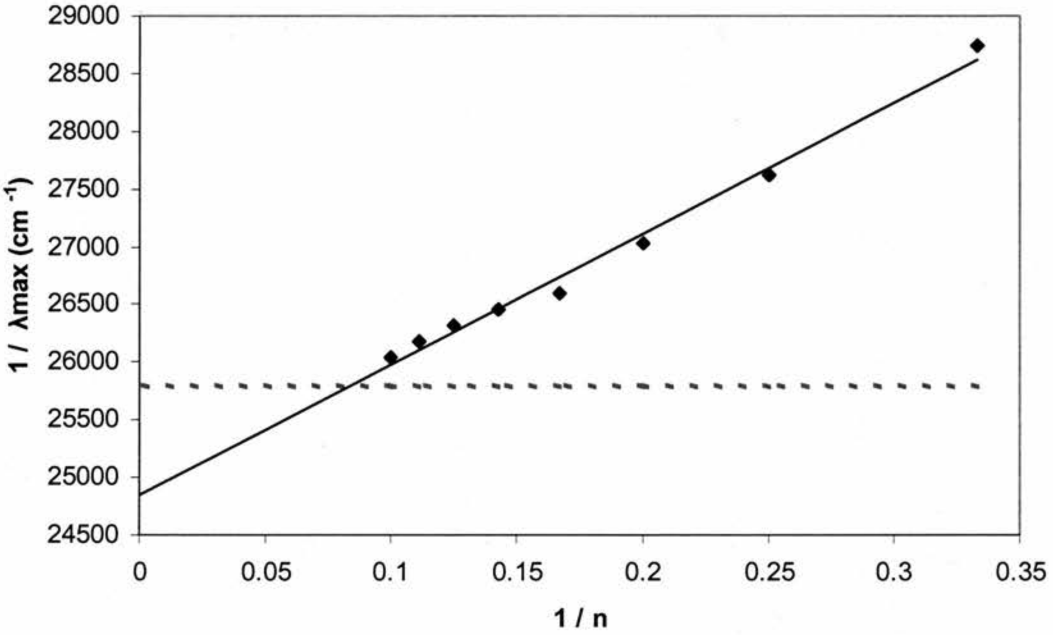
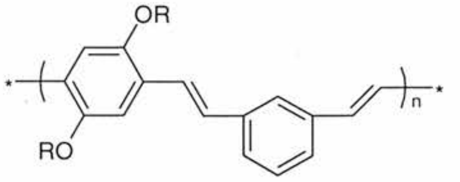


Figure 2.5: Plot to extrapolate effective conjugation length of poly(9,9-dihexylfluorene) using data from Miller et al.[25]

2.4 *Meta* Links as Conjugation Breaks

Meta linkages have been utilised as conjugation breaks in PPV[26] and PF.[27]



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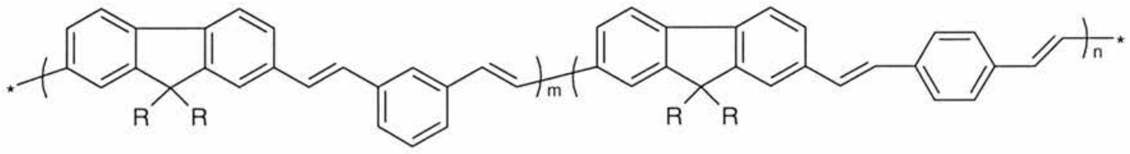

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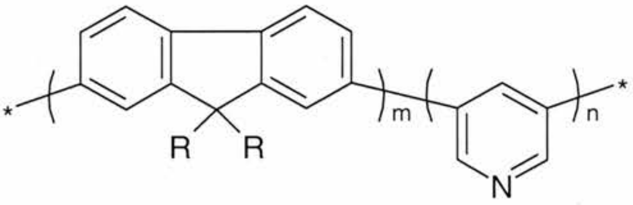
In the case of PPV **38**, the *meta* linkage increased the solubility of the polymer and also enhanced the photoluminescence quantum efficiency by a factor of 4.5 relative to the all-*para* linked polymer. The formation of excimers and the reasons for the increased photoluminescence efficiency were not discussed in this paper.

For the polyfluorene derivative **39** the authors do not report improved optical properties with increasing *meta* linkage content. The long wavelength emission band persists even in solutions diluted to 10^{-5} M. It is therefore hard to imagine that this emission is due to interchain aggregation effects such as excimers.

A paper by W Yang has been published following up the work documented in this chapter showing improved colour stability under EL conditions by the incorporation of *meta* linked pyridines.[28]



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No mention was made in this paper regarding the fluorenone argument. It was found that 0.4 molar equivalents was the optimum ratio of pyridine to fluorene for excimer suppression since 0.5 molar equivalents produced an alternating copolymer and the regioregularity of this polymer was less effective at excimer suppression.

Although *meta* linkages are widely accepted as breaking the conjugation length very few papers have been published as to how the conjugation is broken. There are a number of possibilities. Firstly the *meta* linkage could cause neighbouring units to twist out of plane relative to each other. Alternatively, the *meta* phenylene rings could be randomly twisted along the chain or form a helical structure (Fig. 2.6).

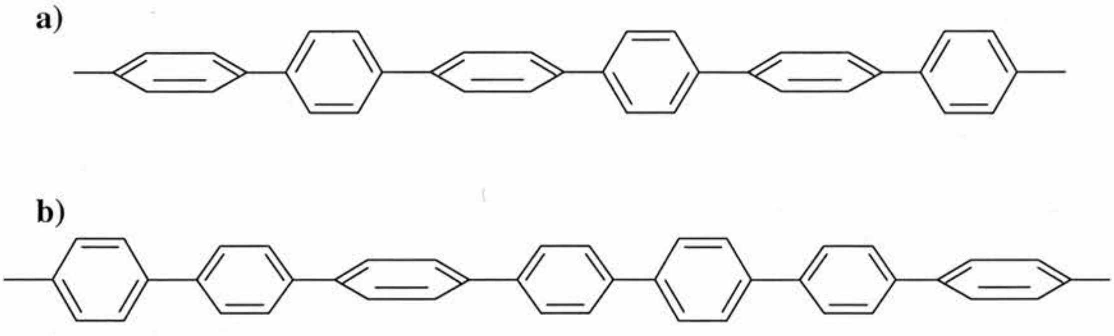


Figure 2.6: a) alternating rings b) helical structure (shown for para linkages)

Finally, the broken conjugation could arise due to the phase relationships at the linked sites and the sizes of the orbital coefficients. An extensive study into the conformational behaviours and electronic properties of *meta* linked phenylenes has been carried out by quantum chemical band calculations.[29] Results of these calculations indicate that polymer chains containing *meta* linkages twist into a helical structure to the same degree as an all *para* chain. Therefore the broken conjugation is apparently not due to twisting of the polymer chains. The authors go on to show that where two consecutive phenyl rings are linked in the *meta* position a nodal plane passes through the molecular orbitals in the HOMO and LUMO. Additionally, a higher band gap exists between the HOMO and LUMO for a *meta*-linked phenyl than for a *para*-linked. This results in weaker π conjugation along the chain (Fig 2.7).

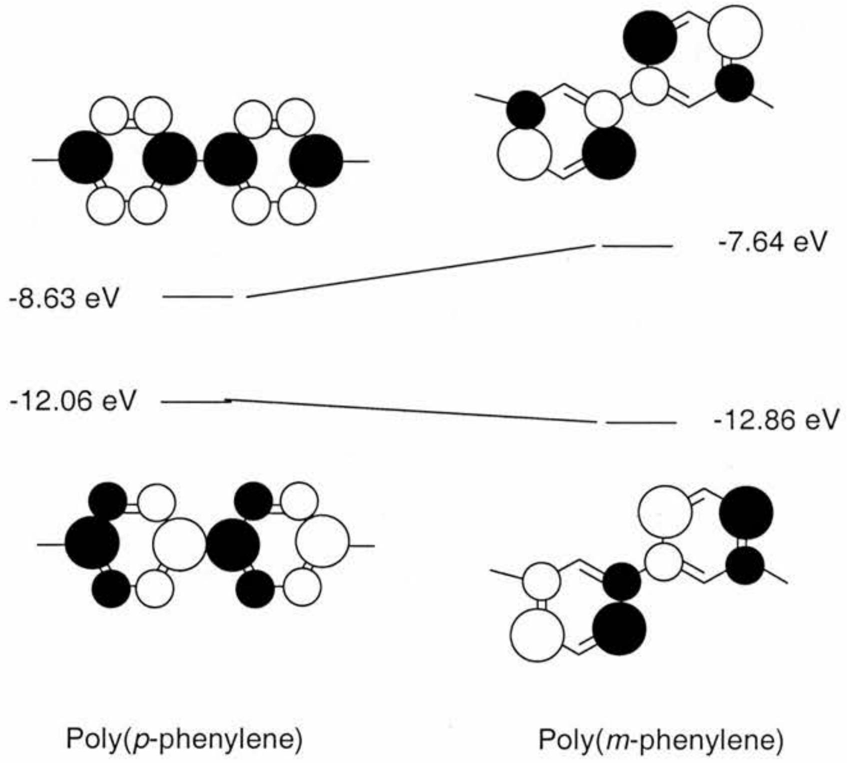


Figure 2.7: Frontier molecular orbital energy diagram for poly(p-phenylene) and poly(m-phenylene) from Ref. 29

In a recent paper by Pogantsch et al.[30], the nature of the excited states for alternating *meta* and *para* phenylene vinylene oligomers and all para phenylene vinylene oligomers have been explored. Figure 2.8 depicts the electron-hole (e-h) two particle wavefunctions for these oligomers derived from quantum chemical calculations. The (e-h) two particle wavefunction is a measure of the probability of finding the electron (or hole) at a particular excited state and areas of light shading indicate a high probability of finding an electron and hole. As can be seen from Figure 2.8 a) the ground state energy is delocalised over several chain units in both the *meta* and all *para* linked oligomers. In contrast, the excited state is localised on a *para*-linked segment (Fig. 2.8 b). Therefore, increasing the chain length or conjugation length does not significantly alter the energy gap between the ground state and first excited state (Fig. 2.9).

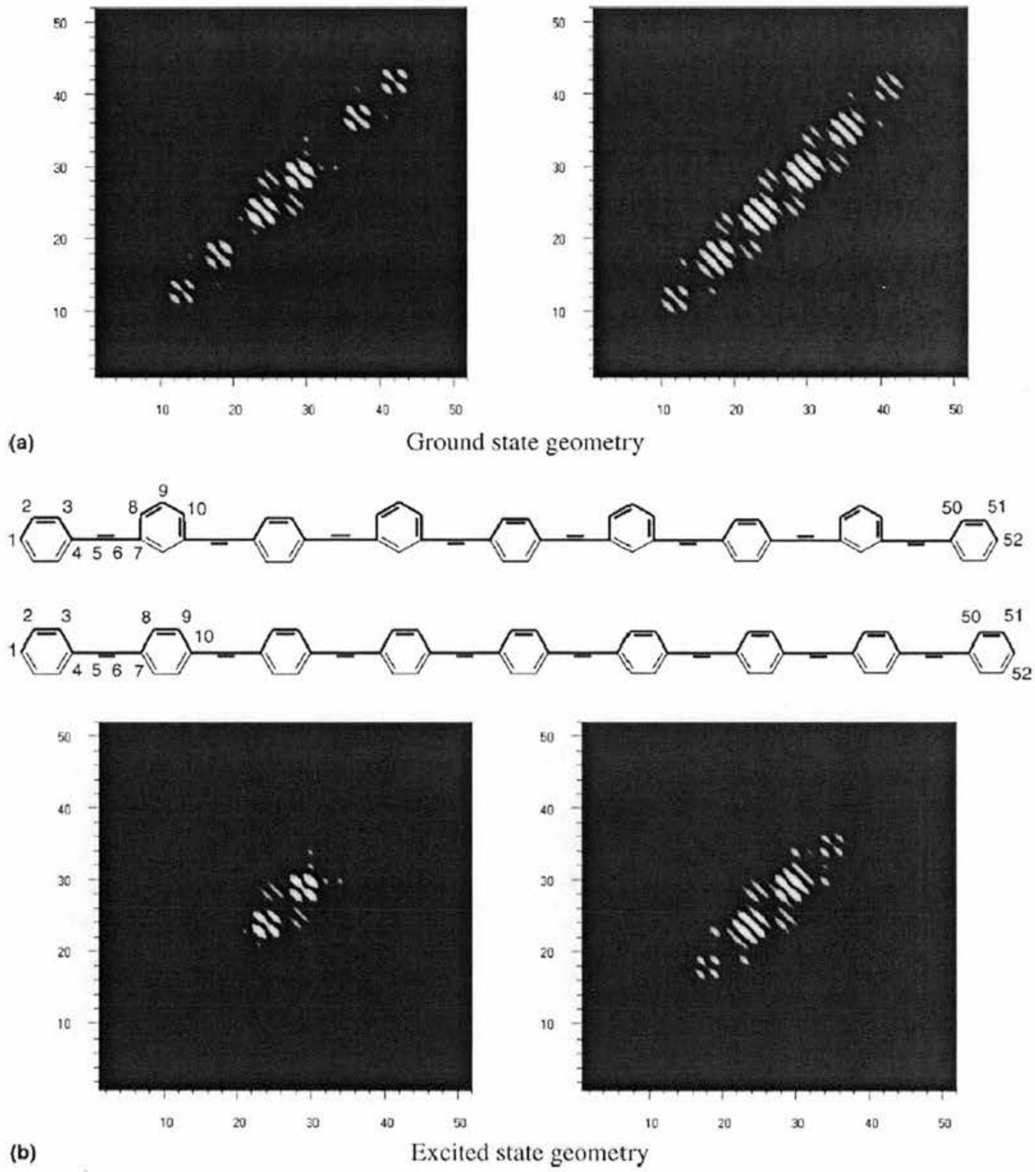


Figure 2.8: Electron-hole two particle wavefunctions for the lowest excited singlet state in meta-linked (left) and para-linked (right) for the ground state (a) and relaxed excited state (b) molecular geometries. Reproduced from Ref. 30.

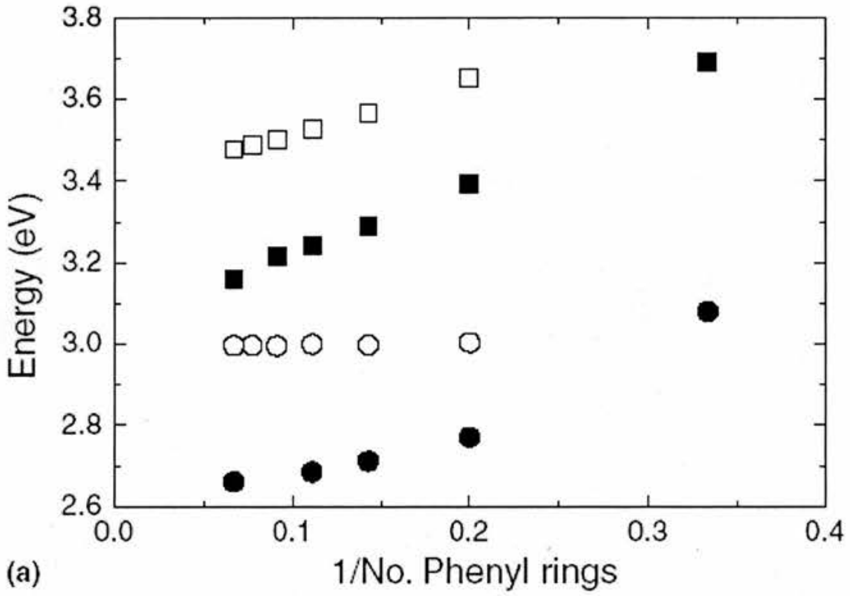


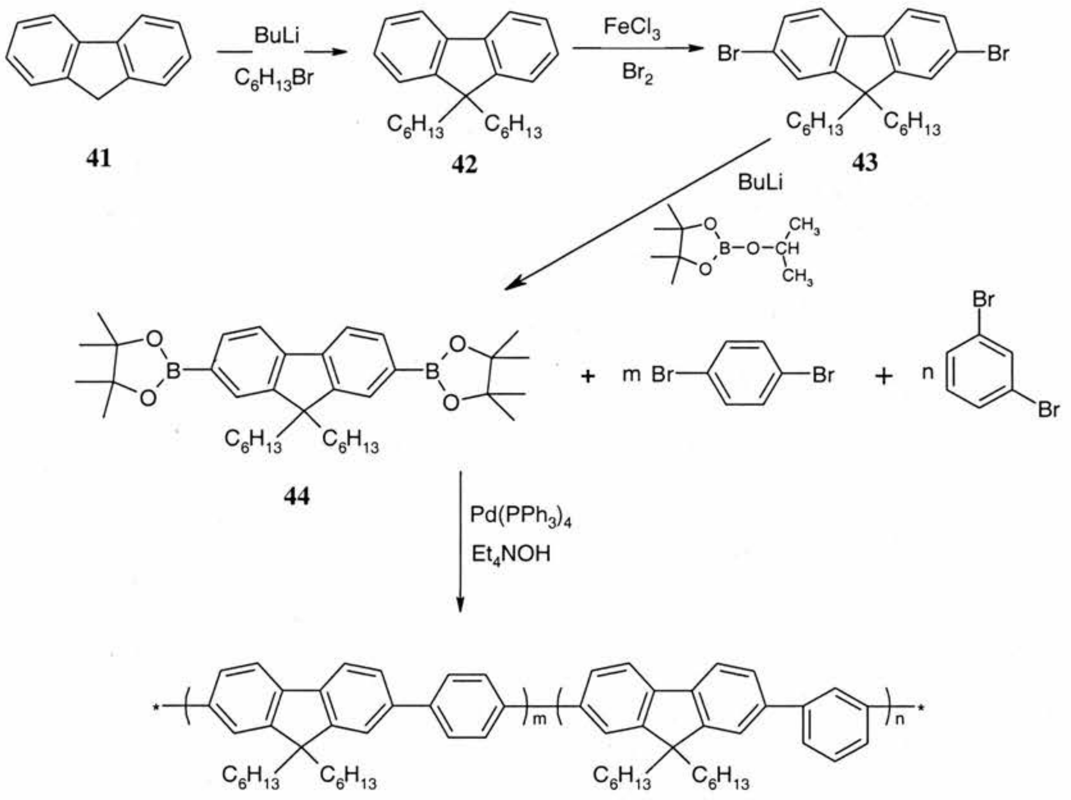
Figure 2.9: Excitation energies as a function of the inverse number of phenyl rings for the lowest excited state. Para-linked (solid symbols, ground state geometry: squares, excited state geometry: circles). Meta-linked (open symbols, ground state geometry: squares, excited state geometry: circles) Reproduced from Ref. 30.

The localised nature of the excited state is highly beneficial for EL devices as the exciton is prevented from migrating to low-energy emitting sites such as excimers or fluorenones.

2.5 Results

2.5.1 Polymer Synthesis

Synthesis of the fluorene copolymers was achieved by the method shown in scheme 2.1. For the purposes of this study the alternating copolymer poly[2,7-(1,4-phenylene)-9,9-dihexylfluorene] was synthesised by Suzuki coupling.[31] Some difficulty was experienced initially in obtaining satisfactorily high molecular weights, which was overcome by modifying the original procedure outlined by Leclerc.[32] Several different modifications were tried, including the use of a phase transfer catalyst. It was found that the best results were obtained through the use of an organic base tetraethylammonium hydroxide (Et_4NOH). Using this base also had the additional advantage of increasing the rate of the reaction, requiring only a few hours to obtain high molecular weights, as opposed to 48 hours which was previously required.



P1 - 7

*Scheme 2.1: Synthesis of copolymers **P1 -7***

This preparation could easily be altered to produce statistical copolymers with varying percentages of *meta* linkages to introduce conjugation breaks without significantly altering the structure of the polymer. Polymers with 0, 5, 10, 25, 50, 75 and 100% *meta* monomers were synthesized since it was expected that a small percentage of *meta* linkages would greatly decrease the contribution from excimers.

Table 2.2 Molecular weights of synthesized polymers

Polymer	Feed Ratio *Para* Phenylene	Feed Ratio *Meta* Phenylene	Mn	Mw	PD
1	1	0	11200	18500	1.652
2	0.95	0.05	12500	35300	2.823
3	0.9	0.1	24600	94500	3.835
4	0.75	0.25	6200	19500	3.139
5	0.5	0.5	8600	12800	1.486
6	0.25	0.75	19100	36700	1.919
7	0	1	3200	16100	5.006

The singlet peak from the *meta* phenylene (Figure 2.10 shown in red) is clearly visible at δ7.9 ppm in the ^{1}H NMR allowing confirmation of the relative quantities of *meta* linkages. For **P2**, **P3** and **P4** the singlet peak was clearly visible but quite small in comparison to the rest of the peaks and therefore the exact ratio of *meta* to *para* phenylene could not be accurately measured by ^{1}H NMR.

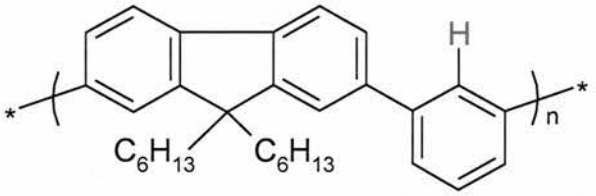


Figure 2.10: Proton giving rise to singlet in ^{1}H NMR

2.5.2 Optical Properties in Solution

As was shown in previous conjugation length studies the absorbance spectra (Fig. 2.11) show a shift to shorter wavelength due to the shorter conjugation length of the polymers. Details are given in Table 2.3.

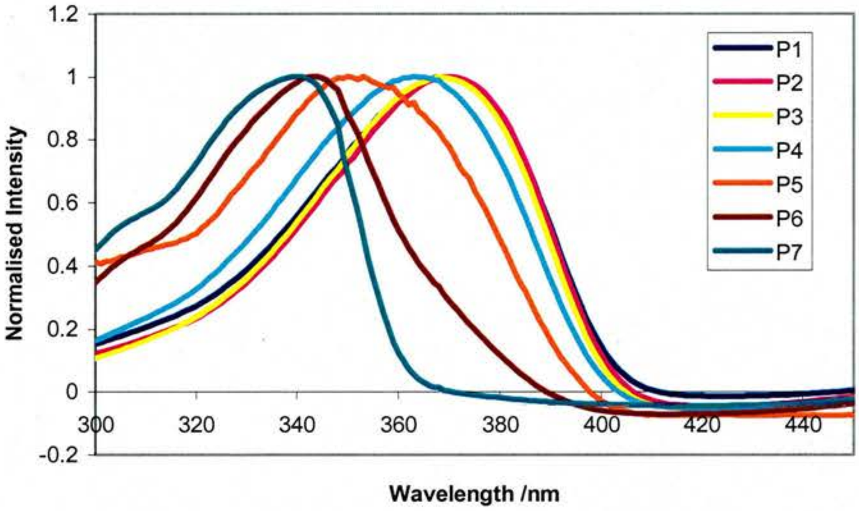


Figure 2.11: Absorption spectra of varying meta link content P1 – P7 (for details of polymer labelling see Table 2.2)

The photoluminescence spectra of dilute solutions show a λ_{em} of 422 nm for the all *para* polymer P1 corresponding to the blue colour expected of polyfluorenes. A characteristic hypsochromic shift for shorter conjugation length polymers is also as expected (Table 2.3). Small percentages of *meta* linkages do not significantly alter the emission spectra of the polyfluorene due to energy transfer from short to longer conjugated segments.[28] This is in accordance with the findings of Pogantsch who reports that the excited state is localised on the *para* segments and that the emission energy does not change significantly with chain length.[30] No long wavelength emission is observed in the photoluminescence spectra (Fig. 2.12) which is in accordance with the polymer chains being well separated in solution and therefore not forming excimers or aggregates.

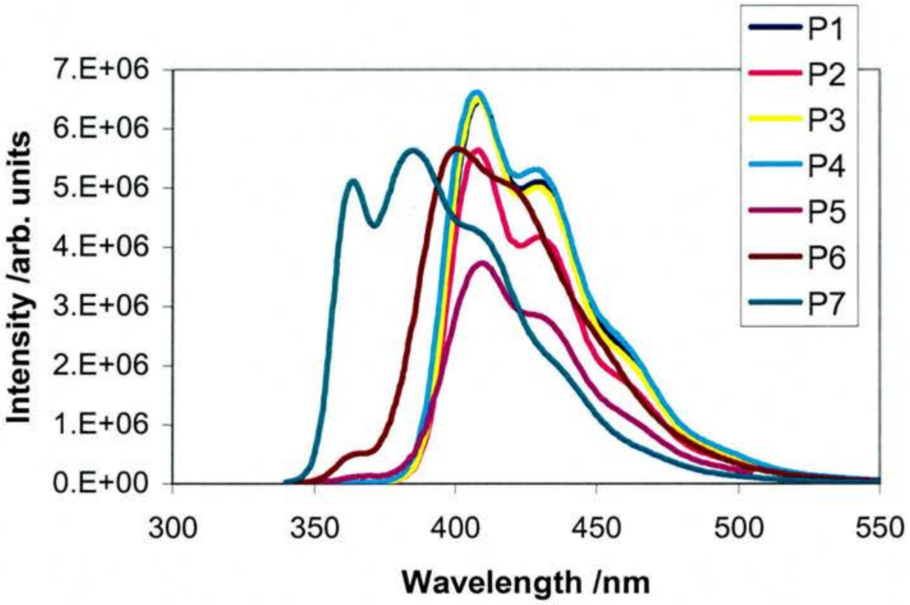


Figure 2.12: Photoluminescence spectra of varying meta link content P1 – P7 (for details of polymer labelling see Table 2.2)

Table 2.3: Absorption and PL response of polymers in THF

Polymer	Absorption λ_{max}	Emission λ_{max}
1	368	409
2	368	408
3	368	408
4	363	407
5	353	405
6	345	401
7	341	385

2.5.3 Optical Properties as Thin Films

Thin films of the polymers were prepared by spin coating the polymer from chloroform solutions (20 mg/ml) onto glass substrates. The absorption and emission spectra of the pristine films closely resembled the solution spectra and no long wavelength band was observed for any polymer. Excimer emission has generally been observed in the literature after heating for 1 hour.[33] **P1** was annealed in air at 150 °C and the emission spectrum recorded. Although a slight increase in relative intensity was observed at 530 nm no significant peak was observed and it was deemed necessary to anneal the film for much longer periods of time: 24 hours and 120 hours. After annealing overnight a peak at 510 nm begins to emerge and after a period of 5 days this peak overshadows the original polyfluorene peak (Fig. 2.13).

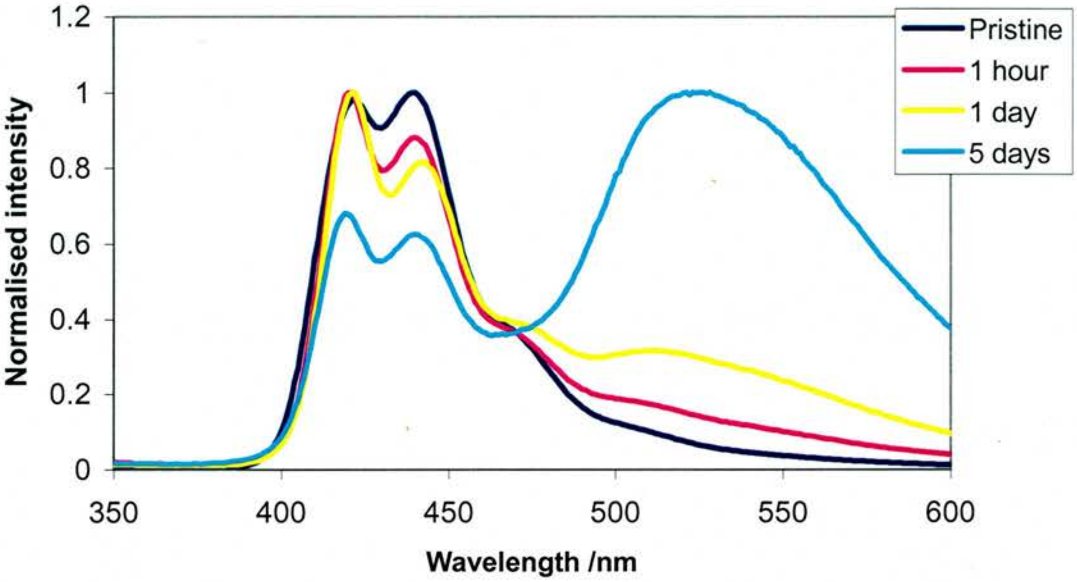


Figure 2.13: Thin film PL spectra of P1 annealing over time (λ_{ex} = 335 nm)

Thin films of all of the various *meta* polymers were then studied. The emission maxima for the films are compared to those in solution (Table 2.3) and found to be similar. For those polymers with only a small quantity of *meta* incorporation the spectra closely resemble the all-*para* linked polymer with a small excimer peak at 540 nm developing after one hour of being annealed (Fig. 2.14) which grows larger after longer annealing time (Fig. 2.15). For those polymers with high *meta*-linkage incorporation (i.e. 0.75 and 1 mole *meta*) this excimer band is suppressed.

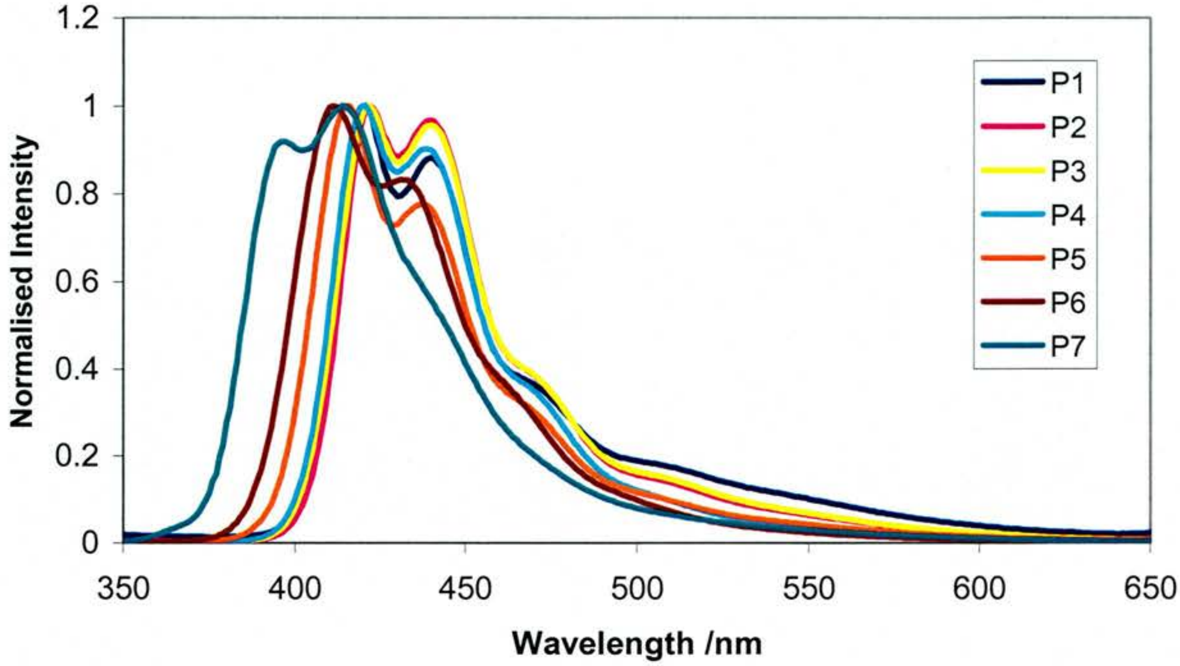


Figure 2.14: PL spectra of thin films of varying meta link content P1 – P7

(for details of polymer labelling see Table 2.2)

annealed for 1 h (λ_{ex} = 335 nm)

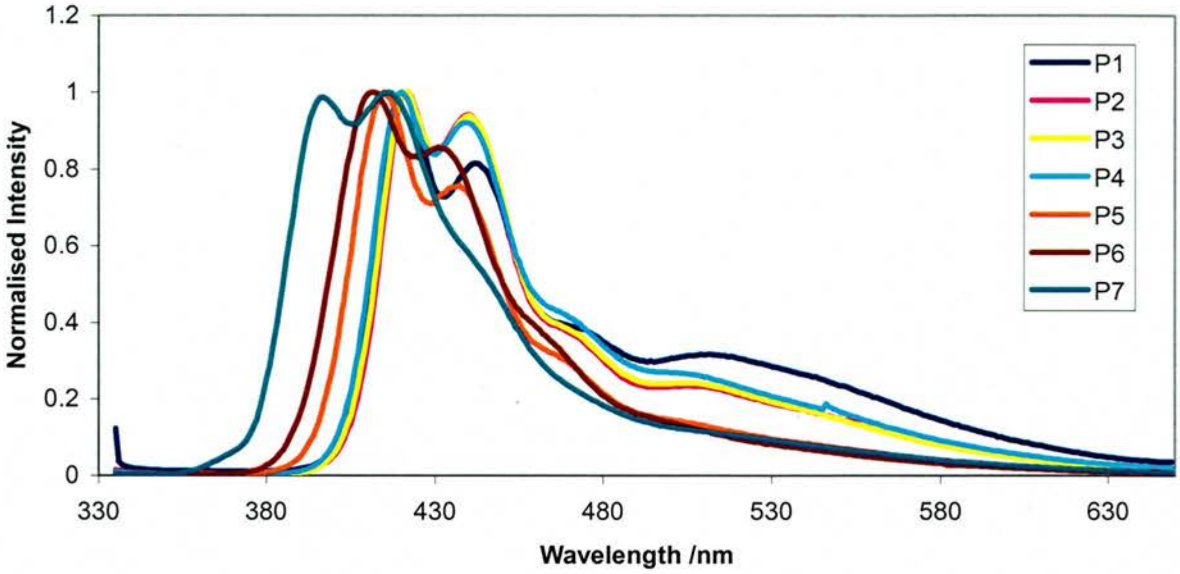


Figure 2.15: PL spectra of thin films of varying meta link content P1 – P7 (for details of polymer labelling see Table 2.2) annealed for 1 day (λ_{ex} = 335 nm)

After annealing thin films of the all *para* polymer for 5 days and then leaving the films exposed to air for a couple of months the thin film spectra no longer show any resemblance to that of a polyfluorene spectrum (Fig. 2.16). Indeed, the only observable emission is from the long wavelength region near 530 nm attributed to either excimer or fluorenone emission. The polymer from the thin film can be washed off the substrate with THF and a solution photoluminescence spectrum of the same sample recorded. The solution spectrum shows only emission from polyfluorene and no long wavelength emission which would be consistent with the excimer theory i.e. the polymer chains are being aligned during the annealing process to form excimers. However when the films are washed off the substrate the chains are free to move about in solution, no longer closely packed and aligned and therefore no excimer formation is observed.

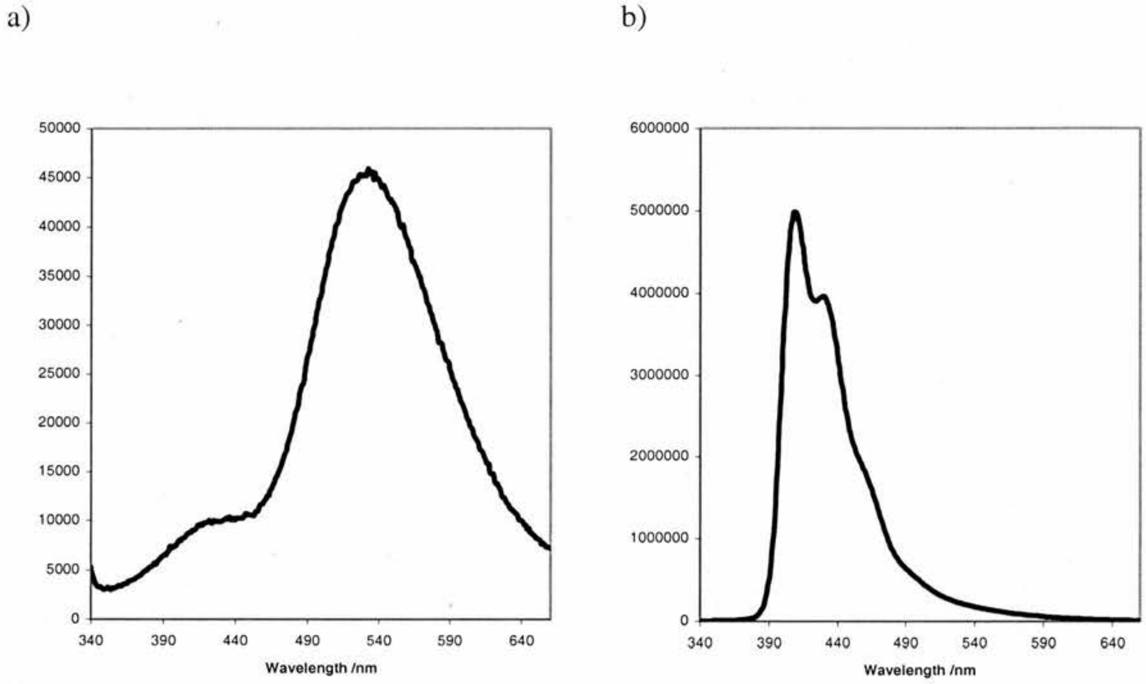


Figure 2.16: a) Thin film PL of P1 after annealing for 5 days b) Solution PL after washing off substrate

2.5.4 Electroluminescence

All of the polymers were then tested in an EL device to obtain electroluminescence data. Devices were of a multilayer structure consisting of; a glass substrate with a layer of indium tin oxide (ITO) as the anode, PEDOT as a hole transporting layer, the emissive polyfluorene layer and a calcium cathode which was covered by a layer of aluminium to protect the calcium from oxidation.

Unfortunately, although the devices had external quantum efficiencies of approximately 0.05% (comparable to literature results for polyfluorenes) the turn on voltages were very high: in the region of 20 V.

Electroluminescence spectra (Fig. 2.17) showed a large peak at 540 nm making the devices appear white to the naked eye. Polymers P6 and P7, which have shorter conjugation lengths, show considerably less long wavelength emission which can be attributed to the prevention of excimer formation. However, there does still exist a small peak.

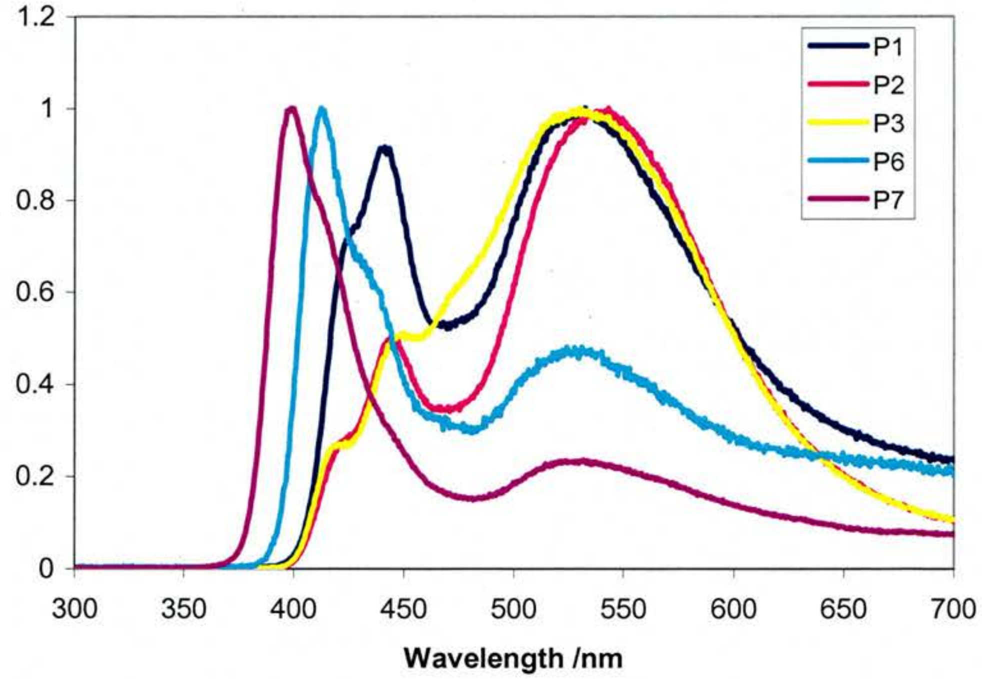


Figure 2.17: Electroluminescence spectra of varying meta link content P1 – P7 (for details of polymer labelling see Table 2.2)

The energy band gap for the fluorenone is lower than that of the polymer; therefore, only a very small amount of fluorenone needs to be present in the sample to give a large peak in the spectrum as excitons or charges migrate along the chain until they come to the lowest energy gap. The incorporation of conjugation breaks, although designed to prevent excimer formation, may also help to prevent fluorenone emission since the charges cannot migrate along the chains as far. Alternatively, the fluorenone or excimer may actually be formed during the operation of the device due to the high turn on voltages. This latter hypothesis is confirmed by the EL spectrum of **P7** taken after five minutes operation (Fig. 2.18). In the initial spectrum the contribution from an excimer peak is significantly smaller than the contribution from the same device five minutes later implying the excimer / fluorenone peak is formed during the device operation.

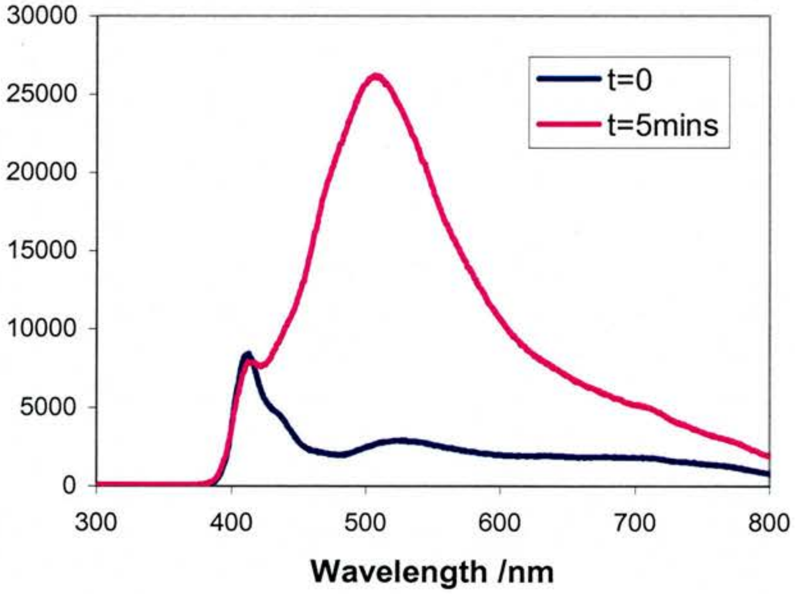


*Figure 2.18: EL of **P7** taken before and after 5 minutes of operation*

2.5.5 Annealing Studies of Thin Films of All-*Para* Polymer P1

The glass transition temperature was found to be 127 °C for the all *para*-linked polymer **P1** (see Appendix 1 for DSC trace). Polymer 1 could then be annealed above and below the glass transition temperature to see how this affected the formation of the long wavelength peak. Annealing above the glass transition temperature should allow the chains to move facilitating the formation of excimers.

Thin films of the all-*para* polymer **P1** that were annealed at 140 °C under an inert atmosphere for varying lengths of time did not show the long wavelength peak until it had undergone 72 hours of annealing (Fig. 2.19).

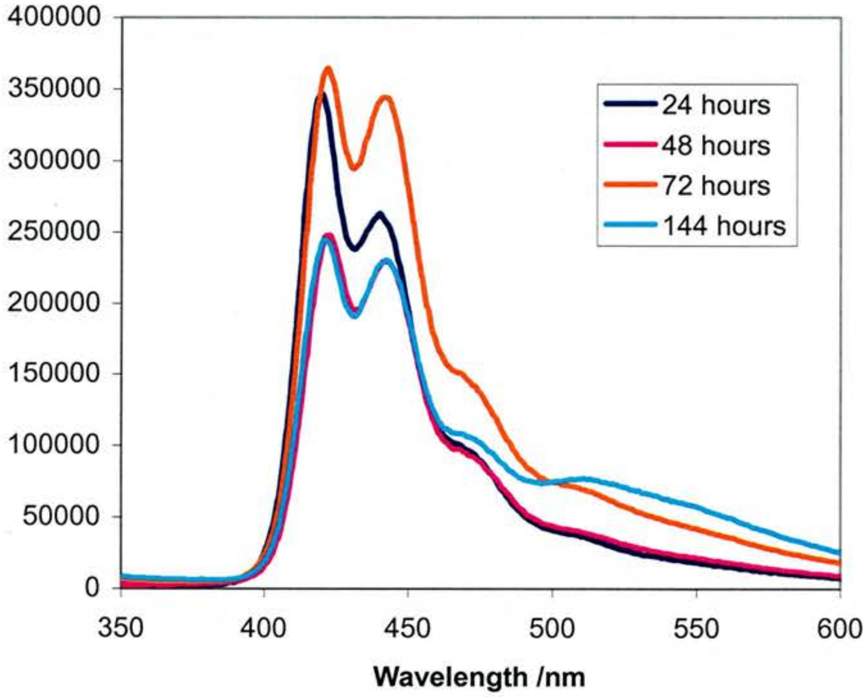


*Figure 2.19: PL Spectra of **P1** annealed under argon over time*

This sample was degassed after every spectrum was recorded and therefore oxygen could be introduced at this stage. It is also feasible that the long wavelength peak is due to a superposition of both fluorenone and excimer peaks. The excimer peak, however, is a lot slower to form due to it requiring time for the chains to move and form aggregates.

Several substrates were spin-coated with **P1** in air and each substrate was exposed to a different set of conditions (Table 2.4). Substrates were heated either above or below T_g or left at room temperature. For half of the samples this was simply carried out in the presence of air, however, the other half were placed in Schlenk flasks evacuated and placed under an atmosphere of argon. The photoluminescence spectra of these films were recorded after 24 hours and 72 hours of being subjected to the various different conditions. The results of these experiments are summarised in Table 2.4 and the actual graphs given in Appendix II.

At 80 °C the troublesome peak at 500 nm only appears in those samples annealed in air. This would seem to indicate that carbonyl moieties are being formed on the polymer. For this argument the formation of a peak at 140 °C under an inert atmosphere appears to be anomalous. Air leakage could explain this phenomenon, however repeat experiments also developed peaks at 500 nm under these conditions and support the excimer theory. In this instance the excimer peak is formed for polymers which have been annealed for extended periods above the glass transition temperature.

Table 2.4: Evidence of long wavelength emission peak from polymer P1 under different conditions

Time/h	Atmosphere	Temperature	Emission Peak at 540 nm ?
24	Air	Room Temp	No
72	Air	Room Temp	No
24	N_2	Room Temp	No
72	N_2	Room Temp	No
24	Air	80 °C	Small
72	Air	80 °C	Medium
24	N_2	80 °C	No
72	N_2	80 °C	No
24	Air	140 °C	Small
72	Air	140 °C	Medium
24	N_2	140 °C	No
72	N_2	140 °C	Small

2.5.6 Infra-Red Studies

In order to examine in more detail the origin of the long wavelength peak, a thin film of the all-*para* polymer **P1** was spin coated onto a salt plate used in infra-red spectroscopy.

The infra red spectrum for the pristine film was recorded and showed no carbonyl stretching frequency as anticipated. The film was then annealed in air for 1 h, 24 h, and so on, as was done for the measurement of the PL spectra in the previous section (Fig. 2.20).

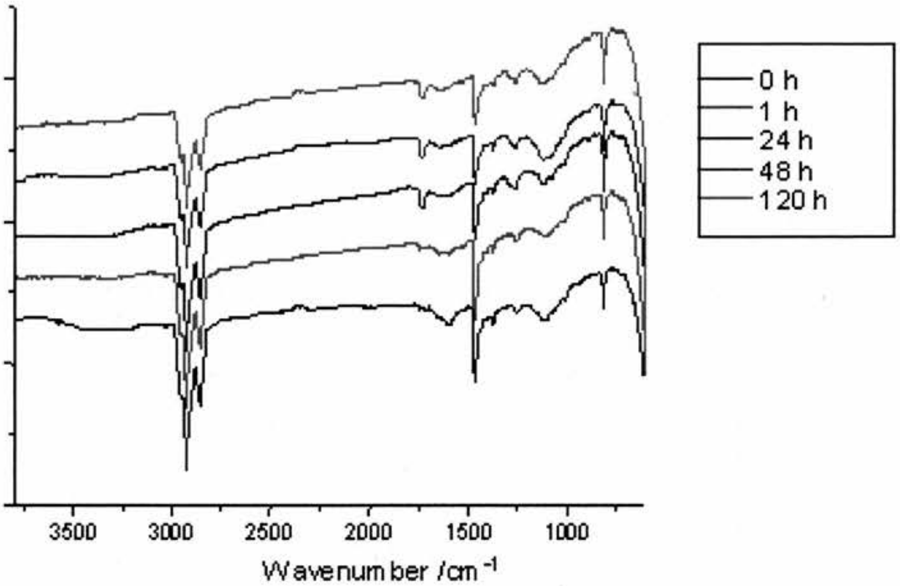


Figure 2.20: IR spectra of P1annealed in air

Over this period a small peak at 1740 cm^{-1} emerges which can be attributed to a C=O stretching frequency. Samples annealed under an argon atmosphere at 140 °C for the same periods of time did not display this peak. This implies that carbonyl moieties are formed in the presence of oxygen (Fig. 2.21).

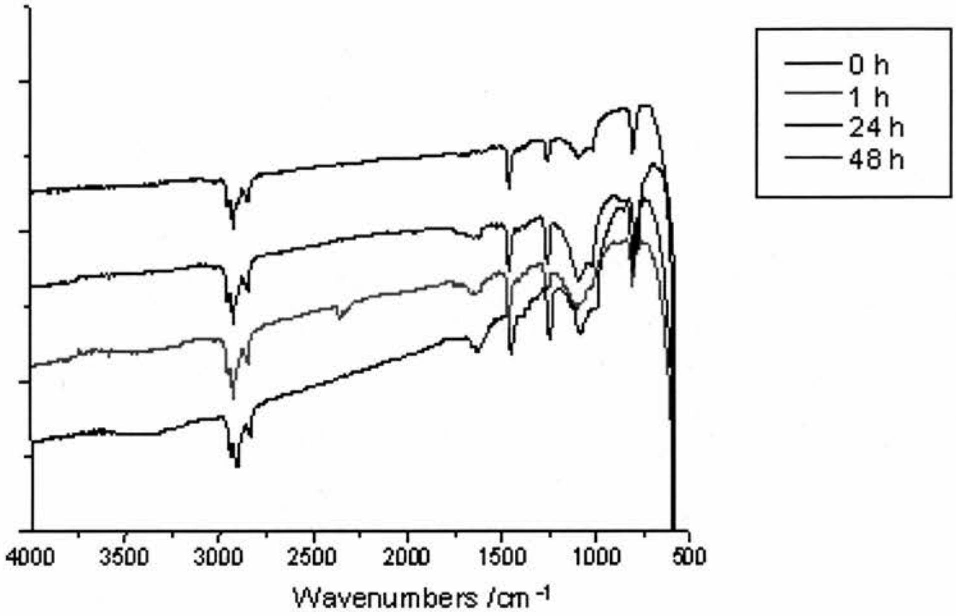


Figure 2.21: IR spectra of ***P1*** *annealed under argon*

2.6 Discussion of Fluorenone vs Excimer Explanations for Long Wavelength Emission

The initial aim of this thesis was to prepare fluorene copolymers, which could prevent the troublesome long wavelength peak caused by excimer and / or fluorenone moieties. During the course of this work thin films of the polymers produced were subjected to various different experiments to determine when the additional long wavelength emission peak formed and if the incorporation of *meta* linkages was successful at maintaining the colour stability. Despite the wealth of literature on this subject and several groups presenting arguments for one case or the other no conclusive evidence has been published as to the origin of the long wavelength peak. In our studies we have found that the long wavelength emission peak formed during the PL conditions has an emission maximum at 510 nm for shorter annealing periods and 540 nm after annealing for 5 days or many months. This raises the question that the long wavelength peak observed may in fact be an aggregate of a peak at 510 nm and a more dominant peak at 540 nm. The paper by Miller et al. argues the case for both fluorenone and excimer formation being the cause for the long wavelength band appearing on annealing. In addition, this group report a quickly-forming emission peak due to fluorenones for polymers end-capped with 2-bromofluorene and a slow forming peak due to excimers for those end capped with 2-bromo-9,9-dihexylfluorene. This would suggest that carbonyl formation occurs quickly relative to excimer formation but this could be affected by temperature since thermal oxidation is likely to occur at high temperatures.

Under EL conditions this secondary peak had a maximum at 540 nm for **P1**, **P2**, **P3** but was shifted to shorter wavelengths for **P6** and **P7**. The latter may be caused by the whole spectrum shifting to shorter wavelengths due to polymers **P6** and **P7** containing shorter conjugation lengths. The long wavelength peak is found to be more dominating in EL than in PL, which was originally thought to be due to the charges in EL migrating across the film and consequently the charge carriers are trapped in the lowest energy state. Another explanation is given by Xong et al. who report that the calcium in EL devices can catalytically oxidise the fluorene to fluorenone increasing the number of fluorenone defects or the rate at which they are generated.

Infra-red analysis in this study indicates that a small amount of fluorenone is being formed as shown by a peak forming in the carbonyl stretching range. Our experiments have shown that extensive annealing of thin films in air leads to exclusive long wavelength emission PL suggesting either extensive fluorenone or excimer formation. However, when the polymer is washed off the substrate the lack of any evidence for the long wavelength peak in solution photoluminescence suggests that fluorenone cannot be the only factor responsible for the poor colour stability of the polyfluorene. Annealing studies also support the argument for both systems operating with the peak at 500 nm forming during annealing in air at elevated temperatures. Under an inert atmosphere the long wavelength peak is still formed but only at temperatures above the glass transition temperature.

Finally, powdered polymer samples that have been left in air for many months after their initial preparation, emit exclusively the polyfluorene emission both in dilute solution and as a thin film. It is only samples that have been cast as thin films, which degrade over time to produce the peak at 500 nm. This suggests that carbonyl moieties are not responsible for the emission at 500 nm since the fluorenone moieties would form in the powdered state as well.

The work carried out in this thesis indicates that both excimer and fluorenone formation can occur I believe that the peak at 500 nm is formed by the superposition of peaks due to excimer and carbonyl formation.

2.7 Conclusions

The experimental evidence from this supports the argument that the long wavelength emission is caused by a small amount of fluorenone moieties in the polymer (introduced in the synthesis or after prolonged exposure to oxygen) and also due to excimer formation (especially when annealed in oxygen or argon at higher temperature). Regardless of the cause of the long wavelength emission band, this study has highlighted that the introduction of conjugation breaks can successfully suppress this troublesome band. The optimum incorporation of *meta* linkages in terms of the colour of emission and molecular weight, is achieved by incorporating 75% *meta* linkages. Full incorporation of *meta* linkages leads to a regioregular alternating copolymer which does successfully suppress the long wavelength band. However, the emission colour is significantly shifted towards the ultraviolet relative to the original *para* linked polyfluorene. Secondly, a *meta* linkage incorporates a kink onto the polymer backbone which appears to be detrimental to achieving high molecular weights.

In the case of excimers the shorter conjugation lengths preventing excimer from forming suppress the troublesome band. The argument for *meta* linkages suppressing fluorenone emission is that the conjugation breaks along the polymer backbone reduce the charge transport rate in the polymer and the exciton cannot migrate to the fluorenone. The fluorenone impurities are effectively isolated from the rest of the polymer.

2.8 Experimental

All starting materials were obtained from Aldrich or Lancaster, were reagent grade and used without further drying or purification except where stated otherwise. Tetrahydrofuran was distilled over sodium and benzophenone under an inert atmosphere.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Av-300 in deuterated chloroform solutions, operating at 299.998 MHz for ^{1}H and 75.45 MHz for ^{13}C. Infra-red spectra were recorded as KBr discs or as thin films of neat polymer on NaCl plates, on either a Perkin Elmer Paragon 1000 or a Nicolet Avatar 360 FTIR spectrometer.

Molecular weights were recorded on a Polymer Laboratories Gel Permeation Chromatography 120 Integrated GPC system with Polymer Laboratories gel 5 μm mixed column relative to polystyrene standards.

Absorption Spectra were recorded either in THF or as a thin film on a quartz substrate using a Varian Cary 300 Bio uv-vis machine. Photoluminescence spectra were recorded either as a dilute solution in THF or as a thin film on quartz substrates with a Fluoromax 2 from the Honba Group.

9,9-dihexylfluorene 42

Fluorene (5.28 g, 31.8 mmol) was placed in a round bottomed flask under a nitrogen atmosphere. This was then dissolved in dry THF (50 ml). The reaction flask was then cooled to –78 °C in a dry ice / acetone bath for 15 minutes whereupon butyl lithium in hexanes (27 ml, 66.7 mmol) was then added dropwise by syringe. The mixture was stirred for 45 minutes before hexylbromide (11 ml, 79.4 mmol) in dry THF (10 ml) was then also added dropwise by syringe. The mixture was stirred overnight and then poured into 150 ml of water. The aqueous layer was extracted with diethyl ether (2 x 50 ml) and the combined organic extracts were washed with brine and then dried over magnesium sulphate. The solvent was removed under reduced pressure and the excess octyl bromide was removed using the Kügel Rohr apparatus. A yellow oil was obtained (10.22 g, 96.2%).

^{1}H NMR δ (ppm) 7.65 (d, 2H), 7.25 (m, 6H), 1.8 (m, 4H), 0.9 - 1.1 (m, 12 H), 0.75 (t, 6H), 0.6 (m, 4H) . ^{13}C NMR δ (ppm) 151.05, 141.49, 130.56, 127.35, 126.72, 123.21, 54.32, 40.85, 35.41, 33.66, 31.93, 24.09, 14.45.

2,7-dibromo-9,9-dihexylfluorene 43

9,9-dihexylfluorene (6.1 g, 18.2 mmol) was dissolved in chloroform (50 ml) to which anhydrous ferric chloride (0.0503 g, 0.31 mmol) was added. The flask was wrapped in aluminium foil and placed in an ice bath. Bromine (2 ml, 38.3 mmol) was then added to the mixture and the flask was then allowed to warm to room temperature and stirred overnight. The solution was then poured into 150 ml of distilled water, to which 2M sodium thiosulphate solution was added. The aqueous layer was then extracted with chloroform (2 x 50 ml) and the combined organic extracts were dried over magnesium sulphate. The excess solvent was then removed under reduced pressure to afford a red viscous liquid which crystallised when left in the fridge for a few days. The crude product was then recrystallised in ethanol to give white crystals (7.99 g, 89%).

^{1}H NMR δ (ppm) 7.35 - 7.5 (m, 6H), 1.85 (m, 4H), 0.95- 1.1 (m, 12 H), 0.75 (t, 6H), 0.55 (m, 4H). ^{13}C NMR δ (ppm) 152.95, 139.46, 130.56, 126.57, 121.90, 121.54, 56.08, 40.62, 31.87, 30.00, 24.05, 23.00, 14.44.
I.R. 1252 cm^{-1}, 1123 cm^{-1}, 822 cm^{-1}, 701 cm^{-1}

2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene 44

The dibromo-9,9-dihexylfluorene (2.04 g, 4.14 mmol) was placed under a nitrogen atmosphere, dissolved in dry THF (50ml) and then cooled to –78 °C in a dry ice / acetone bath. Butyl lithium (3.5 ml, 8.7 mmol) was then added dropwise by syringe. The mixture was then left to stir at –78 °C for thirty minutes before 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.11 ml, 10.3 mmol) was then added rapidly to the reaction mixture. This was then allowed to warm to room temperature and was stirred for 24 hours. The reaction was worked up by pouring the contents of the flask into 150 ml of distilled water and extracting the aqueous layer with diethyl ether (3 x 50 ml). The organic extracts were then washed with brine and dried over magnesium sulphate. The solvent was removed under reduced pressure to yield an off white oily solid, which was recrystallised in ethanol to give a white powder. (1.67 g, 68.7 %, mp 184 – 186 °C).

^{1}H NMR δ (ppm) 7.6 - 7.75 (m, 6H) 1.8 (m, 4H) 1.25 (s, 24H) 0.8 - 1.1 (m, 12 H) 0.7 (t, 6H) 0.45 (m, 4H). ^{13}C NMR δ (ppm) 150.86, 144.31, 134.04, 129.30, 119.78, 84.11, 55.57, 40.49, 31.84, 30.02, 25.34, 23.96, 22.97, 14.42.
I.R. 2929 cm^{-1}, 2857 cm^{-1}, 1610 cm^{-1}, 1467 cm^{-1}, 1355 cm^{-1}, 1145 cm^{-1}, 1080 cm^{-1}, 819 cm^{-1}, 739 cm^{-1}

Tetrakistriphenylphosphine palladium

Palladium chloride (0.1083 g, 0.61 mmol) and triphenylphosphine (0.8037 g, 3.1 mmol) were placed in a schlenk tube which was then evacuated and filled three times. Dimethyl sulphoxide was then added and the reaction mixture heated until dissolution of the reagents (approximately 140 °C). Hydrazine hydrate (0.13 ml, 2.7 mmol) was then added slowly whereupon bubbles were given off. This was then allowed to cool to room temperature and ethanol was added. The precipitate was filtered on a Bűchner funnel under a stream of argon. The precipitate was washed with two portions of ethanol and two portions of ether to give a yellow powder.

^{31}P NMR (C_6D_6) δ (ppm) 26.589

General procedure for Suzuki coupling of polymers

The aryl dibromide (0.207 g, 0.877 mmol) and 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene (0.5094 g, 0.869 mmol) were placed in a round bottomed flask which was then flushed with argon. To this toluene (8 ml) fresh from the still and degassed tetraethylammonium hydroxide solution (5 ml) were added by syringe. This was then stirred for a further ten minutes before the catalyst tetrakistriphenylphosphine palladium (0.0201g, 0.017 mmol) was quickly added. The mixture was then refluxed under argon for 6 hours with vigorous stirring. Once cool the reaction mixture was the poured into methanol and the precipitate collected by filtration. The crude product was then washed with methanol, dilute hydrochloric acid and then methanol again. Purification was achieved by washing the polymer with acetone in a Soxhlett apparatus to remove any catalyst residues or oligomers.

Poly(1,4-phenylene-9,9-dihexylfluorene) P1

A yellow powder was obtained (0.3438 g, 96.8%)

^{1}H NMR δ (ppm) 7.5 - 7.75 (m, 10H), 1.4 (m, 4H), 0.95 - 1.1 (m, 12H), 0.75 (t, 6H).

^{13}C NMR δ (ppm) 152.21, 140.90, 140.57, 140.01, 127.99, 126.37, 121.88, 120.51, 55.72, 40.88, 31.90, 30.16, 24.25, 23.01, 14.43.

I.R. 2923 cm^{-1}, 2851 cm^{-1}, 1460 cm^{-1}, 808 cm^{-1}

Mn = 11210 Mw = 18520 PD= 1.652

P2

0.2616 g, 53.5%

^{1}H NMR δ (ppm) 7.9 (s, 1H), 7.8 (m, 78H), 7.65 – 7.5 (m, 115H) 2.0 (m, 80H), 1.0 (m, 240H), 0.7 (m, 200H). ^{13}C 152.21, 140.91, 140.57, 140.01, 127.99, 126.38, 121.88, 120.52, 55.72, 40.90, 31.91, 30.16, 24.28, 23.02, 14.44

Mn = 12500 Mw = 35290 PD= 2.823

P3

0.81 g, 94.9%

^{1}H NMR δ (ppm) 7.96 (m, 10H), 7.8 – 7.86 (m,), 7.64 – 7.72 (m,) 1.4 (m, 4H), 0.95 - 1.1 (m, 24 H), 0.75 (t, 6H).

^{13}C 162.57, 152.20, 140.89, 140.56, 140.00, 129.19, 128.63, 127.98, 127.60, 126.36, 121.87, 120.51, 55.71, 40.89, 31.89, 30.15, 24.25, 23.00, 14.42

Mn = 24640 Mw = 94500 PD= 3.835

P4

0.2887 g, 63.8%

^{1}H NMR δ (ppm) 7.9 (s, 1H), 7.75 (m, 14), 7.65 – 7.55 (m, 25) 2 (m, 16H), 1.05 (m, 48 H), 0.7 (m, 40H).

^{13}C 152.19, 140.89, 140.55, 140.00, 127.98, 126.65, 126.36, 122.11, 121.87, 120.51, 55.70, 40.91, 31.89, 30.15, 24.25, 23.01, 14.43

Mn = 6200 Mw = 19460 PD= 3.139

P5

0.24 g, 56.5%

^{1}H NMR δ (ppm) 7.9 (s, 1H), 7.75 (m, 6H), 7.7 – 7.4 (m, 13 H), 2.0 (m, 8H), 1.0 (m, 24H), 0.7 (m, 20H). ^{13}C 127.98, 121.87, 120.51, 31.90, 23.01, 14.43

Mn = 8602 Mw = 12780 PD= 1.486

P6

0.3397 g, 80.8%

^{1}H NMR δ (ppm) 7.9 (s, 3H), 7.8 (m, 10H), 7.65 – 7.5 (m, 27H) 2.0 (m, 16H), 1.05 (m, 48H), 0.7 (m, 40H). ^{13}C 152.19, 142.75, 140.63, 140.57, 140.03, 129.66, 127.99, 126.65, 122.12, 121.88, 120.50, 55.79, 40.93, 31.90, 30.16, 24.27, 23.01, 14.43

Mn = 19140 Mw = 36730 PD= 1.919

Poly(1,3-phenylene-9,9-dihexylfluorene) P7

0.47 g, 72.5%

^{1}H NMR δ (ppm) 7.9 (s, 1H), 7.75 (d, 2H), 7.65 – 7.5 (m, 7 H), 2.0 (m, 4H), 1.0 (m, 12H), 0.75 (m, 10H). ^{13}C 152.20, 142.76, 140.64, 140.58, 129.67, 127.62, 126.66, 122.14, 120.51, 55.80, 40.94, 31.91, 30.17, 24.27, 23.01, 14.43

Mn = 3222 Mw = 16130 PD= 5.006

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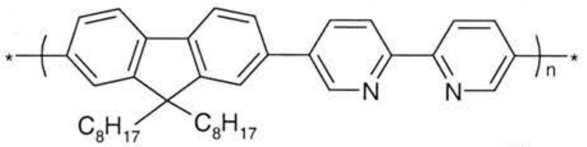
Chapter 3

Polyfluorene Based Metal Ion Sensor

3.1 Introduction

Conjugated polymers demonstrate a wide and varied number of different applications as well as different topics of research interest. One thread that has been comparatively unexplored is that of alternating copolymers where one monomer is based on a well-known ligand (e.g. bipyridine, phenanthroline, acetyl acetonate etc), which is capable of coordinating to a metal ion.

One such example was a study carried out by Liu et al. In this case three similar conjugated polymers based on fluorene and bipyridine were prepared and tested for their metal ion sensing capabilities.[1]



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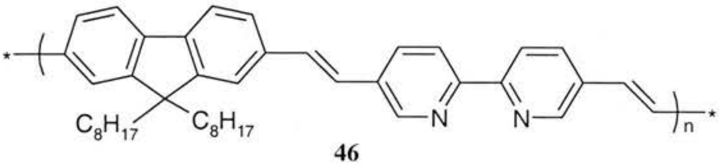

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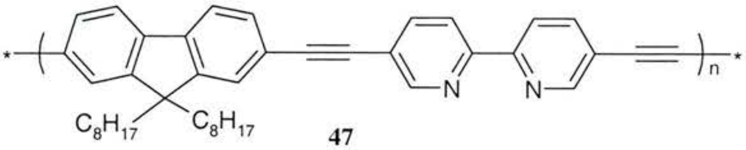

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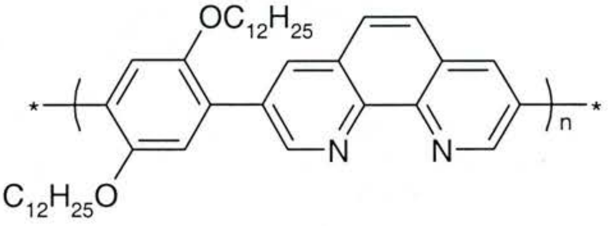
None of the three polymers showed any ion response to the alkali metal ions or the alkaline earth metals except for magnesium. Transition metals, however, produce a very sensitive ionochromic effect in all three polymers. The metal ions could be divided into three distinct groups; metals that completely quenched the luminescence (e.g. nickel), those that partially quenched the luminescence without altering the emission maxima (e.g. aluminium) and those that partially quenched the luminescence and also displayed a red shift in the emission spectra (e.g. manganese). The authors also report differing sensitivities to the metal ions between the polymers, which is explained by differences in the stiffness in the backbone of the polymer. Polymer **45** contains a single C-C bond has the most flexible backbone and also displays the most sensitive ionochromic effect. Polymer **47** with the acetylene and consequently least flexible backbone displays the weakest ionochromic effect. The authors have explained this phenomenon in terms of the flexibility of the backbone permitting the bipyridine units to become planar. The two aromatic rings of the bipyridine unit lie at an angle to each other and as a result the bipyridine is not planar and acts as a conjugation break. However, on coordination of a metal ion such as palladium, nickel or zinc the bipyridine unit is forced into a planar conformation and the conjugation length of the polymer is increased resulting in a bathochromic shift in the absorption and photoluminescence spectrum. The ease of forming the planar bipyridine is related to the ease of binding metal ions and therefore accounts for the differing sensitivities of the three polymers studied.

A second conjugated polymer metal ion sensor has also been reported by Yamamoto et al., This polymer is based on PPV and phenanthroline **48** and was also shown to be an effective metal ion sensor.[2]



48

The phenanthroline moiety is also a widely used chelating ligand capable of binding to a large number of metal ions. However, difficulties have been encountered in the synthesis of high molecular weight polymers because of the insolubility of the phenanthroline moiety.

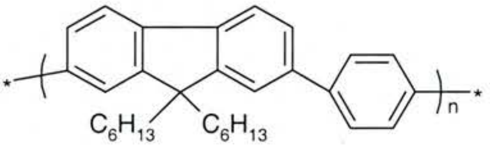
The recent paper by Yamamoto et al. demonstrates that it is indeed possible to synthesize a relatively high molecular weight polymer based on phenanthroline if the second monomer has long alkyl groups attached to enhance the solubility. The polymer **48** was synthesised by Suzuki coupling with a molecular weight of 7000. In contrast to polymers **45 – 47,** polymer **48** displayed good sensitivity to alkaline and alkali earth metals as well as the transition metals. This can be attributed to the high coordinating ability of the phenanthroline relative to bipyridyl.

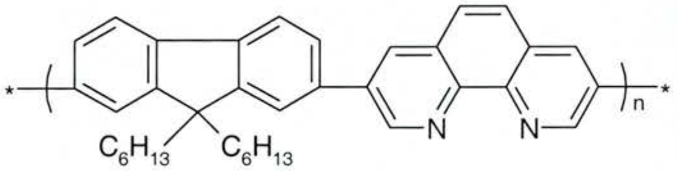
A third metal ion sensor paper was also recently published whilst work in this area was being carried out in our group. The paper by Zhang et al., describes the properties of two alternating copolymers based on fluorene and a bipyridyl unit or a phenanthroline unit to coordinate to the metal ions.[3] Both of these polymers display bathochromic shifts on coordination to some metal ions. This throws into doubt the validity of Liu's argument that the red shift is accounted for by the induced planarity of the bipyridyls increasing the conjugation length. Zhang proposes instead that each metal ion and its polymer complex have a distinct electronic structure and energy level.

3.2 Results and Discussion

3.2.1 Synthesis

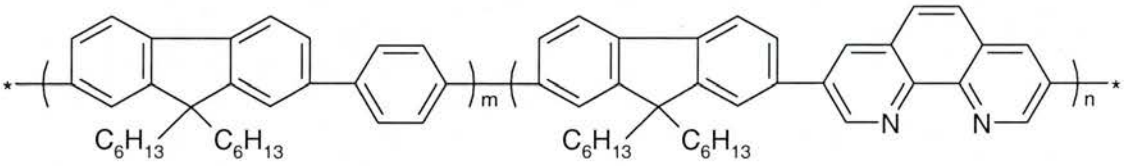
Three polymers were synthesized in order to compare the absorption and emission characteristics of the phenanthroline bearing polymer.





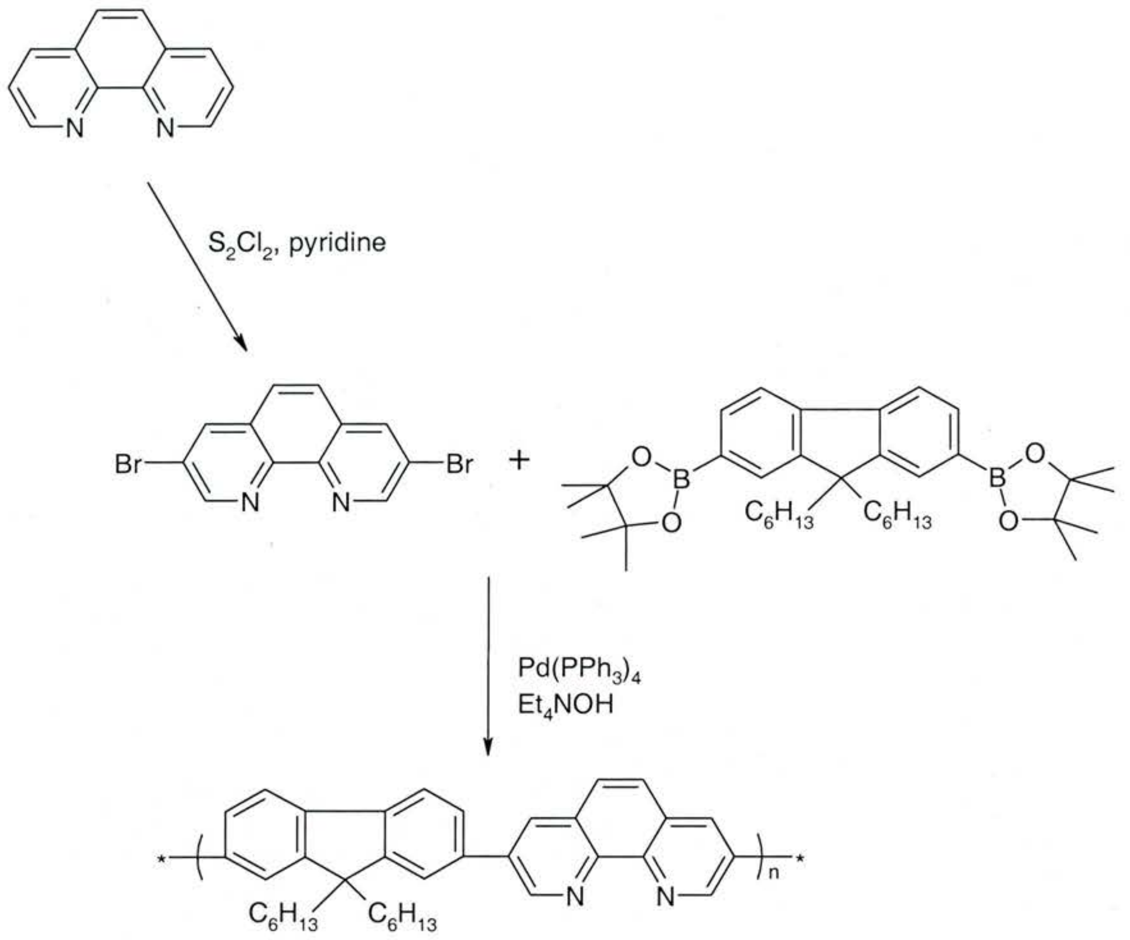
P8

P9



P10

These are the benchmark polymer poly(1,4-phenylene)-2,7-(9,9-dihexylfluorene) **P8,** which was prepared in Chapter 2; poly(3,8-phenanthroline)-2,7-(9,9-dihexylfluorene) **P9;** and a statistical copolymer **P10.** These were also synthesized by Suzuki coupling[4] from the appropriate dibrominated monomers within the Crayston group by Christian Münther as shown in Scheme 3.1.



*Scheme 3.1: Synthesis of **P9***

All three polymers were soluble in chloroform, toluene and THF, although polymers **P9** and **P10** were less soluble than **P8,** presumably due to the planarity and stacking of the phenanthroline units.

Molecular weights of all three polymers were determined by gel permeation chromatography in chloroform except for polymer **P8** where the elution solvent was THF. Polymers **P9** and **P10** have relatively low number average molecular weights with high polydispersities, which may arise due to partial precipitation of these polymers during the reaction.

Table 3.1: Properties of polymers synthesized

Polymer	Mn	Mw	PD	λ_{max} /nm	ε (ml g^{-1} cm^{-1})	λ_{em} /nm
P8	11200	18500	1.652	364	121500	408
P9	6600	21700	3.3	378	88900	410
P10	4800	26500	5.6	378	114200	413

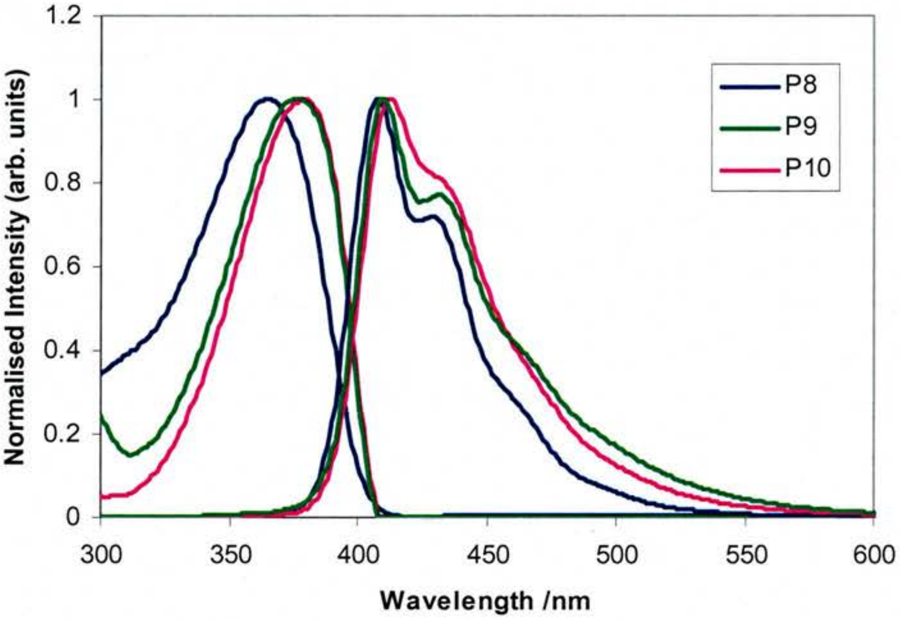


*Figure 3.1: Normalized absorption/emission characteristics of polymers **P8-P10** in THF (λ_{ex} = 335 nm)*

Figure 3.2 demonstrates that the absorption and emission characteristics of all three polymers are very similar. Surprisingly, no energy transfer from the fluorene to the lower energy phenanthroline is observed (which was also observed by Zhang et.al.[3]). This could be accounted for by noting that the n to π^* transition in the phenanthroline is partially forbidden by poor spatial orbital overlap (Fig. 3.2).

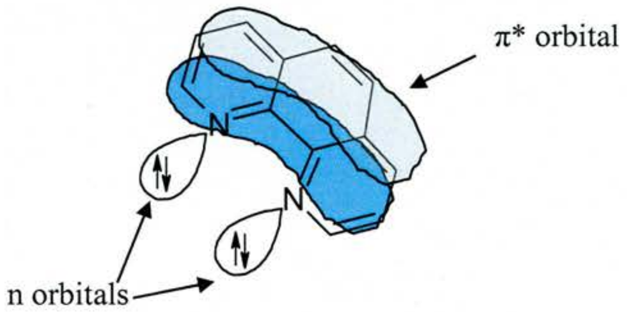


Figure 3.2: Schematic of n and π^* *orbitals in phenanthroline (accurate coefficients not shown)*

3.2.2 Solvent Dependent Optical Properties

In order to investigate the nature of the ground and excited states of polymer **P9** the absorption and photoluminescence spectra were recorded in several solvents of varying polarities. Two solvatochromic indices, Kosower's Z value,[5] and the normalized electronic transition energy E_T^N, are included as a measure of the solvent`s polarity.[6]

Table 3.2: Solvent dependency of ***P9***

Solvent	Z-value	E_T^N	λ_{max} /nm	λ_{em} /nm
Toluene	55.0[a]	0.099	368	403
THF	59.0	0.207	378	409
DCM	64.2	0.309	377	411
DMF	68.5	0.386	379	413
DMSO	71.1	0.444	377	418
Acetonitrile	71.3	0.460	347	403

[a] *extrapolated from plot of Z vs* χ_B *(Ref.7)*

The polymer appeared to be very insoluble in acetonitrile and anomalous results were obtained (e.g. the stray point in Fig. 3.3b). The solvent does not significantly alter the absorption spectrum of **P9** and the ground state of the polymer is therefore non-polar. A slight bathochromic shift or positive solvatochromism is observed in the emission spectra upon increasing solvent polarity (403 nm for toluene → 418 nm DMSO). This indicates that **P9** has a polar excited state, which is stabilised by the polar solvents.

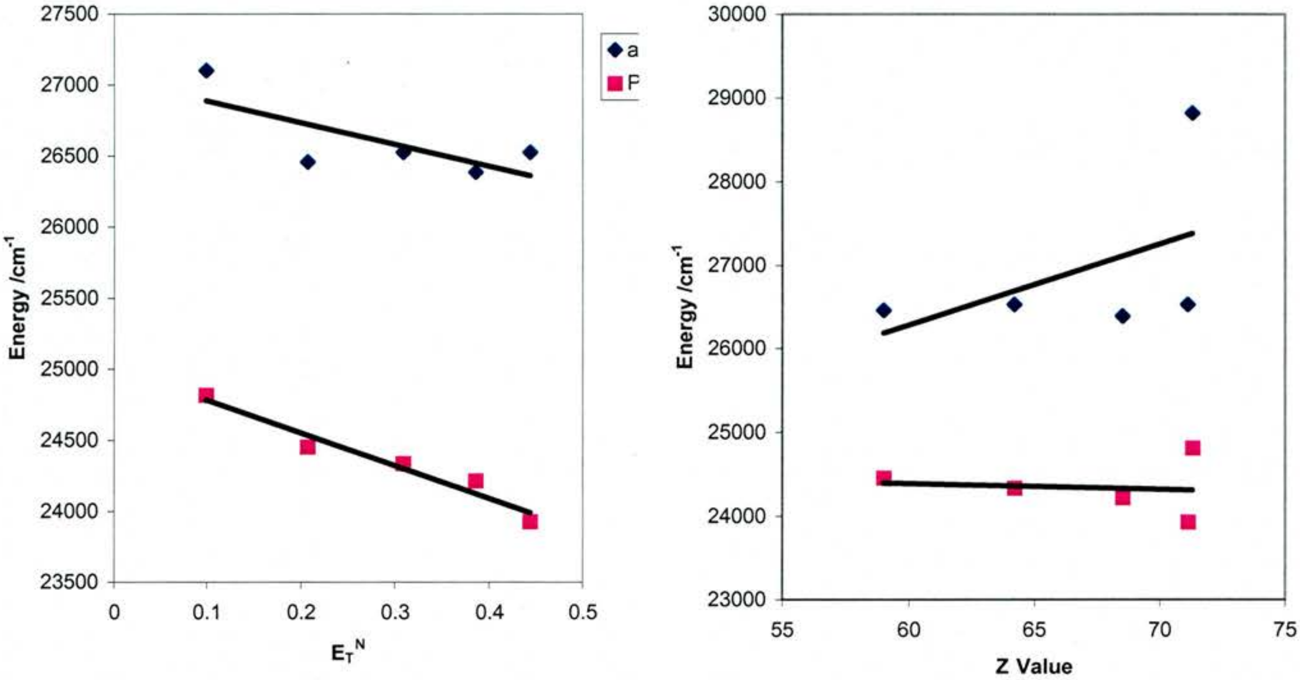
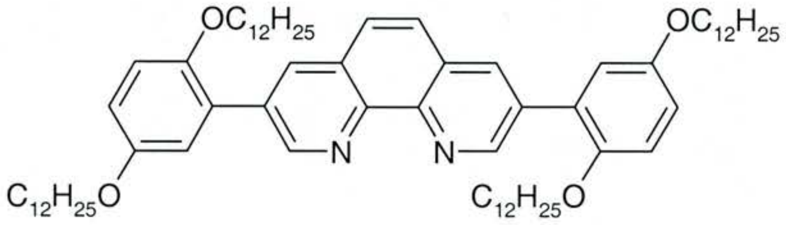


*Figure 3.3: Solvatochromism of absorption and PL of **P9** as a function of a) E_T^N b) Kosower Z Values of the solvent*

Yamamoto also extended his research to include solvatochromism of **48**.[2] A slight bathochromic shift in absorption and a more pronounced shift in photoluminescence (425 nm for benzene → 457 nm in DMF) was observed for more polar solvents which is in accordance with our findings. The solvatochromism was attributed to a charge transfer complex in both the ground and excited state arising from the electron accepting phenanthroline unit and electron donating dimethoxybenzene unit. The oligomer **49** displayed a more pronounced positive solvatochromism (approx. 54 nm). The alternating structure of the polymer reduces the polarity of the charge transfer structure and was thought to cause a reduction in the solvation effect. This could account for the relatively small solvation effect observed in our results. This is compounded by having a less electron-donating group in our case.



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3.2.3 Metal Dependent Optical Properties

Solutions of polymer **P9** in THF were prepared to which was added 20 equivalents of the metal chloride (except zinc bromide and silver nitrate, due to the availability of zinc bromide in the lab and silver chloride is exceptionally insoluble). The mixture was shaken to dissolve the metal chloride and the absorption and emission characteristics were recorded.

Table 3.3: Absorption and emission characteristics for polymer coordinated to metal ions in THF (λ_{ex} = 335 nm).

Metal ion	**λ_{max} /nm**	λ_{EmM}
No ion	378	408
Silver	399	498 (weak)
Aluminium	414	472
Cobalt	415	Q[a]
Copper	312	Q[a]
Iron	338	Q[a]
Lanthanum	396	454
Lithium	378	408
Magnesium	397	435
Nickel	393	Q[a]
Palladium	388	407
Zinc	409	451

[a] *Q – emission was quenched*

The metals could be divided into three groups: those that quenched the luminescence, those that shifted the emission maxima with partial quenching and those that partially quenching the luminescence without incurring the shift in emission spectra. The complete quenching of luminescence occurs in the case of the transition metal ions cobalt, copper, iron and nickel. These metals contain partially filled accessible d orbitals of a suitable energy level that an energy or electron transfer can take place from the polymer to the metal. The metal has low lying energy levels which can dissipate the excited stated energy non-radiatively.[8]

There are two possible energy transfer mechanisms that can occur in a polymer. Firstly, Dexter transfer shown in Figure 3.4 for an elongated octahedral metal. This is sometimes referred to as a double electron exchange mechanism and orbital overlap of the two components is required, accordingly Dexter transfer is limited to short range or through bond interactions.[9] Spin selection rules apply and consequently the spin must be conserved.

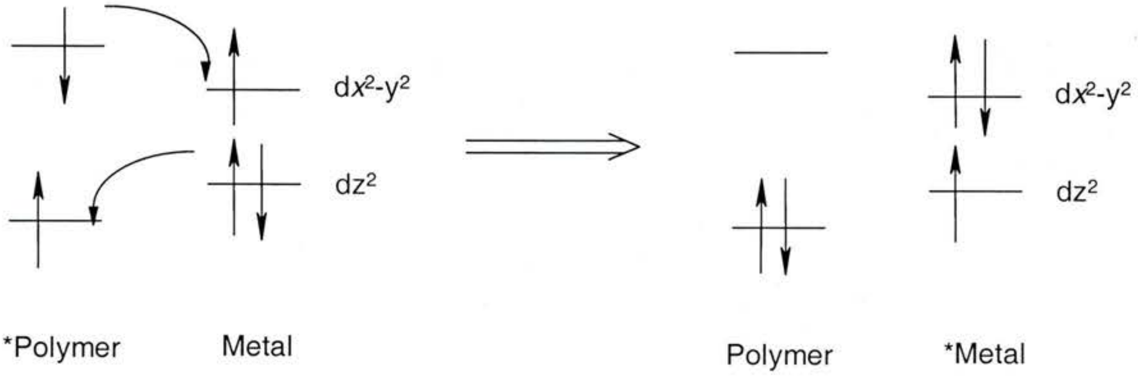


Figure 3.4: Dexter transfer from an excited polymer to a d^9 metal

Secondly, long range (<10 nm) dipole-dipole interactions termed Förster transfer can occur whereby an exciton is transferred in the transaction. In this case the individual spins of the components must be conserved.

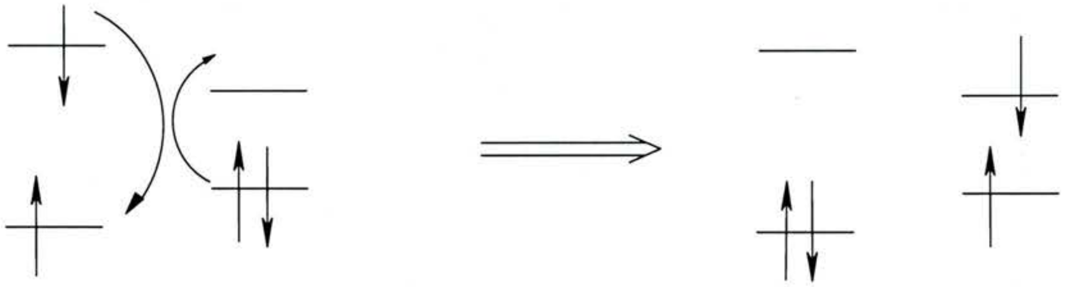


Figure 3.5: Förster energy transfer

Both Förster and Dexter energy transfer processes result in circulation of electrons and do not alter the charge distribution.

Electron transfer can also occur from an excited polymer to a non-excited transition metal which is shown for a d^9 metal ion in Figure 3.6.

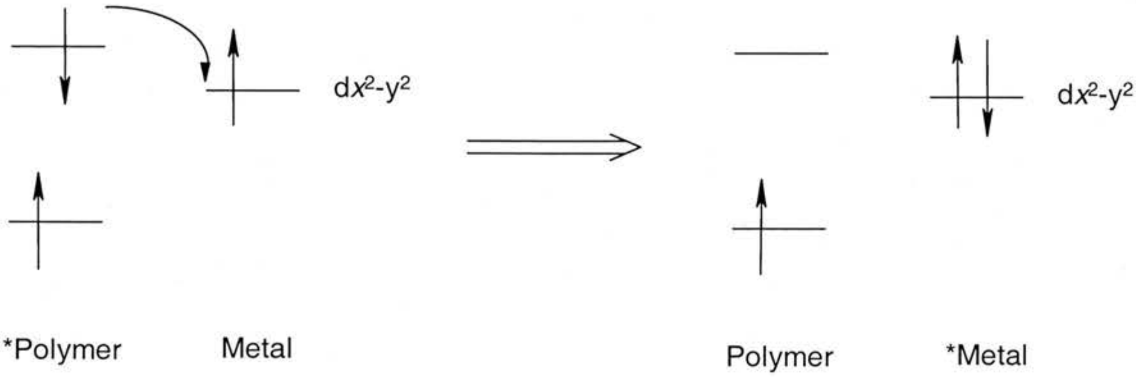


Figure 3.6: Electron transfer from an excited polymer to a d^9 metal

To determine which quenching process is occurring demands extensive spectrofluorimetric experiments at 77 K. Freezing the solution in liquid nitrogen and observing any fluorescent emission in the solid state under ultraviolet light can achieve a qualitative method of determining which process is occurring.[8]

The electron transfer quenching mechanism involves a redistribution of electrical charge which in turn induces the surrounding solvent molecules to rearrange. By freezing the solution solvent molecules are held rigid and prevented from rearrangement, which prevents the electron transfer. Energy transfer simply circulates electrons and involves no alteration of the charge distribution. Solvent molecules are therefore unaffected by energy transfer process. Consequently, systems in which the solvent has been immobilised will begin to fluoresce if electron transfer quenching is occurring. In contrast quenching by Dexter / Förster transfer is still effective in frozen solutions and no light emission will be observed. Photoluminescence was not restored for frozen polymer solutions containing nickel chloride, which implicates Dexter (energy) transfer quenching.

In the second group of metals the luminescence is partially quenched without perturbing the emission maxima; these consist of lithium and palladium. The effect of these metal ions on the polymers in the literature has proved to be contrasting. In the paper by Liu et al, palladium is reported to weakly quench the luminescence and induce an obvious red shift in the emission maximum. Conversely, the findings of Yamamoto indicate the fluorescence is completely quenched. These differences may be an effect of the different counter ions used by different groups and was briefly touched on in the paper by Zhang. Further exploration of this area needs to be studied in order to establish this theory further. In the case of lithium, there are no accessible d orbitals but some orbitals may still overlap with the polymers orbitals albeit less efficiently than the first group of metals. Therefore, some energy or electron transfer may occur but not in sufficient quantity to completely quench the luminescence.

Palladium on the other hand does have partially filled d orbitals, so one might expect complete quenching of the luminescence as in the first group of metals. This doesn't seem to be the case and may be due to palladium binding and causing the polymer to precipitate out of solution reducing the intensity of emission. Alternatively, the palladium chloride may decompose and precipitate out as palladium metal so only a small quantity of palladium chloride is available in solution to quench a fraction of the polymer chains leaving the rest of the polymer chains luminescent.

The third group, which both partially quench the luminescence and shift the emission maximum, consists of silver, aluminium, lanthanum, magnesium and zinc. These metals have a high charge to mass ratio and do not efficiently overlap with the polymers orbitals hence only partial quenching is observed. However due to their highly charged nature the polymers energy levels are disturbed and light of a different wavelength is emitted.

3.2.4 Acid Experiment

An experiment was carried out to determine the effect of 1 drop of acid on the absorption and emission characteristics of the polymer.

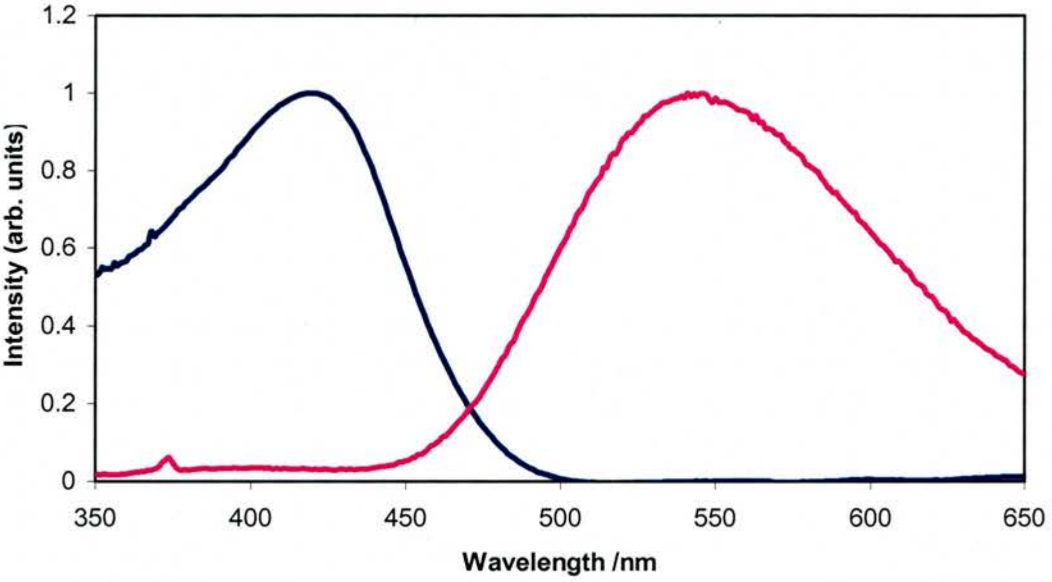


Figure 3.6: Absorption & photoluminescence spectra of P9 and 1 drop of HCl in THF(λ_{ex} = 335 nm)

Figure 3.6 clearly shows that on addition of 1 drop of concentrated hydrochloric acid both the absorption and emission spectra are significantly shifted to longer wavelengths with respect to the original **P9** Figure 3.2. The emission intensity is also significantly quenched relative to **P9** Figure 3.7.

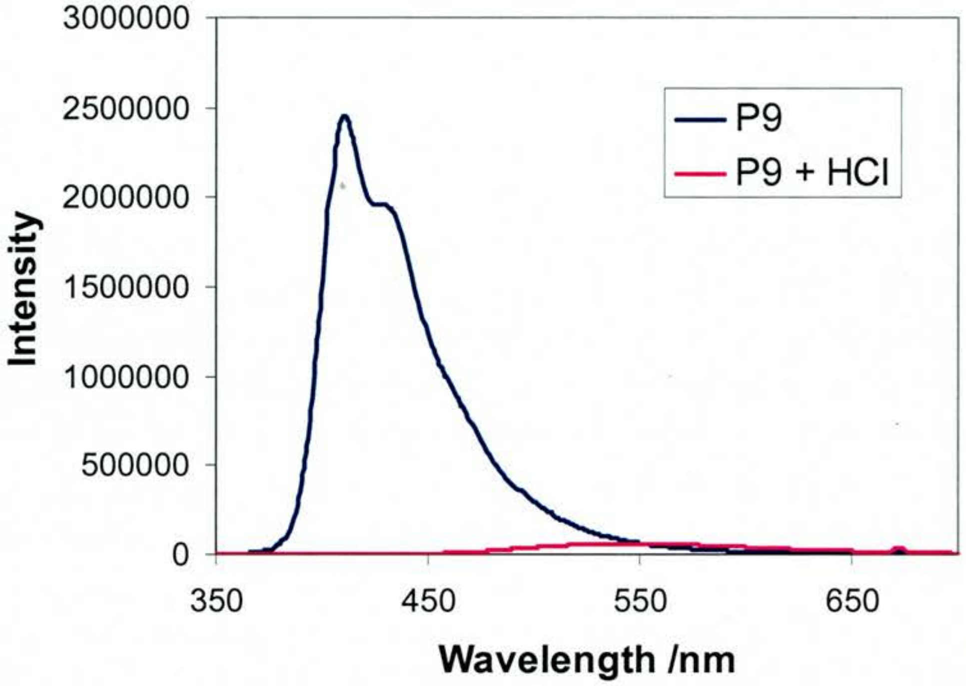


Figure 3.7: Photoluminescence spectra of P9 before and after addition of 1 drop HCl in THF (λ_{ex} = 335 nm)

The shift in the emission spectrum arises due to protonation of the nitrogen and a subsequent charge transfer from the fluorene to the phenanthroline. This effect has been observed in other conjugated polymers such as a pyridine containing PPV. The study by Yamamoto also reports quenching of the polymer luminescence on addition of trifluoroacetic acid, which is attributed to interference in electronic states on protonation.[3]

3.2.5 Quenching of Luminescence by Nickel

The effect of nickel chloride on the polymer was chosen to investigate the quenching process in more detail. This was achieved by preparing a standard solution of the polymer in THF of 2 x 10^{-5} M and titrating against a $NiCl_2$ solution in methanol. The titration was necessarily carried out in two solvents due to the insolubility of either reagent in the corresponding solvent. A control experiment in which methanol was added to a solution of the polymer in THF was carried out. No change was observed in the emission maxima upon addition of this level of methanol.

Table 3.4: Nickel Titration

Volume of $NiCl_2$ in MeOH	Volume of solution / L	M x10^{-5}	Max Abs nm	Max Pl nm
0	0.22	0	381	435
12 uL	0.220012	0.2295	388	437
32uL	0.220032	0.61182	403	442
68uL	0.220068	1.29987	405	Q
520 uL	0.22052	9.9199	407	Q
2.02 ml	0.22202	38.2747	408	Q

Q - quenched

The absorption spectra showed a slight bathochromic shift on coordination of the nickel (Figure 3.8). The emission maximum of the photoluminescence spectrum also showed a slight shift before the emission was completely quenched by the nickel.

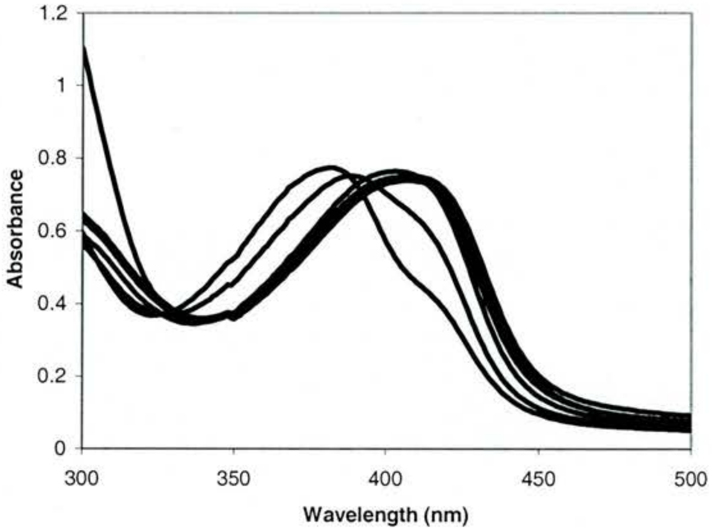


Figure 3.8: Changes in absorption spectrum of ***P9*** *in THF for various concentrations of* $NiCl_2$.

As can be seen from Figures 3.9 and 3.10 the intensity of both the absorption maximum and emission maximum decrease with increasing amounts of nickel chloride.

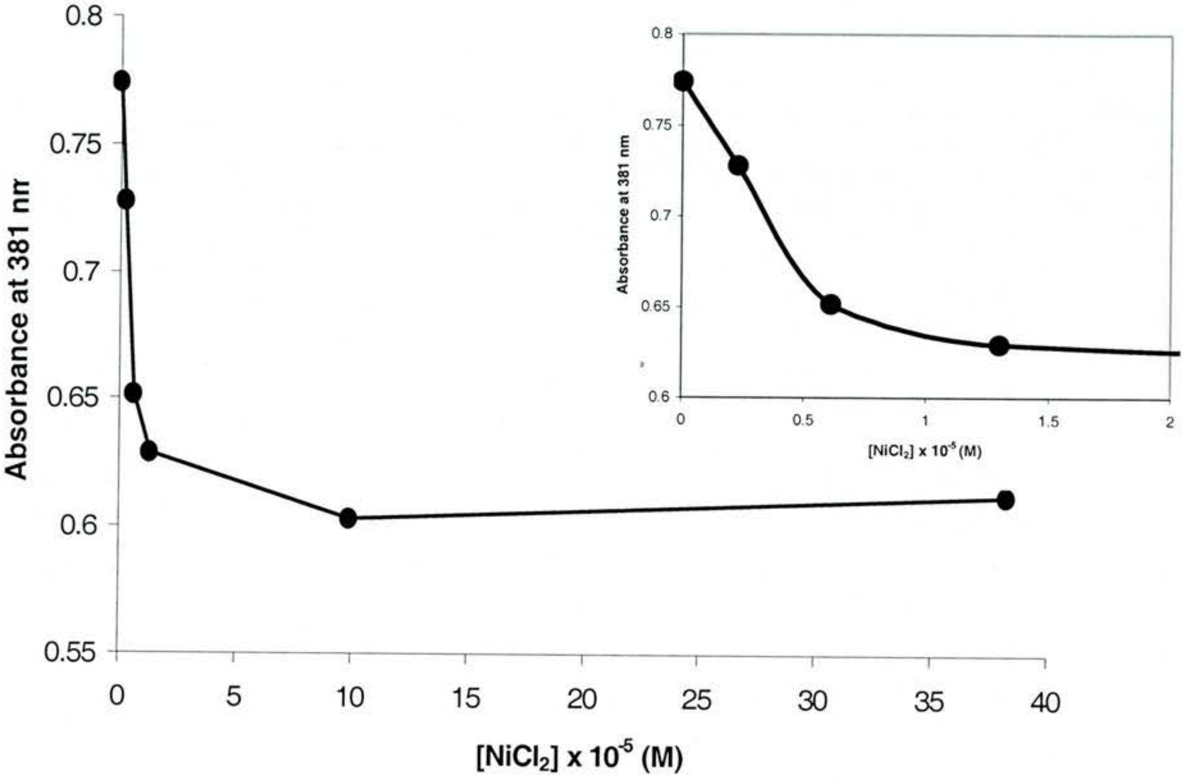


Figure 3.9: Absorption intensity of ***P9*** *in THF as a function of nickel concentration.*

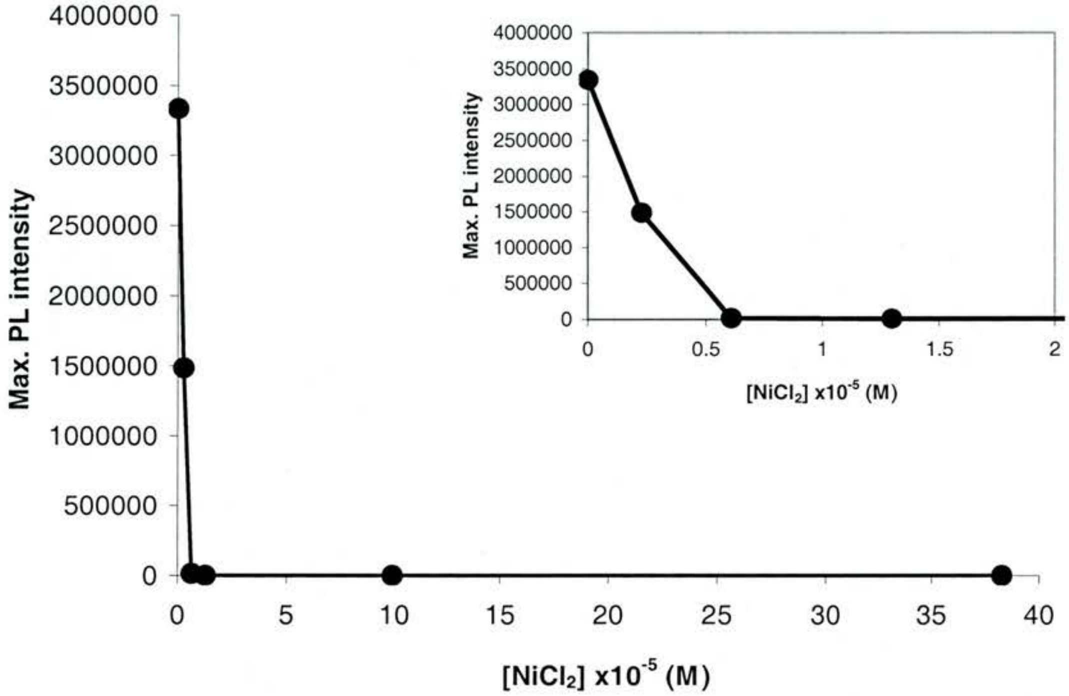


Figure 3.10: Emission intensity (at λem =435 nm) as a function of nickel concentration

The concentration of nickel chloride that would result in a 1:1 ratio of nickel to phenanthroline is 2 x 10^{-5} M. As Figure 3.10 indicates complete quenching has occurred by 0.6 x 10^{-5} M, which corresponds, to one nickel for every 3 or 4 phenanthroline units. One explanation for this is that the nickel binds to 3 or 4 phenanthroline units in an octahedral structure. However it is more likely that this quenching occurs due to a molecular wire effect where the singlet excited state is delocalised along the polymer backbone and therefore every site does not need to be bound to nickel, moreover one would expect that one nickel per polymer chain would be sufficient to completely quench the luminescence. In this example quenching does not occur until several equivalents of nickel per polymer chain has been added. This may arise due to inefficient mixing of the polymer solution during the titration and therefore several nickel ions may bind to polymer chains near the surface of the solution whilst chains in the depths of the solution are not exposed to any nickel until higher concentrations have been added.

3.2.6 Optical Properties of Thin Films

THF is a relatively poor solvent for polymer **P9,** and therefore solutions of the polymer **P9** in chloroform (5mg/ml) were prepared. One equivalent of the metal halide dissolved in methanol was then added. These solutions were then spin cast onto quartz substrates (1200 rpm) and their absorption and emission characteristics were recorded.

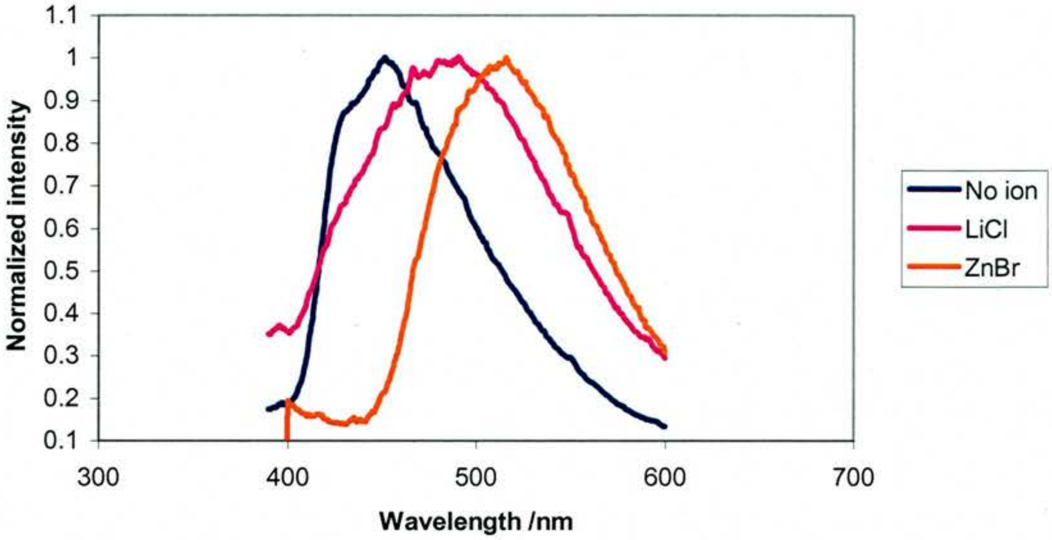


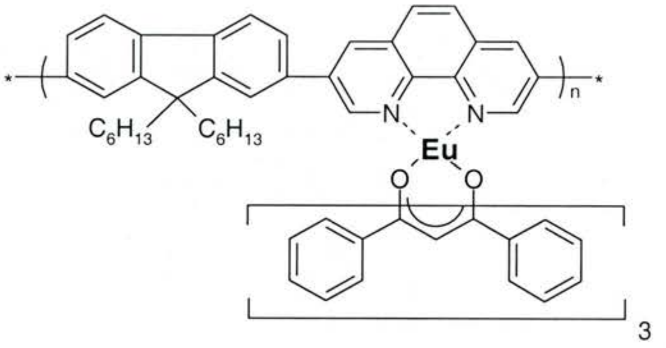
*Figure 3.11: Normalized thin film emission from polymer**P9** and metal ion doped **P9***

Films were relatively thin despite the low revolutions per minute of the spin caster and therefore the intensities of the photoluminescence spectra were also low and relatively noisy. The thin film of the polymer **P9** shows a significant bathochromic shift of approximately 50 nm in the thin film relative to the solution photoluminescence spectra. This may be due to an aggregation effect of the polymer in the solid state or due to more efficient energy transfer in the solid state and therefore the emission observed arises from the phenanthroline moieties.

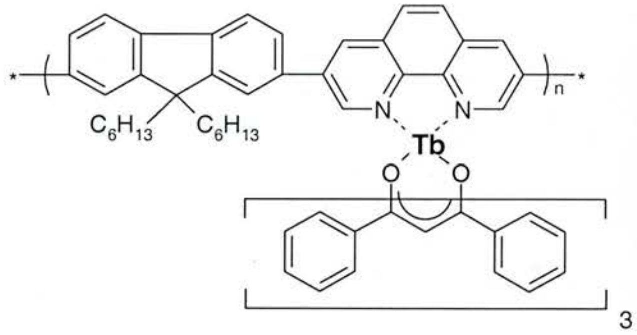
It is clear from Figure 3.11 that the emission spectrum is significantly shifted on coordination of both lithium and zinc. This contrasts with the solution phase results in which the lithium doping was not observed to alter the emission maximum. A probable reason for this is that the Li^+ ion is strongly solvated by the THF / MeOH solvent.

3.3 Rare Earth Metal Coordination

Attempts were made in conjunction with project student M VanRyssen to design organic light emitting diodes that displayed the three primary colours red, blue and green. Since the polymer itself emits blue light, it was necessary to coordinate two different metals that would tune the emission colour to green and red by energy transfer to the metal. Lanthanide metals have been shown to not completely quench the luminescence and red europium and green terbium complexes are well known in the literature.[10] Therefore, the aim of this section of the project was to synthesize polymers **P11** and **P12**.



P11



P12

3.3.1 Synthesis of Europium Bound Polymer P11

Polymer **P11** was synthesized by coordination of europium chloride to polymer **P9** using a method similar to that utilised by Yamamoto.[2]

Table 3.5: Molecular Weights of Polymers

Polymer	Mn	Mw	PD
P9	4700	8200	1.739
P11	5500	9600	1.756

Molecular weights of both polymer **P9** and **P11** were found to be extremely low due to the partial precipitation of polymer **P9** in the polymerisation reaction. Upon complexation **P11** displayed improved solubility relative to **P9** due to the disruption of that π stacking in the planar phenanthroline units. The proton NMR spectrum is more complex and shifted to higher field relative to the uncoordinated polymer (Fig. 3.12). This is due to the paramagnetic nature of the europium. ICP results indicate that only 1 in 12 units are coordinated to europium. Although this is lower than expected, energy transfer from the polymer to the europium should occur resulting in the desired red device.

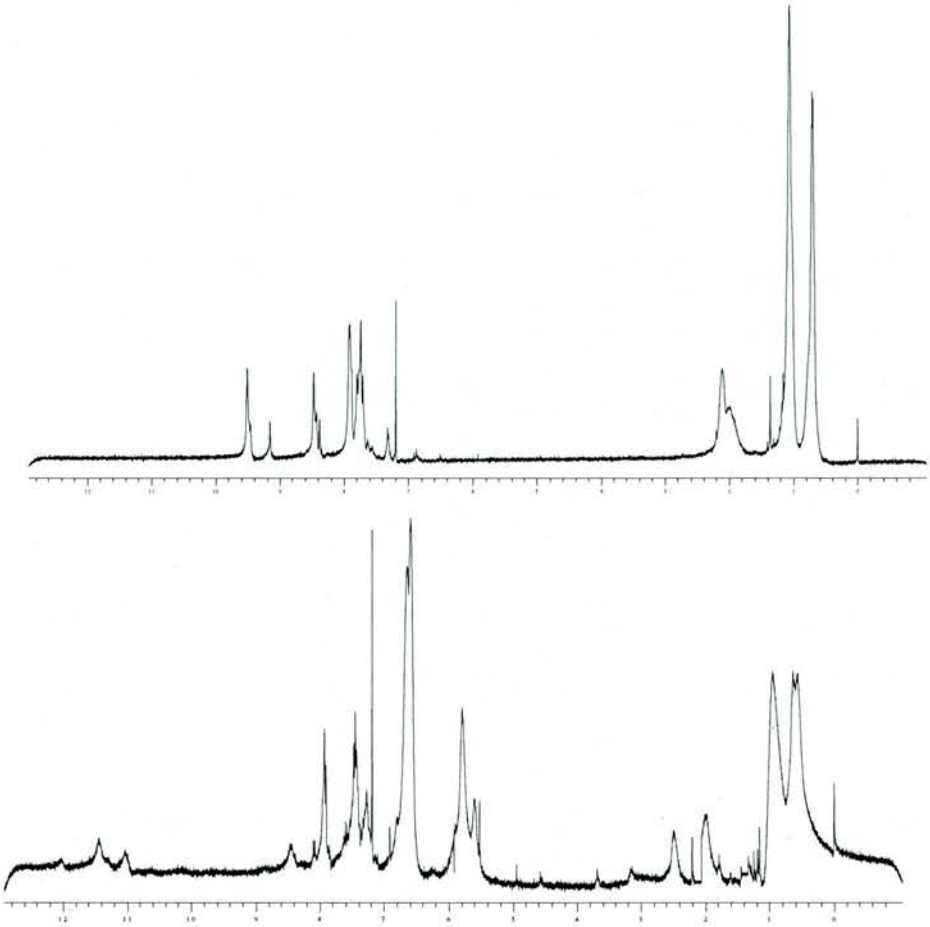


Figure 3.12: Proton NMR spectra of ***P9*** *(top) and* ***P12*** *(bottom)*

3.3.2 Optical Properties of Europium Bound Polymer P11

The absorption spectrum of **P11** was recorded in THF and displayed a maximum of 355 nm. This was found to be blue shifted relative to the uncomplexed polymer 375 nm. The photoluminescence spectrum recorded at a concentration of 0.005 mg/ml appeared to have an identical photoluminescence spectrum to the uncomplexed polymer on first inspection. However in addition to the blue emission a relatively small peak at 620 nm can be seen (Fig. 3.13).

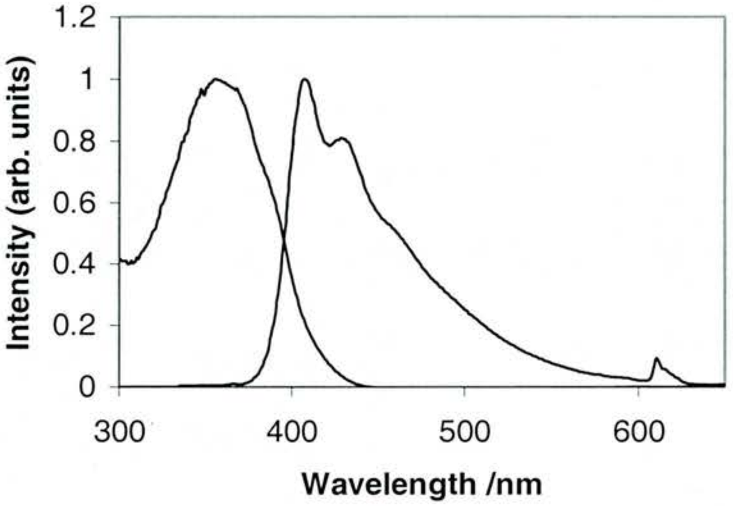


Figure 3.13: Absorption and photoluminescence spectra of a dilute solution of P11 in THF (λ_{Ex} = 335 nm)

Samples of **P11** prepared for NMR analysis were observed to fluoresce red light under a uv lamp therefore a study of the effect of concentration on the solution emission properties was carried out. Samples were prepared of 0.005, .0.01, 0.10 and 1.00 mg /ml of **P11** in THF, these were excited at 335 nm and the photoluminescence spectra recorded (Fig. 3.14). From this spectrum it would appear that the light was simply being quenched, however in Figure 3.15 the spectra have been normalised. It is clear from this graph that as the solutions become increasingly concentrated, the chains are closer, facilitating energy transfer from the polymer to the europium.

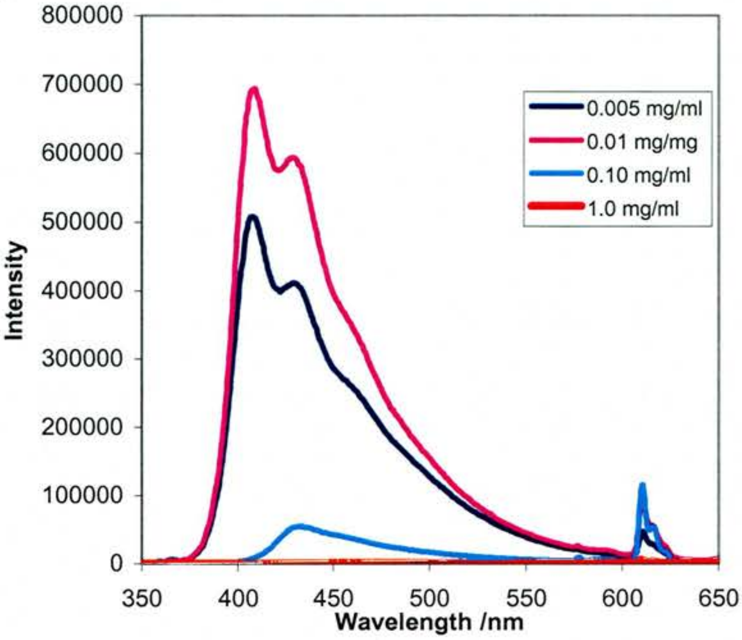


Figure 3.14: Photoluminescence spectra of P11 in THF (λ_{ex} = 335nm)

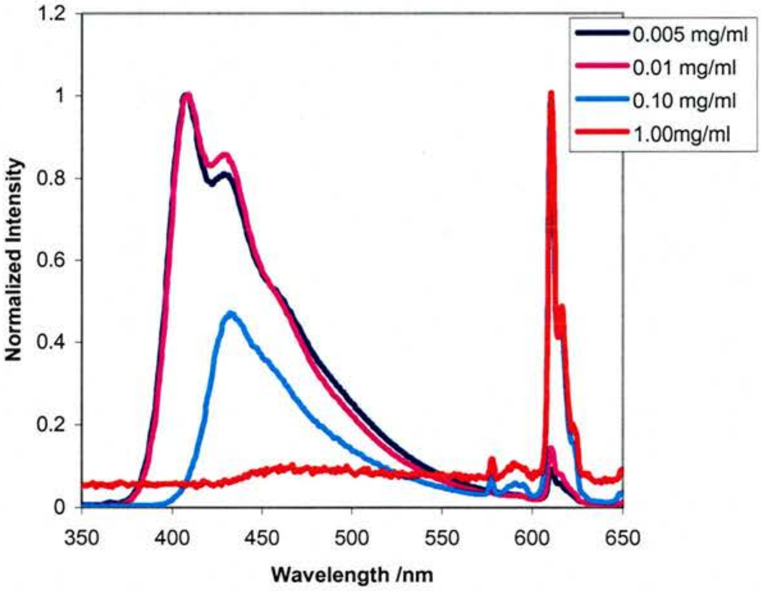


Figure 3.15: Normalised photoluminescence spectra of various concentrations of P11 in THF (λ_{ex} = 335nm)

The polymer was spin coated from a 20 mg/ml chloroform solution onto a glass substrate from which the thin film photoluminescence spectrum was recorded. This was very similar to the concentrated solution PL spectrum with a maximum emission at 612 nm.

Red europium emission displays a very sharp band in contrast to the broad polymer emission. This is in accordance with literature results, and is a result of the contracted nature of the europium's orbitals, which do not interact with the orbitals of the ligands. Energy transfer from the polymer to europium results in emission from discrete energy levels rather than a range of energy levels associated with polymer emission. As a result a characteristic emission pattern is observed with 3 peaks at 579, 592 and 612 nm. These peaks correspond to transitions in the europium atom's *f* orbitals (Figure 3.16).[11]

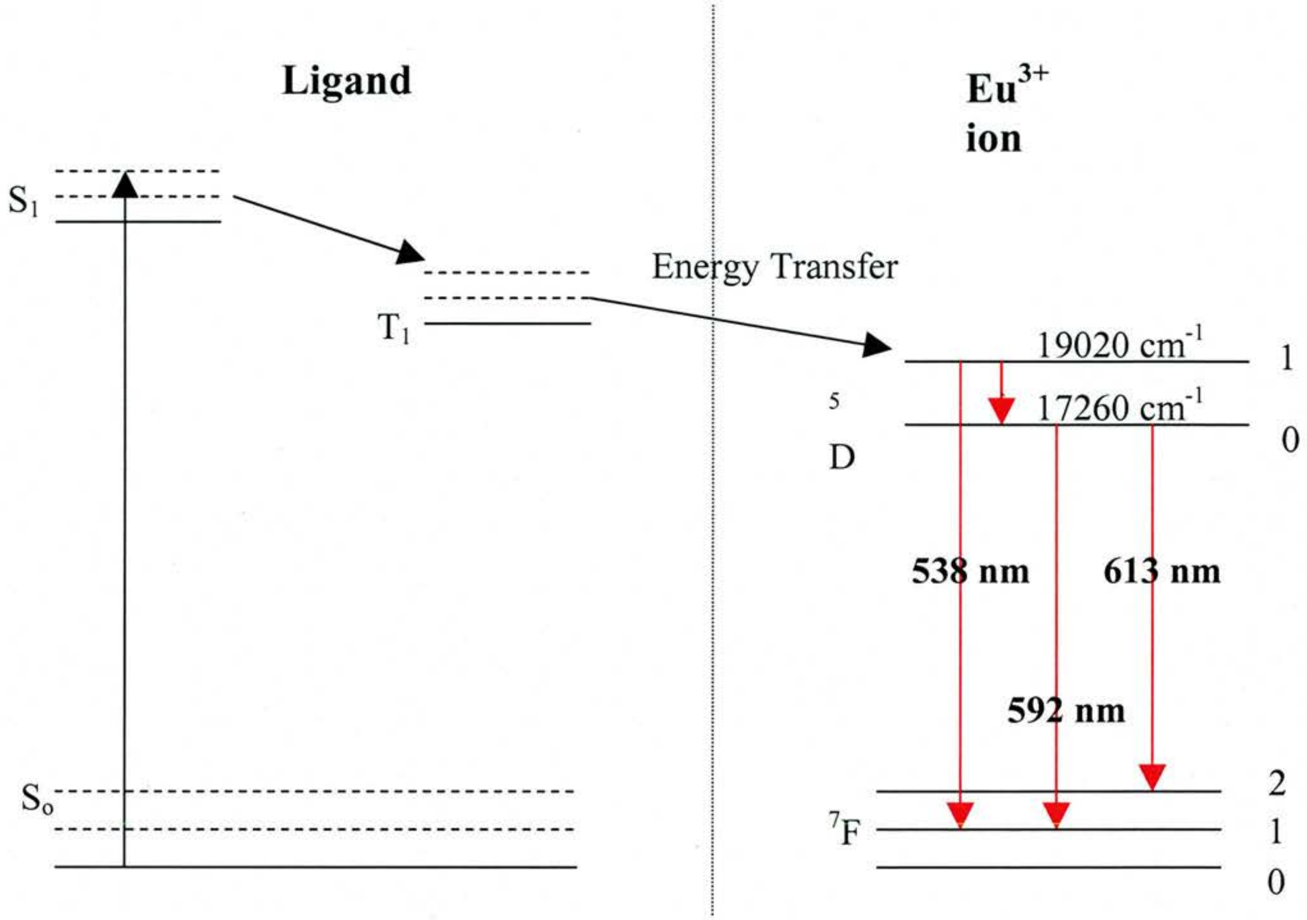
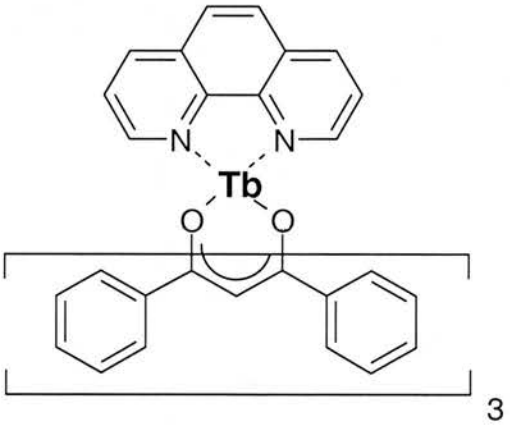


Figure 3.16: Selected energy levels in Eu^{3+} ion (^{5}D term also has J = 2, 3, 4 and ^{7}F also has J = 3, 4, 5, 6 omitted for clarity)

There is a very weak band at 580 nm due to the $^5D_o \rightarrow {}^7F_o$ transition (not shown in Figure 3.16) which is forbidden. The selection rules are ($\Delta S=0$, $\Delta L=0, \pm1$, $\Delta J=0, \pm1$ but $J=0 \;\leftarrow\!|\!\rightarrow\; J=0$).[12] Its appearance indicates that the europium complexed polymer is in a low symmetry environment.[13]

3.3.3 Synthesis of Terbium Polymer with Dibenzoylmethane Ligands

We also attempted to coordinate a terbium complex to the polymer using the same method as used to coordinate the europium. This was attempted twice on two different polymer batches, as it was not clear if the terbium had in fact coordinated to the polymer chain in the first reaction. In addition, the molecular terbium complex tris(acetylacetonato)(1,10-phenanthroline)terbiuim(III) **50** was prepared as an aid to interpreting the polymer's NMR analysis since this information could not be obtained from the literature. Unfortunately, the terbium complex proved to be so paramagnetic that useful NMR data could not be obtained. This is due to terbium (III) (f^8) ground term $^7F_6$ having a greater μ_{eff} ($\approx$ 9.3) than europium (III) (f^6) ground term $^7F_0$ (with $\mu_{eff} \approx 3.4$).[14]



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The first coordination reaction resulted in a low molecular weight polymer **P12a** a terbium atom for every 20 polymer repeat units. Unlike the europium bound polymer, which showed increased solubility relative to the uncoordinated polymer, this terbium polymer was insoluble in THF. This is surprising considering the low coordination of the terbium. One explanation for this anomaly is that several polymer chains have been cross linked through the terbium atom. In the second reaction a polymer **P12b** with improved solubility relative to the original polymer was produced. The molecular weight measurements are reported here although there is cause for concern over the accuracy of these figures. The molecular weights were recorded in THF with the exception of **P9b,** which, due to its insolubility in THF, was recorded in chloroform. Surprisingly, **P12b** has a lower molecular weight, which could be accounted for by cleavage of the polymer during the coordination reaction. Alternatively, **P9b** could be measured with a larger molecular weight than is correct due to the polymers aggregating during the analysis caused by their extreme insolubility.

Table 3.6: Molecular Weights of Terbium Polymers

Polymer	Mn	Mw	P.D
P9a	4700	8200	1.739
P12a	-	-	-
P9b[a]	6600	21700	3.3
P12b	4100	5700	1.403

[a] – *Molecular weight measured in chloroform due to insolubility in THF*

3.3.4 Optical Properties of Terbium Polymer With Dibenzoylmethane Ligands

The absorption and emission spectra for the first terbium polymer **P12a** are shown in Figure 3.17.

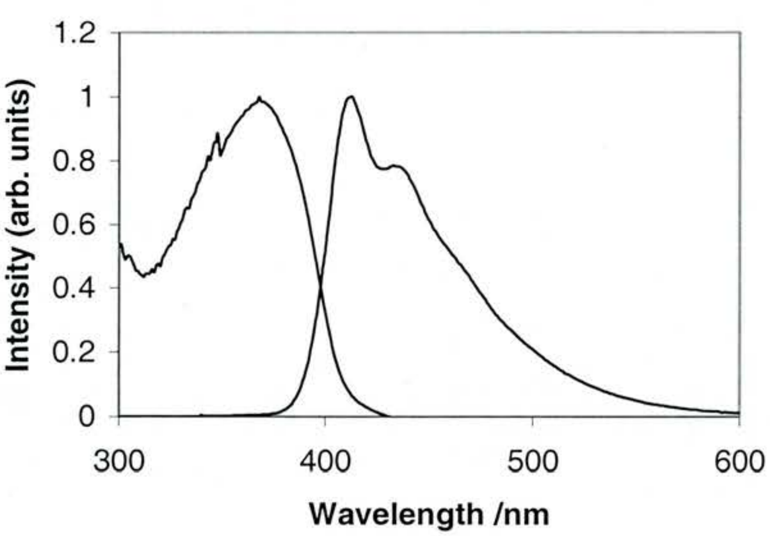


Figure 3.17: Absorption and photoluminescence spectra of a dilute solution of P12 in THF (λ_{Ex} = 335 nm)

The absorption spectrum is slightly shifted to shorter wavelength relative to the uncoordinated polymer. The emission spectrum is blue in dilute solution in agreement with the europium bound polymer. If the concentration is increased, a peak in the green region of the spectrum emerges. However, this peak is extremely broad and is not the set of sharp emission peaks characteristic of terbium emission. The second terbium polymer **P12b** also showed a broad green emission.

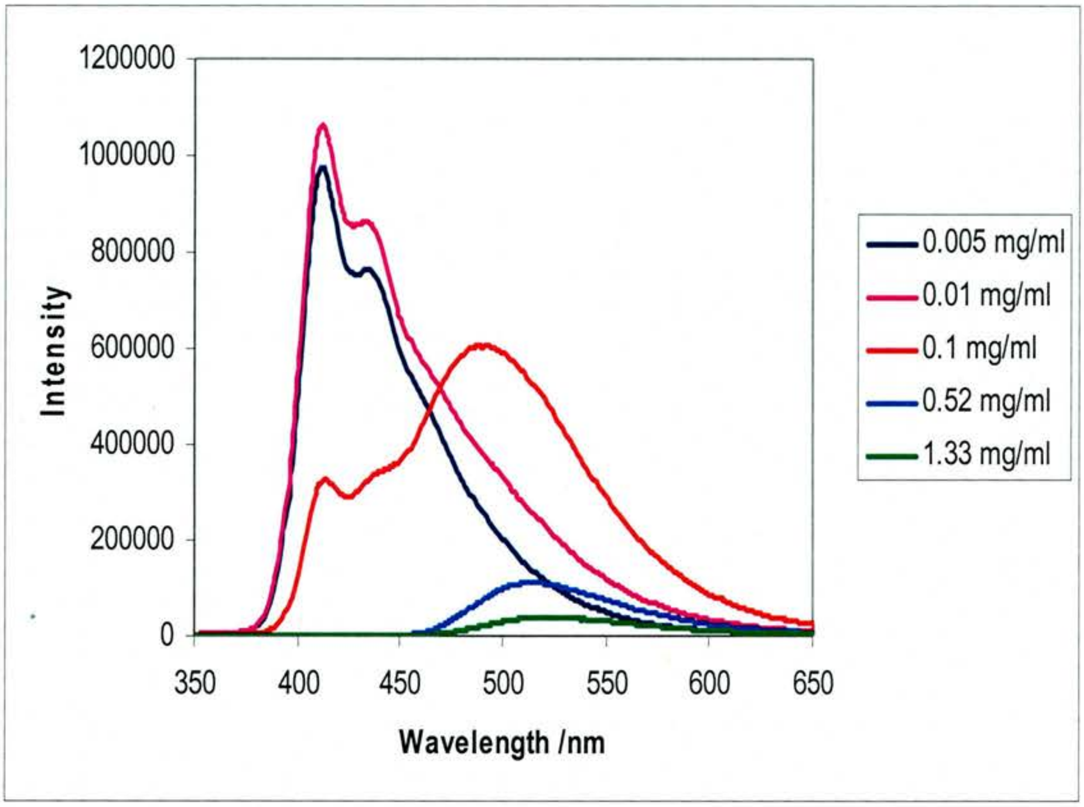


Figure 3.18: Photoluminescence spectra of P12 at various concentrations in THF (λ_{Ex} = 335 nm)

Thin films of the terbium coordinated polymers also give broad green emission similar to the concentrated solution spectra and are not characteristic of terbium emission. There are a few possible explanations for this phenomenon; firstly the green peak could be caused by an excimer or aggregate effect, the lowest unoccupied energy level in the terbium could be too high for the energy to be transferred from the polymer to this energy level in the terbium and the terbium could be uncoordinated and is simply altering the energy levels in the polymer in the same way as lanthanum described in section 3.2.3. Whilst excimers or aggregates do not cause a loss in emission intensity, the partial quenching observed in this instance could be due to self absorption effects, as the solutions in which the green emission is observed are very concentrated relative to the concentrations at which photoluminescence spectra are normally recorded.

3.3.5 Synthesis of Terbium Polymer with Acetylacetonate Ligands

Further literature investigation revealed that unlike europium, dibenzoylmethane ligands do not facilitate energy transfer from the dibenzoylmethane to the terbium highlighted by the energy level diagram in Figure 3.19.[15]

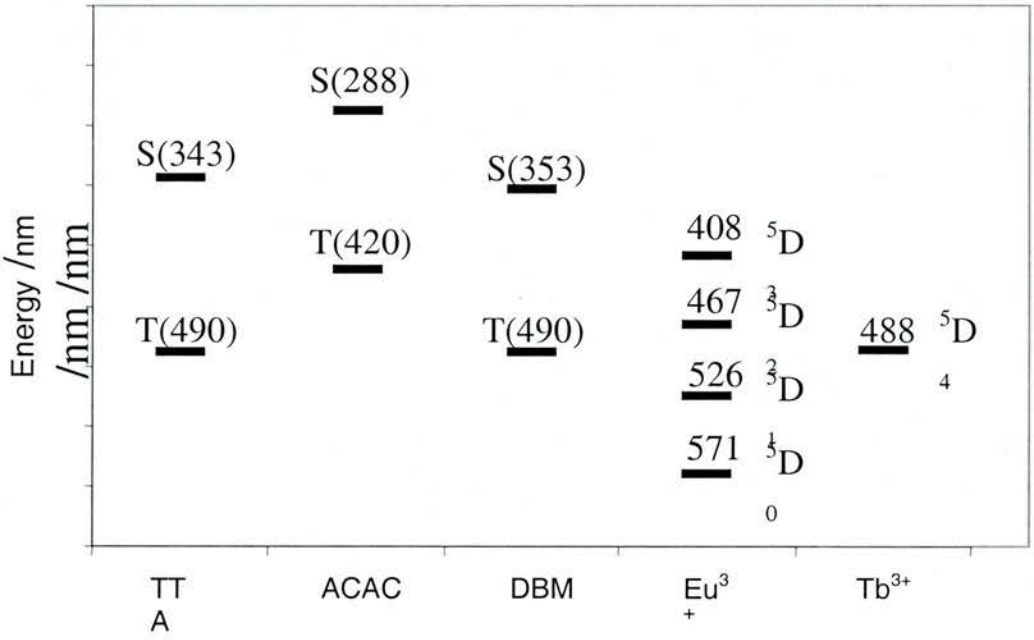
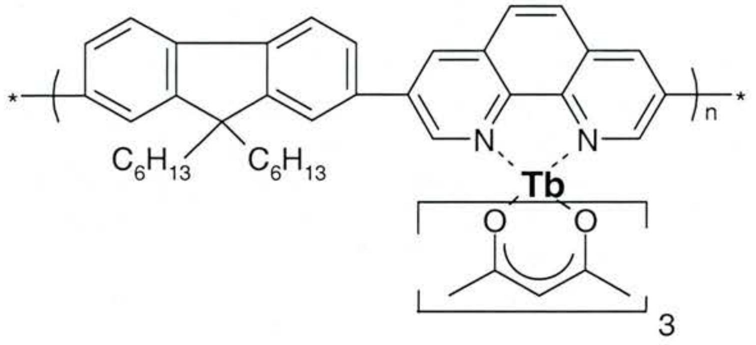


Figure 3.19: Energy levels for Eu and Tb and selected ligands (TTA – tristrifluoro thienyl butanedionato, ACAC – acetylacetonate, DBM – dibenzoylmethane)

Acetyl acetonate (acac), a very similar chelating ligand to dibenzoylmethane in terms of binding capability, has appropriate energy levels to the terbium which allows energy transfer. The terbium polymer **P13** was synthesized by the same method as **P12**. The terbium molecular complex was also synthesized as a reference.



P13

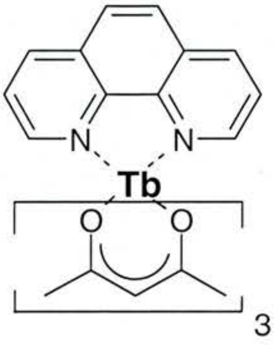


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Table 3.7: Molecular weights of **P9b** and **P13**

Polymer	Mn	Mw	PD
P9b	6600	21700	3.3
P13	9700	26100	2.648

3.3.6 Optical Properties of Terbium Polymer With Acetylacetonate Ligands

In accordance with the literature our prepared molecular terbium complex **51** emitted green light in the characteristic terbium emission with peaks at 491, 548, 582 and 622 nm which correspond to $^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_4$ and $^5D_4 \rightarrow {}^7F_3$ transitions respectively. The solution absorption and emission spectra of the terbium bound polymer are given in Figure 3.20 and shows the blue light emission from the polymer itself. Unfortunately no green terbium emission was observed at either higher concentrations in solution or in thin films of the polymer. Both solution and thin film were excited at higher energy excitation wavelength of 270 nm and again no terbium emission was observed.

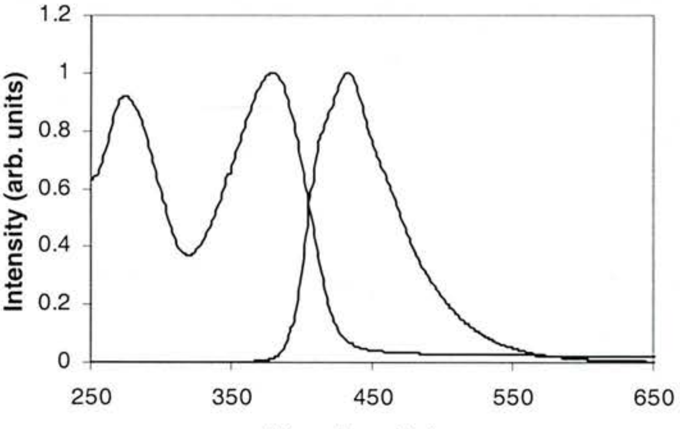
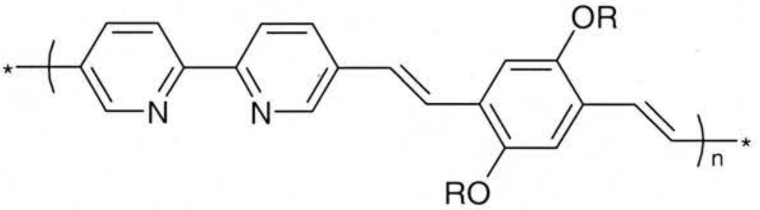


Figure 3.20: Photoluminescence spectra of ***P13*** *in THF (λ_{Ex} = 335 nm)*

Lanthanides such as europium chloride have been coordinated to a bipyridine conjugated polymer **52** the emission characteristics of which can be altered upon the addition of small quantities of methanol. Initially the photoluminescence is quenched by the methanol and eventually the original polymer luminescence is observed. There are two possible explanations for this phenomenon. In the first place methanol binds to the lanthanide on the polymer and alters the rate of energy transfer from the polymer to the lanthanide. Alternatively methanol is an excellent ligand for the lanthanide and causes the lanthanide to dissociate from the polymer.[16]



52

Polymers in this study were precipitated into methanol after the coordination of the lanthanide ions. This was not observed to be detrimental to the europium, however to confirm that the precipitation into methanol was not the cause of the poor optical properties of the terbium, the synthesis of **P13** was repeated. Terbium chloride was added to the reaction mixture dissolved in water and the polymer was precipitated into hexane at the end of the reaction. No improvement in the emission properties was observed using this method of synthesis and is probably due to the bidentate ligands phenanthroline and acetylacetonate having stronger binding capabilities than chlorine or methanol.

3.4 Conclusions / Future work

A conjugated polymer has been synthesised containing a phenanthroline moiety that is capable of coordinating to metal ions. Coordination of metal ions to the polymer induces a shift or quenching of the emission in the photoluminescence spectra. This highly sensitive ionochromic effect would make this polymer a useful metal ion detector.

A red light emitting polymer was obtained by coordination of europium to the polymer, demonstrating the colour tuning capability of the phenanthroline containing polymer. Unfortunately, difficulties were encountered in the preparation of a green light emitting polymer. This is most likely due to inefficient intramolecular energy transfer from the triplet state of the ligand to the $^5D_4$ energy level of terbium. Further investigation is required in order to overcome this problem. A solution could be to attach different ligands to the terbium, use a polymer with a different chelating repeat unit or by using a different green emitting metal such as iridium. The aim of these changes would be to obtain better matched ligand to terbium energy levels facilitating energy transfer.

3.5 Experimental

All starting materials were obtained from Aldrich or Lancaster, were reagent grade and used without further drying or purification except where stated otherwise. Tetrahydrofuran was distilled over sodium and benzophenone under an inert atmosphere.

^1H and ^{13}C NMR spectra were recorded on a Bruker Av-300 in deuterated chloroform solutions, operating at 299.998 MHz for ^1H and 75.45 MHz for ^{13}C. Infra-red spectra were recorded as KBr discs or as thin films of neat polymer on NaCl plates, on either a Perkin Elmer Paragon 1000 or a Nicolet Avatar 360 FTIR spectrometer.

Molecular weights were recorded on a Polymer Laboratories Gel Permeation Chromatography 120 Integrated GPC system with Polymer Laboratories gel 5 μm mixed column relative to polystyrene standards.

Absorption Spectra were recorded either in THF or as a thin film on a quartz substrate using a Varian Cary 300 Bio uv-vis machine. Photoluminescence spectra were recorded either as a dilute solution in THF or as a thin film on quartz substrates with a Fluoromax 2 from the Honba Group.

Tb(dbm)$_3$(phen) 50

1,10-phenanthroline (0.1642 g, 0.911 mmol) and dibenzoylmethane (0.6163 g, 2.75 mmol) were dissolved in 10 ml of ethanol and 3 ml of 1M sodium hydroxide solution. The mixture was then heated to 60–70 °C, terbium chloride hexahydrate (0.3402 g, 0.911 mmol) in 5 ml of water was added dropwise and a yellow precipitate formed. Once cool the remaining solvent was removed under reduced pressure and the crude product was washed with methanol. A green powder was obtained (0.8051 g. 87.3%)

No useful NMR data could be obtained due to the strong *para* magnetism exerted by terbium.

IR 1595, 1550, 1517, 1309, 1220, 1067, 1023, 841, 722 cm^{-1}

λ_{max} (CHCl$_3$) 256, 348 nm

Tb(acac)$_3$(phen) 51

1,10-phenanthroline (0.14 g, 0.777 mmol) and 2,4-pentandione (0.24 g, 2.400 mmol) were dissolved in 10 ml of ethanol. Terbium chloride hexahydrate (0.30 g, 0.803 mmol) in 5 ml of water was added followed by 3 ml of sodium hydroxide solution dropwise. A white precipitate formed. The mixture was heated to 65 °C for 5 h. Once cool the remaining solvent was removed under reduced pressure and the crude product was washed with methanol and water. A white powder was obtained (0.32 g. 64.4%)

No useful NMR data could be obtained due to the strong paramagnetism exerted by terbium.

IR 1597, 1521, 1260, 1016, 918, 759 cm^{-1}

λ_{max} ($CHCl_3$) 229, 266 nm λ_{em} 491, 548, 582 and 622 nm

Terbium Coordinated Polymer (DBM) P12

P9b (0.1049 g, 0.205 mmol) and dibenzoylmethane (0.1390 g, 0.620 mmol) were dissolved in dry THF to which triethylamine was added. Terbium trichloride hexahydrate (0.077 g, 0.205 mmol) in 3 ml of methanol was added and the mixture heated to 50 °C for 5 h. Once cool the solvent was removed under reduced pressure and the crude product was washed with methanol. An orange powder was obtained (0.28 g, 101.6 %).

Mn = 4074 Mw = 5717 PD = 1.403

No useful NMR data could be obtained owing to the paramagnetic nature of the polymer.

IR 1594, 1548, 1516, 1307, 1220, 1066, 1023, 721 cm^{-1}

λ_{max} ($CHCl_3$) 247, 348 nm

Terbium Coordinated Polymer (acac) P13

The same method was used as given above substituting the dibenzoylmethane for 2,4-pentandione

(0.1675 g, 85.9%)

Mn = 9738 Mw = 26140 PD = 2.684

^{1}H NMR δ (ppm) 8.5 (s), 7.4 (s), 6.9 (s), 6.7 (s), 6.2 (s), 1.0 (s), 0.4 (br s), 0.0 (s), -0.4 (s).

IR 1591, 1517, 1018, 920, 825, 728 cm^{-1}

λ_{max} ($CHCl_3$) 273, 377 nm

3.5 References

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Chapter 4

Covalent Attachment of Aluminium Complexes to Polyfluorene Copolymers

4.1 Introduction

In recent years a significant amount of research into doping light emitting polymers with various different metal complexes has been carried out.[1] The doping of polymers with metal complexes has revealed that the properties and efficiencies of these polymers can be significantly improved. For example, doping with iridium complexes has been shown to harvest triplet as well as singlet excited states as iridium is phosphorescent and therefore the external quantum efficiency could theoretically be improved by as much as a factor of 4.[2]

Doping alone does have some drawbacks including poor stability and problems of phase separation of the individual components of the device. The obvious alternative, the covalent incorporation of metal complexes onto the polymer has been largely unexplored. It was therefore considered worthwhile to investigate incorporating metal complexes and not metal ions along the main backbone of the polymer or as pendant groups.

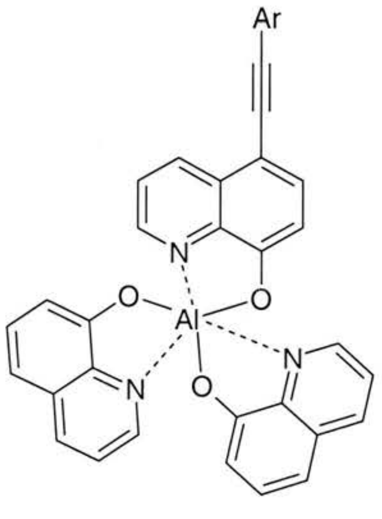
The prime candidate metal complex that we targeted for incorporation was aluminium trisquinolate (Alq_3) **2**. Alq_3 was the first organic small molecule discovered[3] with potential for use in organic light emitting diodes and is still currently used as a light emitting layer or even an electron transporting layer.[4]

Aluminium trisquinolate is relatively insoluble in common organic solvents so it is unfeasible to use solution processing techniques such as spin coating to prepare devices from Alq_3. Since the aluminium 3+ ion is surrounded by 3 bidentate quinolate anions, the net charge of the complex is zero with all of the aluminiums coordination sites filled. This means that Alq_3 can be sublimed at approximately 350 ^{o}C without decomposition.[5] Light emitting diodes can therefore be prepared from Alq_3 using vacuum deposition. Mer and fac geometrical isomers are always present and these are not generally separated when fabricating devices.

The absorption spectrum of Alq_3 consists of two strong bands at 260 and 385 nm and a number of smaller, weaker absorption peaks.[6] The dominant absorption bands have been attributed to ligand centred electronic transitions with the bands at 260 nm and 385 nm being assigned to the ^1B_b and ^1L_a electronic transitions bands respectively.[7]

The photoluminescence emission spectrum is a broad, structureless band with a maximum of approximately 520 nm, therefore Alq_3 emits green light. The first electroluminescent device reported by Tang and VanSlyke emitted light at 550 nm with an external quantum efficiency of approximately 1 %.[3]

Aluminium trisquinolate has been the subject of a vast amount of research and numerous scientific papers have been published. Several groups have focussed their research onto modifying the properties of this material and have demonstrated that the colour of emission can be tuned. For example the emission colour of **53** is controlled by the nature of the aromatic substiutent. With an electron deficient species such as 4,6-dimethoxy-1,3,5-triazine **53a** the photoluminescence emission maximum is 520 nm. The emission maximum is hypsochromically shifted with more electron donating moieties dimethylamine benzene **53b** for example has an emission maximum of 600 nm.[8]



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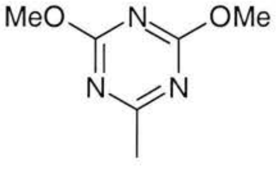
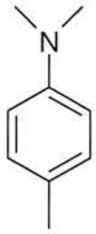
Ar =



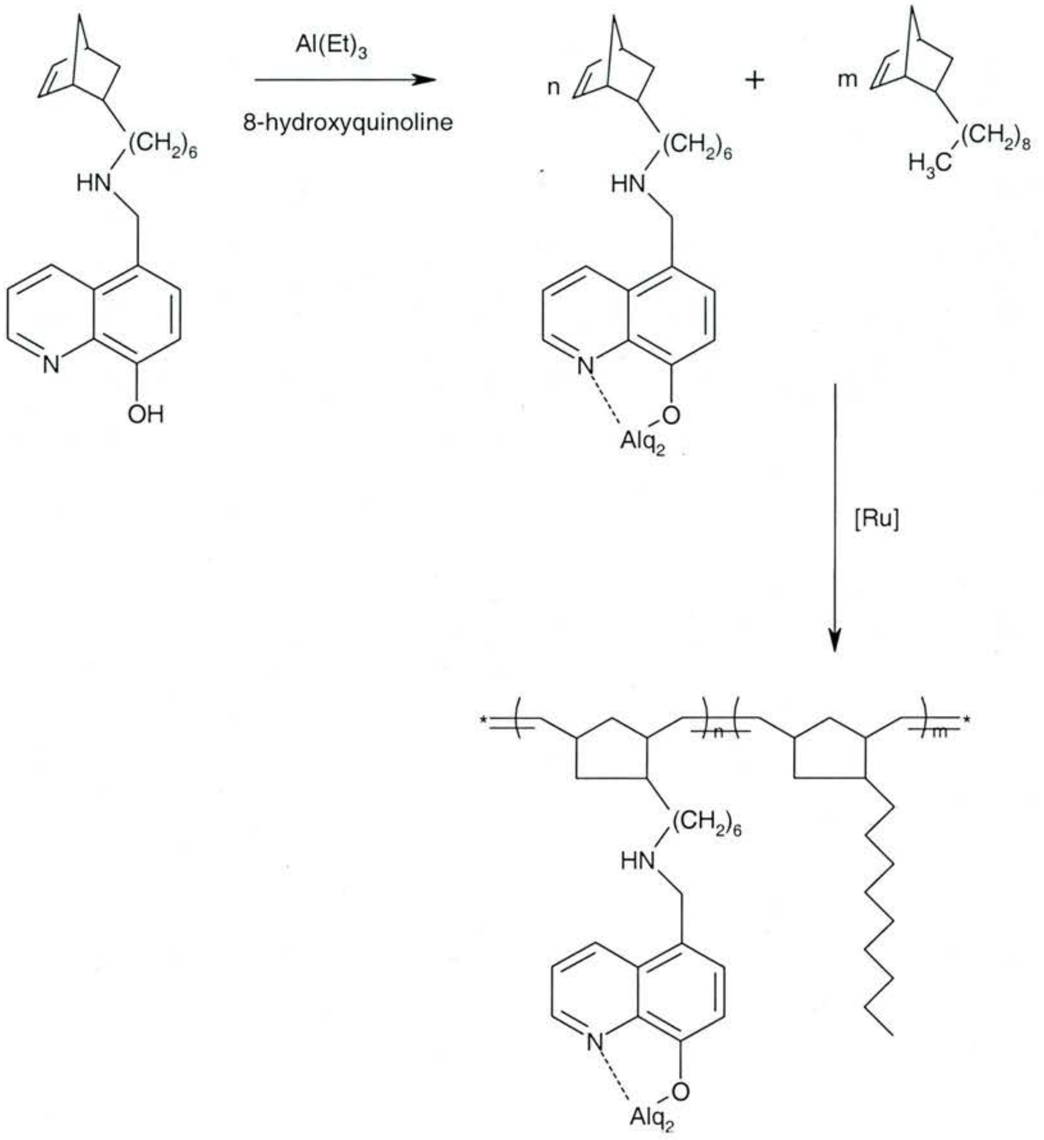
a



b

An aluminium coordinated polymer was first prepared by Hay et al., in 2000. This was achieved by coordinating the aluminium complex as a pendant group to a poly(arylene ether).[9] Work was ongoing to determine the feasibility of using this material for use in an OLED.

A soluble aluminium complexed polymer has recently been prepared by M Weck et al.[10] Quinolate pendant groups were attached to an amino-norbornene derivative to which the aluminium was then coordinated. This is then polymerised by ring opening metathesis polymerisation which can tolerate a variety of functional groups.



54

Scheme 4.1: ROMP synthesis of Alq functionalised polymer

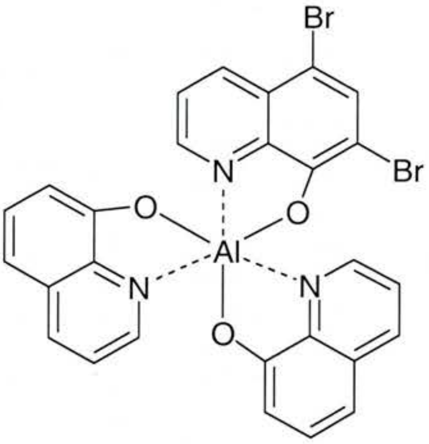
Unfortunately, the initial polymer **54** was insoluble. The solubility was improved on synthesizing a block copolymer with additional long alkyl chains; however, the polymer itself and the solubilising alkyl chains are non-conjugated, and therefore the charge transport properties of this polymer are likely to be comparatively poor. The authors did not comment on this and no devices were prepared from this material.

It was therefore undertaken in this project to prepare a solution processable Alq_3 derivative utilising a conjugated polyfluorene backbone, which should prove to have superior charge-transport properties to the poly(ether) and poly(norbornene).

4.2 Results and Discussion

4.2.1 Coordination Through Hydroxyquinolate Ligand

Several different strategies to incorporate the aluminium quinolate onto the polymer backbone were considered. One concern was the possibility that the polymer chains would be cross-linked through the aluminium complex. The first strategy, therefore, was to synthesize a heteroleptic aluminium complex **55**.



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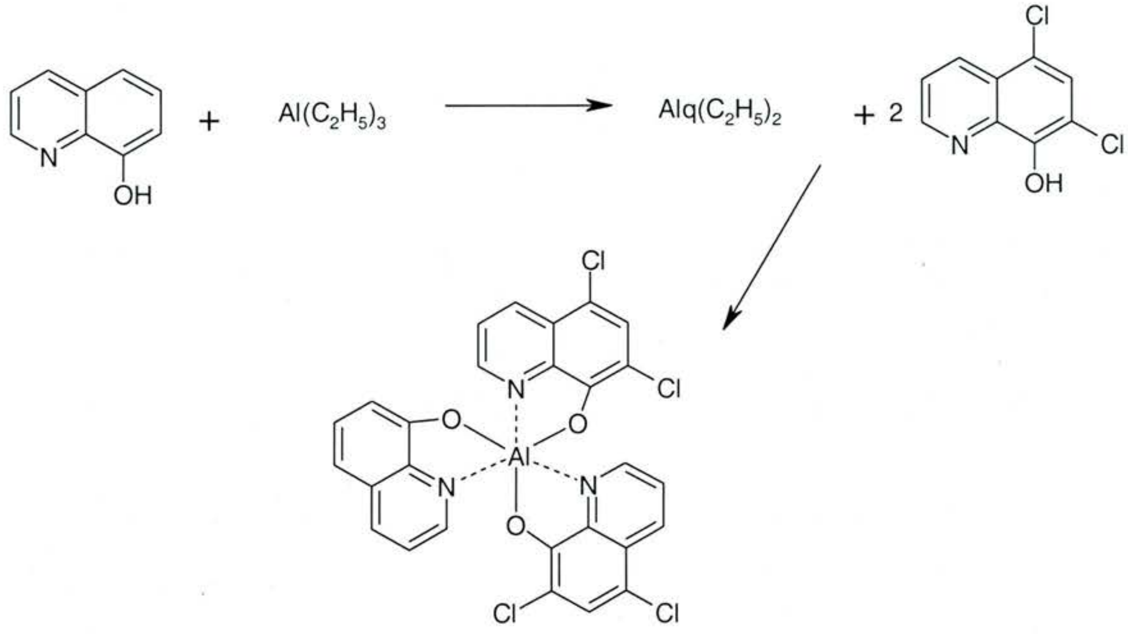
It was proposed to alter a procedure by Do et al in which a heteroleptic aluminium complex with one hydroxyquinoline and two chlorinated hydroxyquinolines was formed.[11]

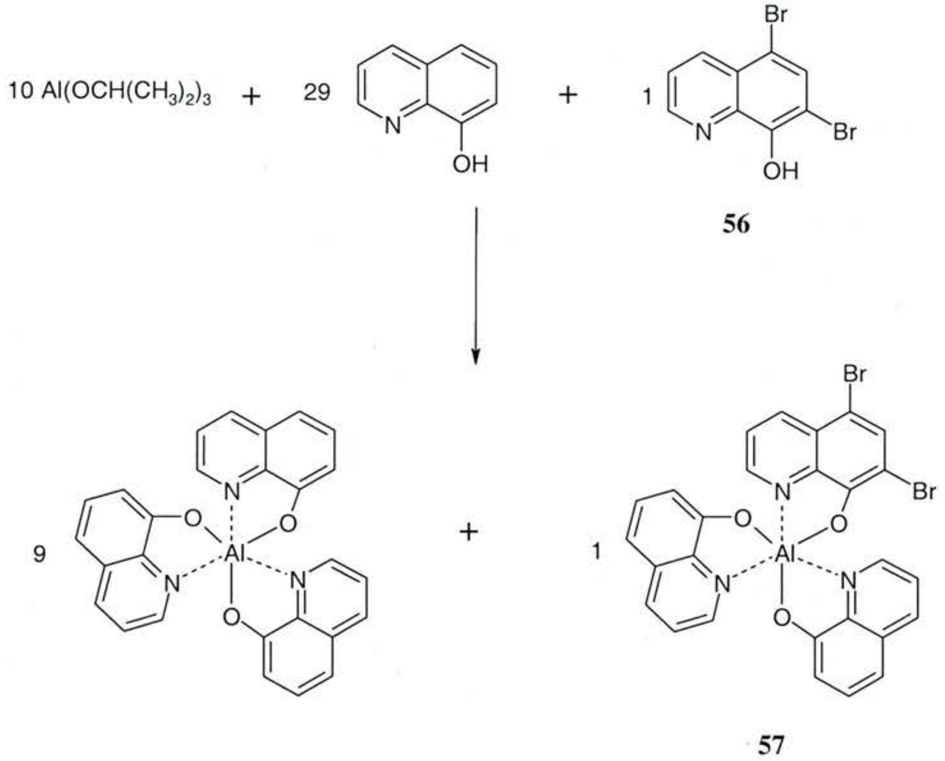


Scheme 4.2: Synthesis of AlqClq$_2$

One difficulty associated with this strategy is that if two equivalents of the dibrominated quinolate are used then cross-linking of the polymer chains through the complex could ensue. Therefore, the procedure was altered to prepare first the brominated AlBrq$(OCH(CH_3)_2)_2$ which would then be reacted with two equivalents of 8-hydroxyquinoline. Unfortunately, the dibrominated hydroxyquinoline proved considerably less soluble than the 8-hydroxyquinoline and concerns over the formation of complexes with two or more functionalised quinolines led us to abandon this approach.

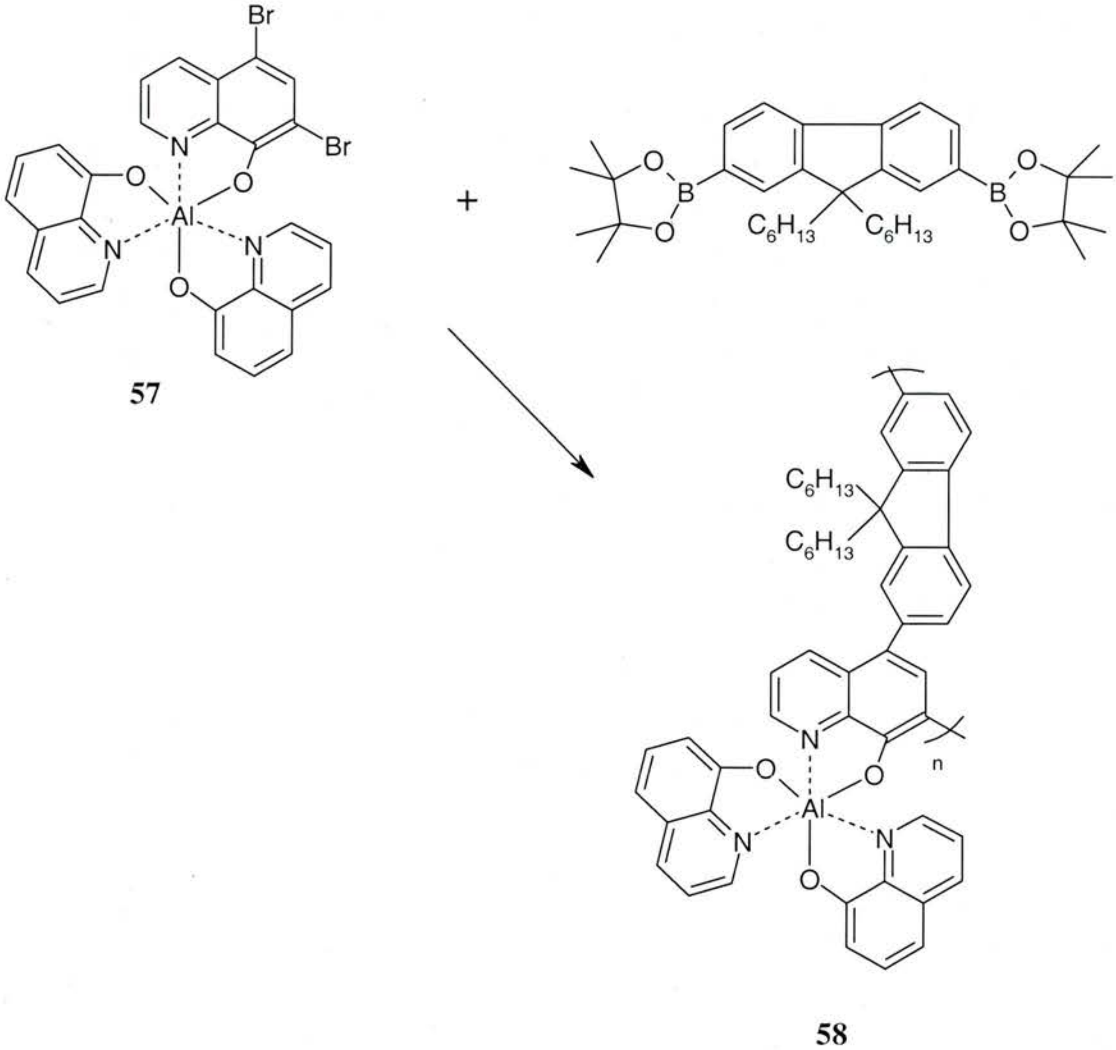
The paper by Weck et al reported the synthesis of an aluminium complex with a 20:1 ratio of non-functionalised ligand to functionalised ligand they were able to reduce the odds of a complex containing two functionalised ligands to less than 0.1% and indeed they observed no cross linking in their polymerisation.

This strategy to form 9 equivalents of Alq_3 and 1 equivalent of Alq_2Brq **57** was adopted in the work outlined in this chapter.



*Scheme 4. 3: Synthesis of Alq_2Brq **57***

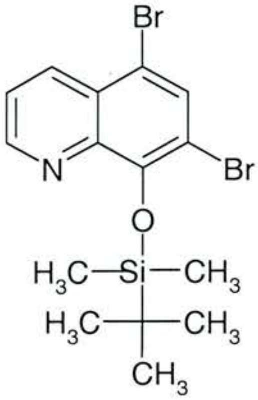
The polymerisation was carried out with both aluminium complexes present as they would be difficult to separate and only the bromine containing complex should be capable of reacting in the polymerisation (Scheme 4.4). The precipitate obtained emitted light at 516 nm. However there was inconclusive proof that an oligomer had been obtained and the precipitate may simply be a mixture of starting materials. This is likely to be due to the insolubility of the aluminium complex in toluene. The absorption spectrum of this precipitate shows two bands at approximately 262 and 388 nm which is consistent with the absorption spectrum of aluminium trisquinolate.



*Scheme 4.4: Attempted polymerisation of Alq$_2$Brq **57** to form oligomer **58***

When the polymerisation is carried out in THF the reaction mixture is no longer biphasic and the complexes appear to dissolve. However, no polymers are formed, which could be a result of the base destroying the Al complex comonomer Alq_2Brq **57**.

A second synthetic strategy was to use the dibrominated quinoline as a monomer **56**. Then the polymer is reacted with aluminium isopropoxide and 8-hydroxyquinoline to form the functionalised polymer. Unfortunately, this too was not successful, and this could have been due to a number of reasons. Firstly, the dibromo monomer **56** seemed to be soluble in the aqueous layer of the polymerisation reaction and is therefore in a different phase from the fluorene monomer, preventing polymerisation. Secondly, the quinolate is a bidentate ligand and is therefore capable of binding to the palladium metal catalyst which could also be detrimental to the polymerisation reaction. To overcome these problems the OH group was protected with a *t*-butyldimethylsilane protecting group which made the quinoline soluble in the organic layer. It was also hoped that the bulky protecting group would prevent the catalyst from coordinating to the monomer.



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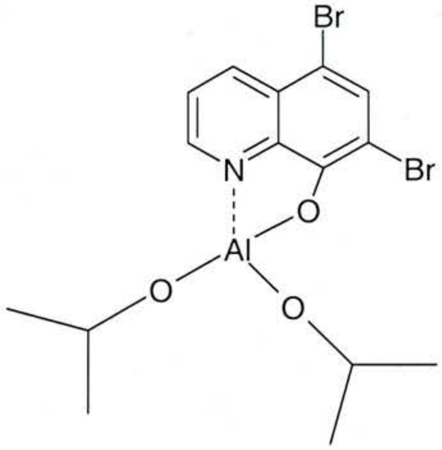
Again, however, no polymer was formed and this was attributed to electronic factors. The Suzuki coupling reaction proceeds faster if electron withdrawing groups are attached to the dibrominated monomer.[12]

It was then attempted to reverse the monomer functionality by attaching boronic ester groups onto the quinoline and coupling this to dibromofluorene. Great difficulties were encountered on trying to form the diboronic ester quinolate and the reaction conditions were varied including choice of base and reaction temperature. From proton NMR it was found that the quinolate could indeed by debrominated using t-BuLi but the diboronic ester could not be isolated.

It was then attempted to synthesize the mono quinolate aluminium complex **60**. It was hoped that **60** would be soluble and that the isopropoxide groups could later be replaced with quinoline groups. However, the crude product obtained proved to be extremely insoluble. A test reaction was carried out with the non-brominated quinolate, however no evidence of the isopropoxide group was evident in the NMR of the precipitate suggesting that the main product formed is aluminium trisquinolate and not **60**.



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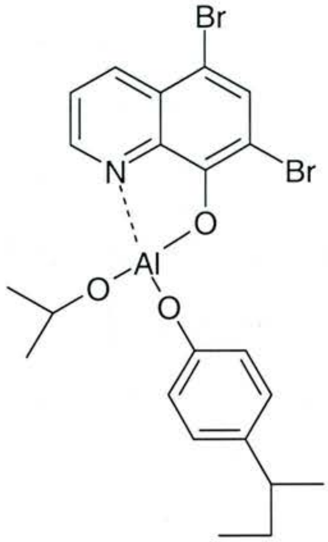
Attempts were also made to prepare a 4-coordinate heteroleptic aluminium complex **61** that would have greater solubility than the aluminium trisquinolate. A modified procedure outlined by Wang et al., was adopted.[13]



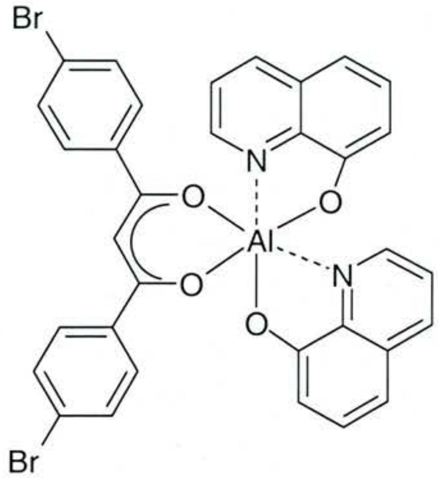
61

Unfortunately, the product **61** could not be isolated from the reaction. This is likely to be due to the insolubility of the brominated quinolate. A precipitate forms during the reaction after the quinolate is added and therefore the product is not in solution to react with the phenol, which is added second. The reaction was also attempted in reverse whereby the phenol was added first with warming. Unfortunately, this did not yield the desired product. A possible explanation for this lies in the fact that we are attempting to replace an Al - O bond with an Al – O bond. In the reaction outlined by Wang the starting material is triethyl aluminium and therefore they are substituting a much weaker Al - C bond with an Al - O bond. It was therefore established that it would be extremely difficult to have three quinolates coordinated to the aluminium.

4.2.2 Coordination Through AcetylAcetonate (acac) Ligand

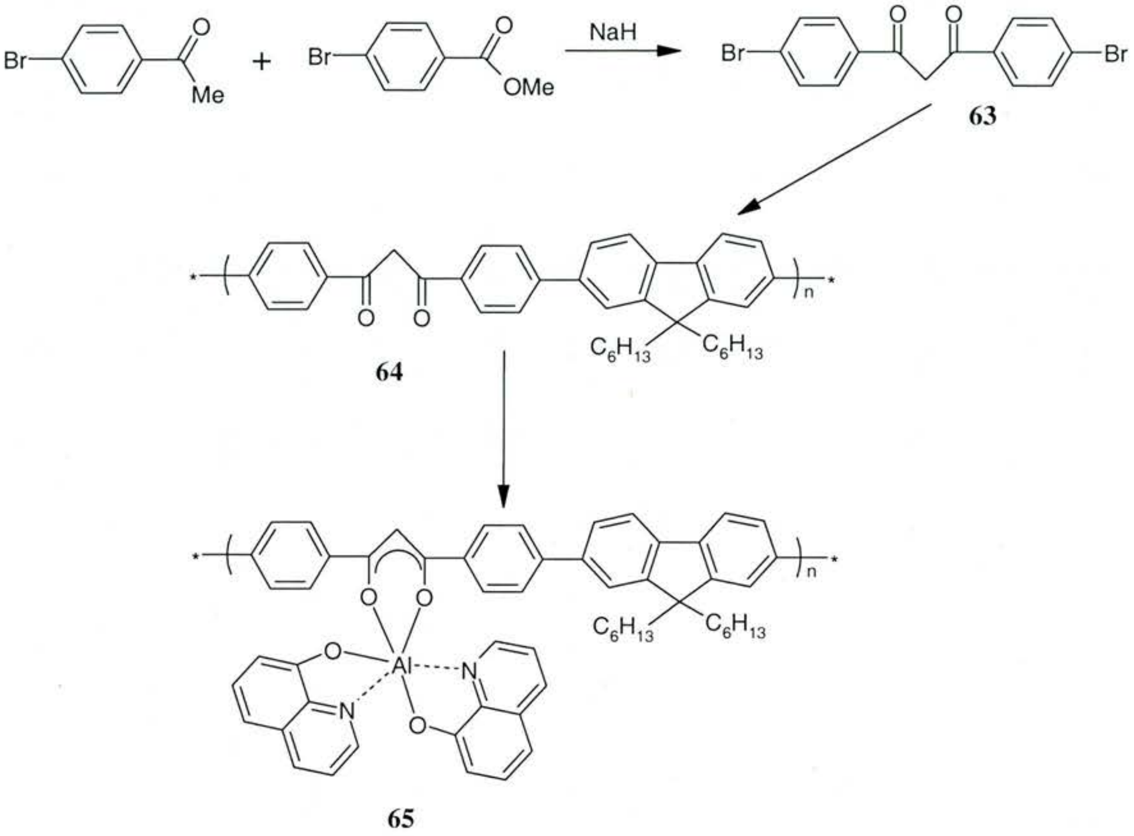
Having unsuccessfully explored many ways of attaching the aluminium complex to the polymer through the hydroxyquinoline moiety our attention turned to an acetyl acetonate (acac) type of ligand. Fluorescence is subject to the lowest energy gap and therefore attaching one or two ligands of higher energy than the hydroxyquinoline will not adversely effect the wavelength of light emitted. Acac is known to bind strongly to aluminium and test reactions confirmed that aluminium binds to two quinolates and one acac regardless of the molar ratios used in the reaction. Attempts to substitute the acac ligand in this complex with the dibrominated quinolate failed presumably because aluminium is a class A metal and therefore binds strongly to the oxygens of the acac. It was therefore anticipated that the acac ligand could be incorporated into the polymer to facilitate the addition of the aluminium and also help to prevent cross-linking since each aluminium would only coordinate to one acac.

Two strategies of using the acac were then considered: the synthesis of **62** which could then be polymerised, or the synthesis of the dibrominated acac ligand **63**, which would be polymerised and then complexed to the aluminium (Scheme 4.5).



62

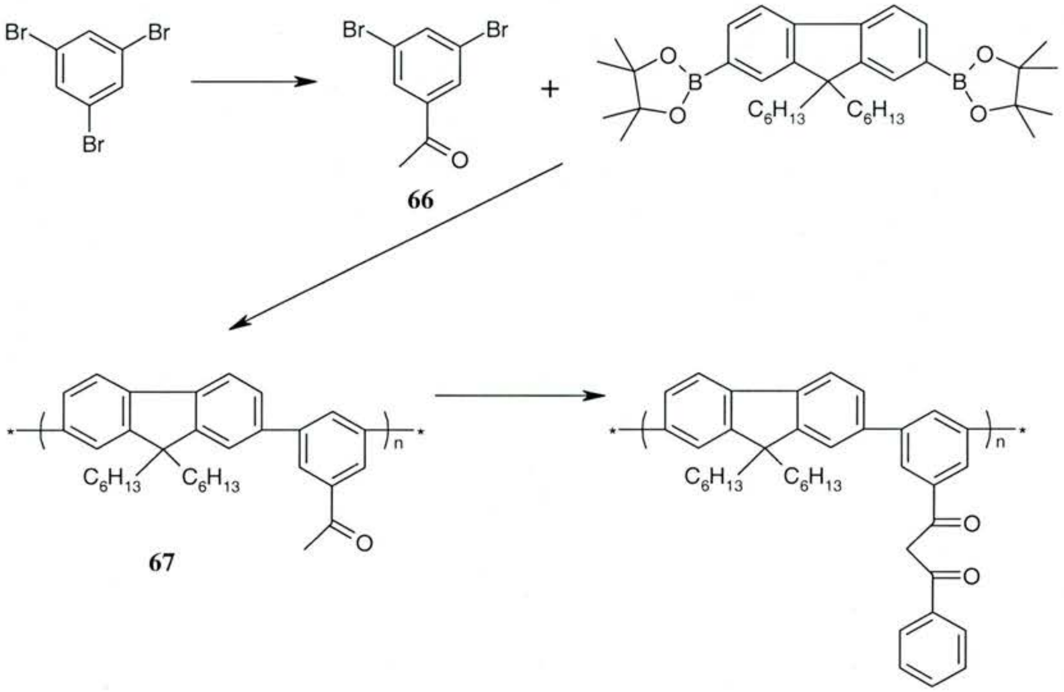
Both strategies required the synthesis of the dibrominated acac type ligand **63**. Attempts to make this ligand involved many different bases including butyl lithium, sodium, sodium methoxide. The ligand was finally prepared, albeit in poor yield, from a crossed Claisen reaction using sodium hydride as a base and methanol as a catalyst (Scheme 4.5).



*Scheme 4.5: Synthesis of Alq functionalised polyfluorene **65***

Unfortunately, neither the polymerisation using **62** nor the strategy of Scheme 4.5 were successful which could be due to catalyst binding to the acac ligand in the first instance or the bromines of the complex not being activated enough for the oxidative addition step in the Suzuki coupling reaction.

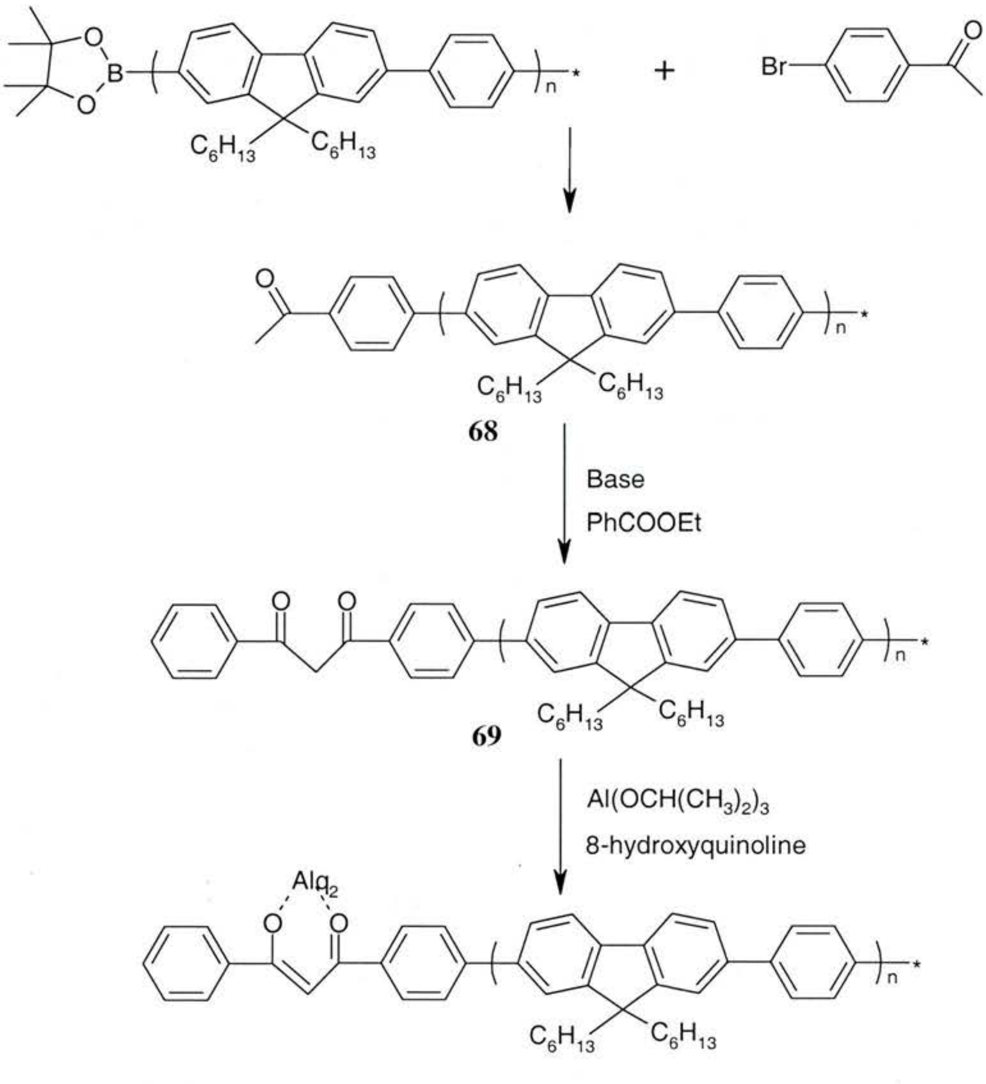
Another method of achieving aluminium coordination as a pendant group is shown in Scheme 4.6. In this method 3,5-dibromo acetophenone **66** was prepared from tribromobenzene. This was then reacted in a Suzuki reaction to form an oligomer **67**. It was then attempted to form the acac moiety by the crossed Claisen reaction detailed above, however the signal due to the methyl group of the acetophenone was still present in the proton NMR and no evidence for the formation of the acac moiety was found.



Scheme 4.6:Synthesis of pendant acac moieties

The introduction of the aluminium quinolate as an end group has also been explored. This method has the additional advantage that any bromines or boronic ester end groups are removed which will help to improve the efficiency of the device. Moreover, the aluminium functionality is at lower energy than the polyfluorene, therefore exciton trapping should occur on the aluminium sites and the observed electroluminescent emission will be solely from the aluminium. The desired yellow emission could therefore be achieved from the inclusion of only a few of the desolubilising aluminium groups.

A polyfluorene with acetyl end groups was synthesized by end-capping the polymer with bromoacetophenone **68**.

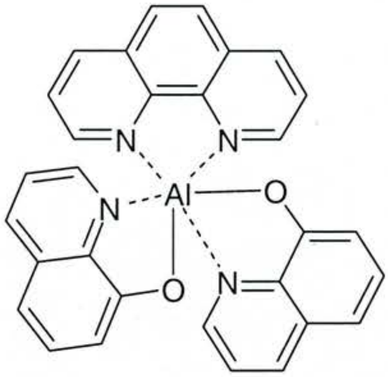


Scheme 4.7: End group Alq functionalisation

Attempts were made to deprotonate the acetyl groups with solid sodium methoxide and sodium hydride, however the complex ^{1}H NMR spectrum obtained from the polymer itself makes it very difficult to assign the end groups even on relatively short chain polymers. Due to inconclusive proof of the end groups reacting to form the acac type functionality **69** it was deemed better to leave this strategy and focus on another method of coordinating the aluminium.

4.2.3 Coordination Through Phenanthroline Ligand

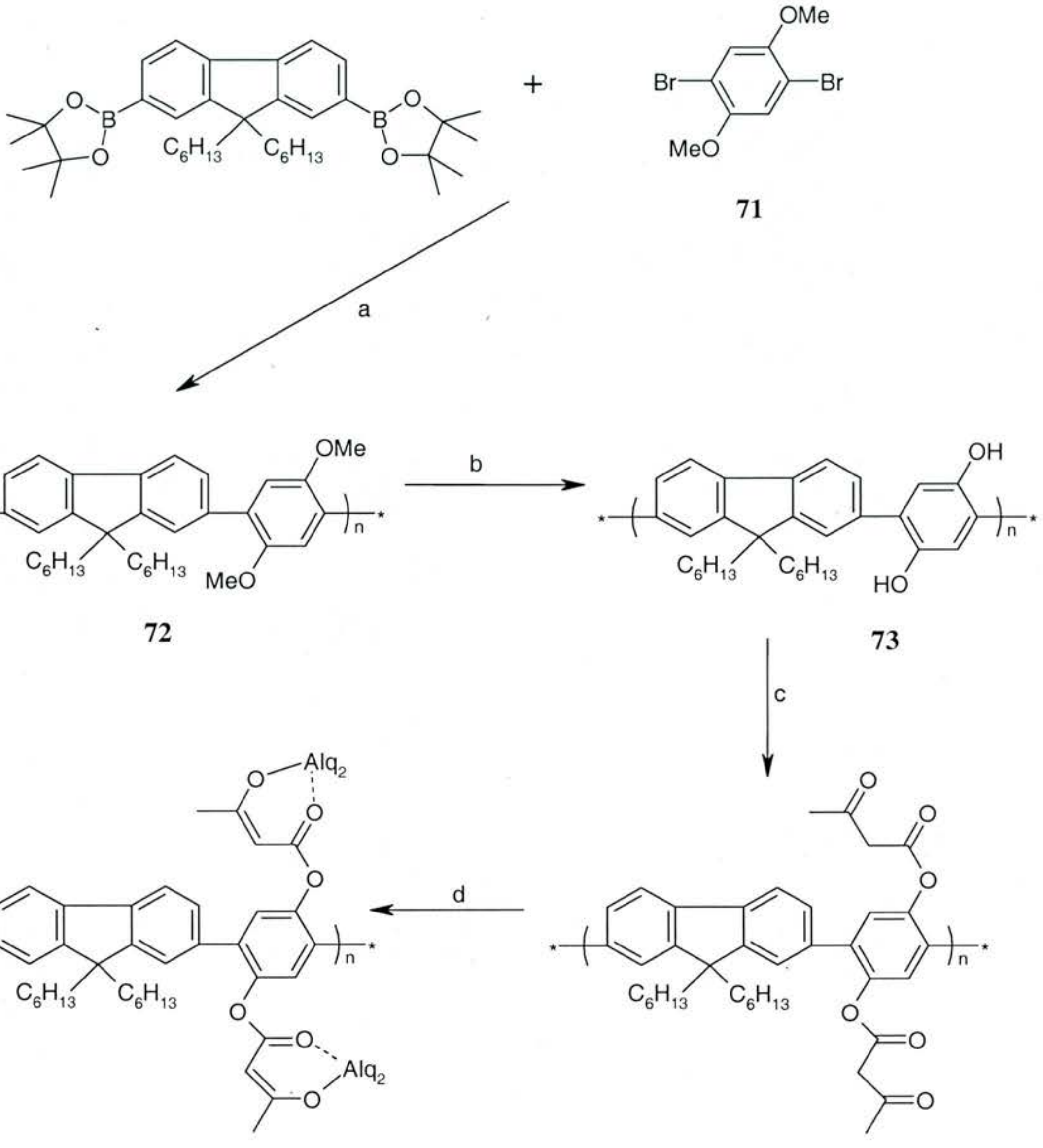
Due to the difficulties encountered in preparing a fluorene based polymer encompassing a covalently bound ligand our attention turned back to the polymer prepared in Chapter 3. This fluorene based polymer incorporates a phenanthroline moiety which is a well known bidentate ligand. No instances were found in the literature of aluminium coordinated to phenanthroline, prompting a test reaction to be carried using molecular phenanthroline in order to determine if aluminium would coordinate. Thus one equivalent of phenanthroline and two equivalents of hydroxyquinoline were used in the reaction **70** as this would be the preferred ratio of reagents in the reaction to coordinate the aluminium to the polymer. During the reaction a yellow precipitate formed, which was soluble in chloroform. Proton NMR consisted solely of peaks arising from the hydroxyquinoline.



70

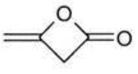
4.2.4 Functionalisation of Phenyl Ring

Several groups have reported the formation of an acetoacetate functional group from diketene and an alcohol in relatively high yields.[14] The alternating fluorene copolymer P1 prepared in Chapter 2 to prepare a fluorene based polymer with hydroxyl functionality was a desirable target. The proposed synthesis for this is shown in Scheme 4.8 and involved Suzuki coupling of 2,5-dibromo-1,4-dimethoxybenzene **71** which could be deprotected by reaction with BBr_3 to yield the hydroxyl polymer **73**.



Scheme 4.8: Functionalisation of Phenyl Ring a) Suzuki coupling b) BBr_3

c)



2,5-Dibromo-1,4-dimethoxybenzene **71** was prepared in good yield by a Friedel-Crafts bromination of dimethoxybenzene. Attempts to polymerise this with the fluorene boronic ester resulted in recovery of the starting materials and no coupling products were observed. Examples have been found in the literature which detail successful Suzuki coupling of 2,5-dibromo-1,4-dimethoxybenzene.[15] The lack of coupling in this instance is not as a result of differing electronic properties caused by the ether groups. Instead this may be due to a bad sample of catalyst or air entering the system as the mixture turned black early on in the reaction indicating that the catalyst had decomposed to palladium metal. Due to time constraints it was not possible to pursue this proposed synthesis. However it is believed that this would be a viable method of binding the aluminium given more time to optimize the reaction conditions.

4.2.5 Functionalisation of Alkyl Chains

One final position capable of functionalisation that was briefly explored are the alkyl chains connected to the fluorene moiety. The proposed synthetic strategy (Scheme 4.9b) involved bromination of the terminal carbon on the alkyl chain, this would then react with bromo-8-hydroxyquinoline. A similar reaction to this has been carried out by Mongin using heptyl bromide and 2,7-dibromo-8-hydroxyquinoline (Scheme 4.9a).[16]

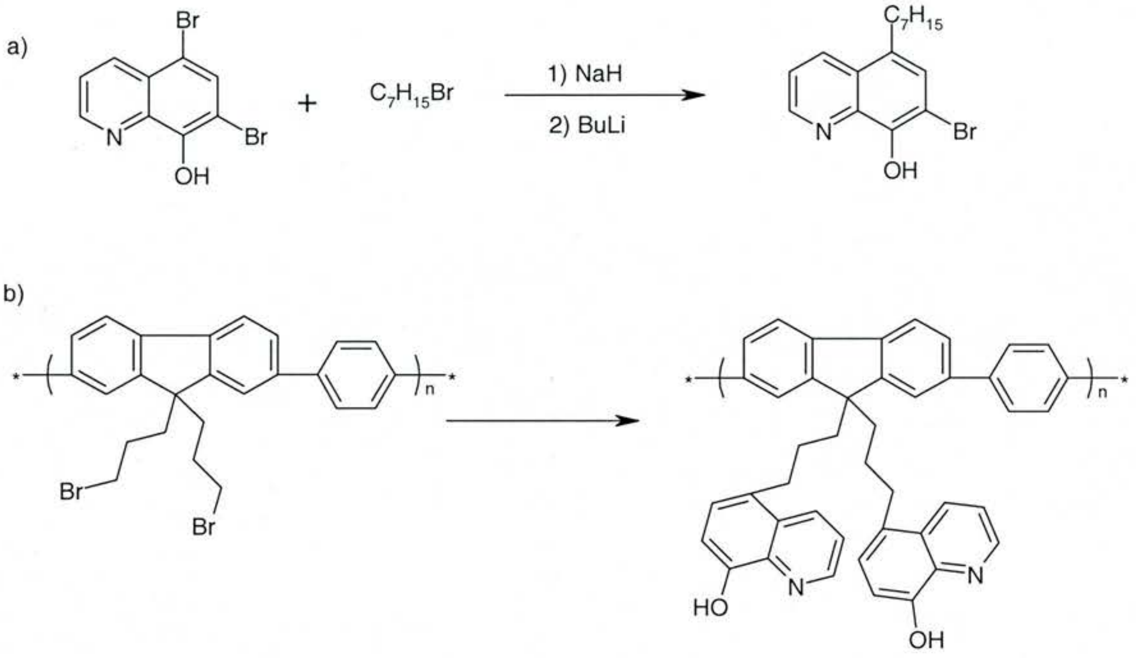
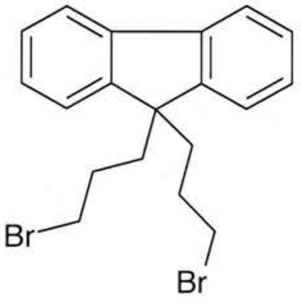
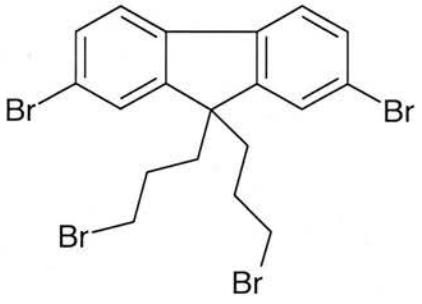


Figure 4.9: Functionalisaton of alkyl chains with hydroxyquinoline

In order to control the polymer structure it was necessary to prepare the brominated alkyl groups in the monomer rather than adding these after the polymerisation. These bromine atoms would not affect the Suzuki coupling polymerisation since aromatic bromines have been shown to react exclusively in the presence of alkyl bromines.[17]

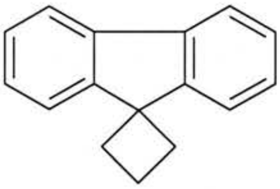


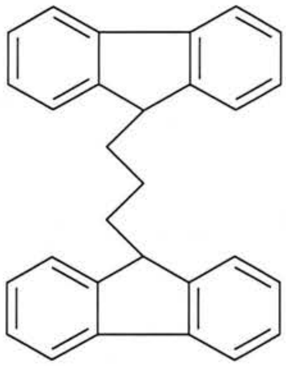
74



75

Two possible methods of preparing the monomer **75** were considered. In the first case the brominated alkyl chains are added to fluorene followed by bromination of the aromatic ring to give **74**. Dibromopropane was selected as the alkyl chain because of its availability in the lab. Deprotonation of the fluorene was achieved by addition of butyl lithium and the dianion generated was dripped into 20 equivalents of dibromopropane by means of a cannula. It was hoped that by using a large excess of dibromopropane the formation of cyclic monomers and dimers could be prevented.





During the process of transferring the fluorenyl anion, the temperature in the cannula could not be maintained at –78 °C, this is likely to result in the destruction of the anion and ultimately the failure of this reaction.

The second method of preparing monomer **75** is to first brominate the fluorene at the 2,7 positions and then attach the alkyl chains using a method given by Liu.[18] The first step of this method was successfully achieved using the Friedel-Crafts procedure. The second stage was attempted a couple of times and whilst the desired product was formed, so too was the mono-alkylated species and also a certain amount of fluorene in which the terminal bromine on the alkyl chain was missing. Attempts at purification by column chromatography were unsuccessful due to the constituents of the mixture being very soluble in common organic solvents and running together on the column. Polymerisation was not attempted on the crude mixture as this would lead to a very complex mixture of repeat units. Some repeat units would then contain an acidic proton that could be oxidatively removed to produce a fluorenone moiety in the polymer. From the work detailed in Chapter 2, this is to be avoided, as it may prove detrimental to the final polymers optical properties.

Due to the nature of the aluminium complex being attached at the end of a saturated alkyl group it may be that this is detrimental to the charge transfer properties of the polymer. Because of this and the difficulties associated in preparing a pure sample of **75** no further work in this area was carried out.

4.3 Conclusions / Future Work

The aim of this chapter was to coordinate aluminium hydroxyquinolate onto a fluorene type polymer backbone. Several different strategies incorporating several ligands were tried to achieve this but unfortunately the inherent difficulties with a synthesis of this nature and time constaints on this work have meant that this goal has not been realised. The knowledge of this area has been extended and a number of important issues have come to light. Firstly, Suzuki coupling of the hydroxyquinoline is not feasible since coupling will occur at only one C-Br group if the hydroxyl functionality is protected. The only remaining alternative, is to utilize the hydroxyquinoline as an end cap for the polyfluorene chain.

Acetylacetonate type ligands were also considered. The synthesis of the 1,3 dicarbonyl moiety proved far from straight forward and investigations need to be carried out to fully understand why these materials did not polymerise. The acac groups may need to be protected during the coupling reaction

It is expected that with more time, the functionalisation of the side chains should prove successful. The resulting polymer would have a conjugated backbone with pendant green aluminium chromophores. These chromophores would be connected through short saturated groups and therefore charge transfer from the polymer backbone to the aluminium may be hindered. Under EL conditions this may not be a problem due to the hopping mechanism of charge transfer and light should be emitted from the lowest possible energy gap.

One further possible method of incorporating a ligand onto the polymer is to functionalise the phenyl ring and react it with the diketene. No polymer was obtained in this project and the reasons for this are unclear. With more time it is anticipated that this could be overcome and the desired polymer could be prepared.

4.4 Experimental

All starting materials were obtained from Aldrich or Lancaster, were reagent grade and used without further drying or purification except where stated otherwise. Tetrahydrofuran was distilled over sodium and benzophenone under an inert atmosphere.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Av-300 in deuterated chloroform solutions, operating at 299.998 MHz for ^{1}H and 75.45 MHz for ^{13}C. Infra-red spectra were recorded as KBr discs or as thin films of neat polymer on NaCl plates, on either a Perkin Elmer Paragon 1000 or a Nicolet Avatar 360 FTIR spectrometer.

Molecular weights were recorded on a Polymer Laboratories Gel Permeation Chromatography 120 Integrated GPC system with Polymer Laboratories gel 5 μm mixed column relative to polystyrene standards.

Absorption Spectra were recorded either in solution in THF or as a thin film on a quartz substrate using a Varian Cary 300 Bio uv-vis machine. Photoluminescence spectra were recorded either as a dilute solution in THF or as a thin film on quartz substrates with a Fluoromax 2 from the Honba Group.

2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene 44

The boronic ester was prepared as outlined in Chapter two.

Synthesis of Alq_3 and Alq_2Brq mixture 57

Aluminium isopropoxide (1.84 g, 9.0 mmol), 5,7-dibromo-8-hydroxyquinoline (0.27 g, 0.9 mmol) and 8-hydroxyquinoline (3.79 g, 26.1 mmol) were placed in a 3 necked round bottom flask and flushed with argon. Dry THF (20 ml) was then added and the mixture was warmed to 40 °C for 2 hours. The yellow precipitate (3.29 g) was filtered and used without further purification.

^{1}H NMR δ (ppm) 8.80 – 8.72 (d, 3H), 8.24 - 8.10 (m, 3H), 7.48 – 7.28 (m, 6H), 7.16- 7.0 (m, 6 H)

λ_{max} 260 , 388 nm, λ_{em} 517 nm

Attempted Polymerisation of Alq_2Brq 58

The Alq_3 / Alq_2Brq mixture (0.427 g, 0.63 mmol of Alq_2Brq) and 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene (0.3692 g, 0.63 mmol) were placed in a 3 necked round bottomed flask and placed under an argon atmosphere. Tetrakistriphenylphosphine palladium (0.0073g, 0.0063 mmol) was then added followed by dry THF (40ml). This was then stirred at room temperature for 10 minutes before an aqueous solution of tetraethylammonium hydroxide (10 ml) was added. The mixture was then heated to 80 °C for 2 days. Once cool the reaction mixture was poured into methanol and the precipitate collected by vacuum filtration. The pale yellow powder weighed 0.52 g.

λ_{max} 262 , 388 nm, , λ_{em} 516 nm

Attempted Polymerisation of boronic ester 44 with ligand 56

Carried out by general Suzuki coupling method outlined in Chapter 2. No polymer obtained

5,7-dibromo-8-(tert-butyl-dimethyl-silanoxy)-quinoline 59

5,7-dibromo-8-hydroxyquinoline (2.0435 g, 6.75 mmol), t-butyl-dimethyl chlorosilane (1.2200 g, 8.09 mmol) and imidazole (1.1481 g, 16.9 mmol) were placed under an inert atmosphere and dissolved in anhydrous DMF. The reaction mixture was then stirred at 35 °C overnight. The reaction mixture was poured into water and extracted with petrol. The solvent was removed under reduced pressure and once cool the oil became solid. The crude product was recrystallised in methanol to give off white spiky crystals. (2.44 g, 5.8 mmol, 86.7%, mp 74 – 75 °C)

^{1}H NMR δ (ppm) 8.75 (d, 1H), 8.35 (d, 1H), 7.9 (s, 1H), 7.45 (t, 1 H), 1.0 (s, 9H), 0.25 (s, 6H) . ^{13}C NMR δ (ppm) 153.12, 144.14, 138.11, 130.06, 124.92, 114.53, 113.85, 28.72, 22.04, 0.00

TOF MS ES+ 417.97 triplet

IR 2936, 2851, 1570, 1484, 1453, 1386, 1098, 837, 782

Attempted Synthesis of 8-(tert-butyl-dimethyl-silanoxy)-5,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-quinoline

5,7-dibromo-8-(tert-butyl-dimethyl-silanoxy)-quinoline (0.62 g, 1.49 mmol) was placed in a three necked round bottomed flask and flushed with argon. Dry THF was added and the reaction vessel was cooled to –78 °C in a dry ice/acetone bath. Butyl lithium (1.25 ml, 3.12 mmol) was added dropwise . The mixture was stirred at –78 °C for 45 minutes and then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.76 ml, 3.72 mmol) was added. The reaction mixture was allowed to warm to room temperature and was stirred overnight. The reaction mixture was then poured into water and extracted with diethyl ether. The combined organic extracts were dried over magnesium sulphate and then filtered. Excess solvent was removed under reduced pressure. Product could not be isolated.

Attempted synthesis of diisopropoxide aluminium 5,7-dibromo-8-quinolate $AlBrq(OCH(CH_3)_2)_2$ 60

5,7-dibromo-8-hydroxyquinoline (0.83 g, 2.74 mmol) was placed in a 3 necked round bottomed flask and flushed with nitrogen and dissolved in dry toluene (10 ml). To this aluminium isopropoxide (0.56 g, 2.74 mmol) in dry toluene was added dropwise. The mixture was then stirred at room temperature for 1 hour whereupon the precipitate was filtered with suction. The excess solvent of the filtrate was removed under reduced pressure (0.71 g)

Attempted synthesis of diisopropoxide aluminium 8-quinolate $Alq(OCH(CH_3)_2)_2$

To a solution of aluminium isopropoxide (0.47 g, 2.30 mmol) in dry toluene (10 ml) under an inert atmosphere was added dropwise a solution of 8-hydroxyquinoline (0.34 g, 2.34 mmol) in dry toluene (10 ml). The mixture was then stirred at room temperature for 1 h. A yellow precipitate formed which was collected by filtration. (0.24 g). ^{1}H NMR analysis of this compound consisted solely of hydroxyquinoline peaks. Excess solvent was removed from the filtrate by means of a rotary evaporator

Attempted synthesis of 5,7-dibromo-8-hydroxyquinoline-s-butylphenolato aluminium 61

Aluminium isopropoxide (0.41 g, 2.0 mmol) and 5,7-dibromo-8-hydroxyquinoline (0.61 g, 2.0 mmol) were placed in a round bottom flask and flushed with nitrogen. Dry toluene (15 ml) was added and the mixture was stirred at room temperature for 1 hour. During this time a yellow / green precipitate formed. S-butyl phenol (0.30 g, 2.0 mmol) was dissolved in dry toluene (10 ml) and added dropwise to the reaction mixture. The mixture was stirred overnight. The yellow / green precipitate (0.05 g) was filtered but was too insoluble for NMR analysis. The excess solvent was removed from the filtrate under reduced pressure (0.81 g). This was then dissolved in the minimum amount of toluene and precipitated in hexane.

Aluminium Acetylacetonate Di-8-quinolate

Aluminium isopropoxide (0.255 g, 1.25 mmol) was placed in a three necked round bottom flask which was then flushed with argon. To this was added dry toluene (17 ml) followed by neat acac (0.125 g, 1.25 mmol) dropwise. 8-hydroxyquinoline (0.358 g, 2.46 mmol) in dry toluene (8 ml) was then also added dropwise whereupon the mixture gradually turned yellow. This was then warmed to 45 ^{o}C in an oil bath for 15 mins until a precipitate began to form. The precipitate was filtered under suction to yield a pale yellow solid (0.26 g, 50.3%, mp 304 ^{o}C dec)

^{1}H NMR δ (ppm) 8.5 (d, 2H), 8.1 (d, 2H), 7.4 (t, 4H), 7.1 (d, 2H), 6.95 (d, 2H), 5.5 (s, 1H), 1.95 (s, 6H)

^{13}C δ (ppm) 192.91, 159.21, 144.31, 139.49, 139.00, 131.03, 129.53, 121.88, 112.43, 112.10, 102.39, 27.44

λ_{max} 260 , 388 nm, λ_{em} 514 nm

1,4-Bis-(4-bromo-phenyl)-butane-1,3-dione Aluminium 8-quinolate 62

Aluminium isopropoxide (0.0422 g, 0.21 mmol), 1,4-Bis-(4-bromo-phenyl)-butane-1,3-dione (0.0768 g, 2.01 mmol) and 8-hydroxyquinoline (0.0614 g, 4.2 mmol) were placed in a 3 necked round bottomed flask and flushed with argon. Dry toluene (20 ml) was then added and the reaction mixture was heated to 50 °C for 8 hours. The yellow precipitate was collected by suction filtration (0.070 g)

^{1}H NMR δ (ppm) 8.64 (d, 2H), 8.16 (d, 2H), 7.56 (d, 4H), 7.44 (t, 4H), 7.36 (d, 4H), 7.28 (m, 2H), 7.10 (d, 2H), 7.00 (d, 2H), 6.8 (s, 1H)

1,4-Bis-(4-bromo-phenyl)-butane-1,3-dione 63

Methyl bromobenzoate (2.18 g, 10.1 mmol) and bromoacetophenone (0.49 g, 2.46 mmol) were placed under an inert atmosphere followed by dry toluene (20 ml). The flask was then heated to 60°C whereupon a small portion of sodium hydride (0.128 g, 3.20 mmol) (in mineral oil) was added. The mixture was heated for 2 h, once cool excess water was added to quench the reaction. A yellow precipitate was collected. (0.13 g, 13.8 %, mp 194 – 196 °C).

^{1}H NMR δ (ppm) 7.8 (d, 4H), 7.55 (d, 4H), 6.7 (s, 1H). ^{13}C NMR δ 185.14, 134.57, 132.43, 129.06, 127.93, 93.25

Attempted Polymerisation of 1,4-Bis-(4-bromo-phenyl)-butane-1,3-dione 64

The general Suzuki coupling polymerisation outlined in Chapter 2 was used. No polymer was obtained.

3,5-dibromoacetophenone 66

DMAC was stirred over calcium hydride for 2 h at room temperature then vaccum distilled (60 °C, 5 mm/Hg) prior to use. Tribromobenzene (1.60 g, 5.08 mmol) was dissolved in dry diethyl ether under an argon atmosphere and cooled to -78°C in a dry ice / acetone bath. To this was added n-butyl lithium (2 ml, 5.00 mmol) dropwise. The mixture was stirred at –78 °C for a further two hours and DMAC (0.52 ml, 5.60 mmol) was added dropwise. This was then stirred at room temperature overnight. The reaction was quenched by the addition of 10 % hydrochloric acid solution (30 ml). The layers were separated and the aqueous layer was extracted with diethyl ether. The combined organic extracts were dried over magnesium sulphate and the excess solvent removed under reduced pressure. The pure product was isolated by column chromatography in silica rf = 0.375 (eluant: 9:1 hexane:ethyl acetate). A white powder was obtained 0.45 g, 31.9 %.

Mp 62 - 63°C (lit 61 – 63 °C)[19]

^{1}H NMR δ (ppm) 7.9 (s, 1H), 7.75 (s, 1H), 2.5 (s, 3H)

^{13}C NMR δ (ppm) 195.60, 140.14, 138.65, 130.51, 123.8, 27.03

Oligomer (prepared from 3,5-dibromoacetophenone coupled to 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene 44) 67

Prepared by usual Suzuki coupling method outlined in Chapter 2

Yield = 0.3 g

^{1}H NMR δ (ppm) 8.0 – 8.2 (s), 7.9 (s), 7.4 – 7.8 (s), 3.4 (s), 2.0 (s), 1.3 (s), 1.1 (s), 1.0 (s), 0.6 (s)

Poly(1,4-phenylene-9,9-dihexylfluorene) end capped with 4-bromoacetophenone 68

2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene (0.7673 g, 1.308 mmol), 1,4-dibromobenzene (0.2316 g, 0.892 mmol) were placed in a three necked round bottomed flask fitted with a reflux condenser and a septa. This was placed under an argon atmosphere and tetrakistriphenylphosphine palladium (0.0112 g, 0.0097 mmol) was added. Toluene (8 ml) fresh from the still was added and the mixture was stirred at room temperature for 10 mins. Tetraethyl ammonium hydroxide solution (1 M) (5 ml) was degassed and then added to the mixture. This was then heated to 80 °C for 2 h. 4-bromoacetophenone (0.1700 g, 0.854 mmol) was then added and the mixture heated at 80 °C for a further 2 h. Once cool the mixture was precipitated into methanol. A light brown solid was collected by filtration which was washed with methanol and water. (0.5608 g, 91.7%)

^{1}H NMR δ (ppm) 8.0 (d), 7.8 (m), 7.6 (), 2.6(s), 2.0 (s), 1.05 (s), 0.7 (s)

Poly(1,4-phenylene-9,9-dihexylfluorene) end capped with acac moieties 69

A solution of poly(1,4-phenylene-9,9-dihexylfluorene) end capped with 4-bromoacetophenone (0.3299 g, 0.109 mmol) and ethyl benzoate (3 ml) in toluene (5 ml) was heated to heated to reflux. Sodium hydride in mineral oil (0.0329 g, 0.823 mmol) was then added and the mixture heated for a further hour. Once cool the reaction was quenched by the addition of water. The crude product was collected by precipitation in methanol. (0.3258 g)

^{1}H NMR δ (ppm) 8.0 (d), 7.8 (m), 7.6 (m), 2.6(s), 2.0 (s), 1.05 (s), 0.7 (s)

Attempted synthesis of diquinolato(1,10-phenanthroline)aluminium(III) complex Al(phen)q_2 70

Aluminium isopropoxide (0.50 g, 2.45 mmol), 1,10- phenanthroline (0.46 g, 2.55 mmol) and 8-hydroxyquinoline (0.71 g, 4.89 mmol) were placed in a round bottomed flask and flushed with argon. To this dry toluene (15 ml) was added and the mixture was heated to 50 °C for 5h. A yellow precipitate (0.94 g) was collected by filtration.

1,4-dibromo-2,5-dimethoxy-benzene 71

1,4-dimethoxybenzene (1.59 g, 11.5 mmol) and anhydrous ferric chloride (0.07 g, 0.43 mmol) were dissolved in chloroform (30 ml). The reaction flask was wrapped in aluminium foil and placed in an ice bath. Bromine (1.4 ml, 27.2 mmol) was then added, the reaction mixture was allowed to warm to room temperature and stirred overnight. The mixture was then poured into water and washed with sodium thiosulphate solution (2 M). The layers were separated and the aqueous layer was extracted with dichloromethane. The combined organic extracts were dried over anhydrous magnesium sulphate. The excess solvent was removed under reduced pressure. A pale yellow powder was obtained 3.14 g, 92.2 %. Mp 132 – 133 °C (lit mp 135 – 137 °C)

^{1}H NMR δ (ppm) 7.05 (s, 2H), 3.80 (s, 6H)

^{13}C NMR δ (ppm) 150.90, 117.49, 110.87, 57.41

Attempted polymerisation with 1,4-dibromo-2,5-dimethoxy-benzene 72

Boronic ester (0.4350 g, 0.74 mmol), dibromo-dimethoxy-benzene (0.2173 g, mmol) and tetrakis triphenylphosphine palladium (0.0102 g, mmol) were placed in a 3 necked round bottomed flask and flushed with argon. To this dry, degassed toluene (8 ml) and degassed tetramethylammonium hydroxide solution (4 ml 20% aq. solution) was added. The mixture was then heated to 80 °C for 6 h. Once cool the reaction mixture was poured into methanol. No precipitate formed.

9,9-bis-(6-bromo-hexyl)-9H-fluorene 74

Fluorene (0.55 g, 3.31 mmol) was placed under a nitrogen atmosphere, dissolved in dry tetrahydrofuran (20 ml) and cooled to –78 °C. Butyl lithium (3 ml, 7.50 mmol) was added dropwise and the mixture stirred at –78 °C for 45 minutes. Dibromopropane (12.56 g, 62.2 mmol) was placed in a second flask under a nitrogen atmosphere, dissolved in dry THF and cooled to –78 °C. The fluorene mixture was transferred dropwise to the second flask by means of a cannula. The reaction was then allowed to warm to room temperature and stirred overnight. This was then poured into water and extracted with diethyl ether. The organic layers were dried over magnesium sulphate and the excess solvent removed under reduce pressure. The excess dibromopropane was removed by Kügel Rohr distillation. Purification was attempted on a silica column (eluant hexane: ethyl acetate)

2,7-Dibromo-9,9-bis-(6-bromo-hexyl)-9H-fluorene 75

2,7-Dibromofluorene (0.57 g, 1.76 mmol) and tetrabutylammonium bromide (0.0289 g, 0.09 mmol) were placed under an argon atmosphere to which dimethylsulphoxide (10 ml) was added. 1,3-dibromopropane (0.62 ml, 6.10 mmol) was then added followed by dropwise addition of sodium hydroxide solution (2 g in 2 ml). This was then heated to 40 °C for 6 h. The reaction was quenched with water and extracted with ethyl acetate. The combined organic extracts were dried over magnesium sulphate and the solvent removed under reduced pressure.

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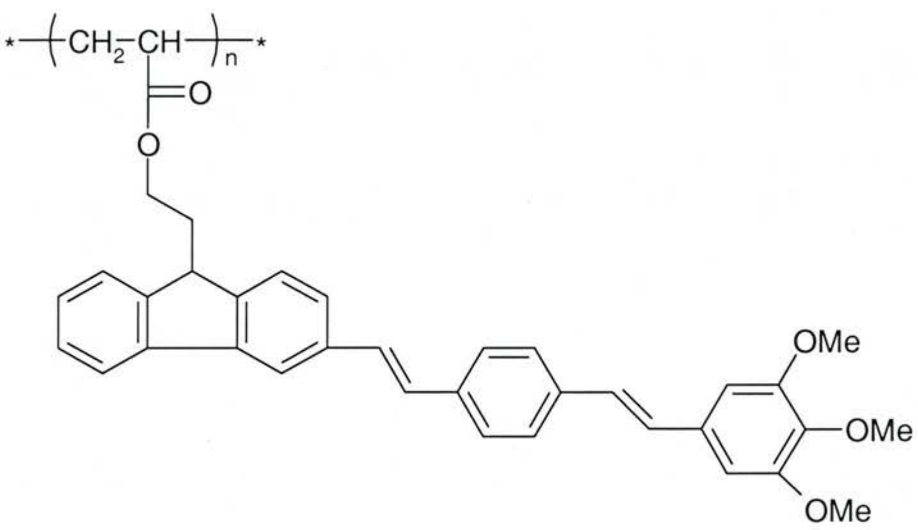
Chapter 5

Covalent Attachment of Aluminium Complexes to Polystyrene

5.1 Introduction

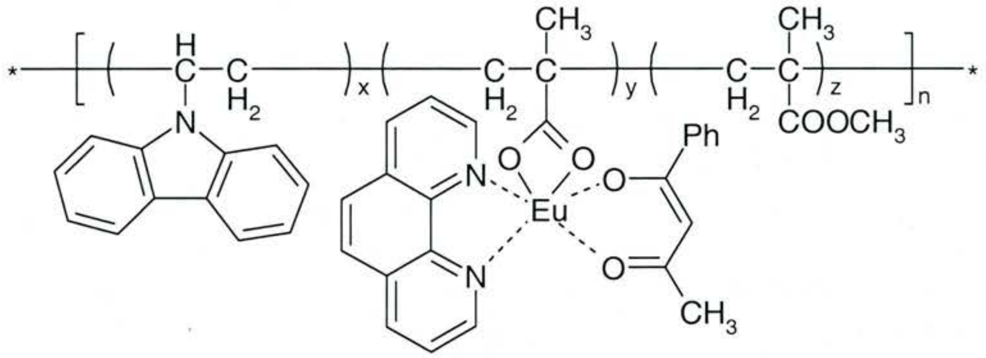
A wide misconception exists that in order for a polymer to be semiconducting it must be conjugated. Polyvinylcarbazole, a non-conjugated polymer, has also been shown to be both semiconducting and electroluminescent.[1] For this class of polymer conduction is facilitated by hopping charge transfer from an aromatic segment from one polymer chain to the next.[2] This highlights the potential for exploring other non-conjugated polymers which possess both semiconducting and light-emitting properties.

An example of this was discussed in chapter 4 and involved the coordination of aluminium to a non-conjugated polymer based on ring opening polymerisation of a norbornene derivative.[3] A review of the literature also revealed a couple of other non-conjugated polymers which are photoluminescent. One such system, based on polymethacrylate, has pendant carbazole units as the light emitting chromophore **76**. These polymers, termed CARBDIS polymers, emit blue light when excited by ultraviolet light with an emission maximum centred at 445 nm. CARBDIS-based polymers are reputedly suitable for use in light emitting diode applications due to their high thermal stability, excellent film forming properties and good charge transport properties; however, no devices or electroluminescent results for this polymer were reported by the authors.[4]



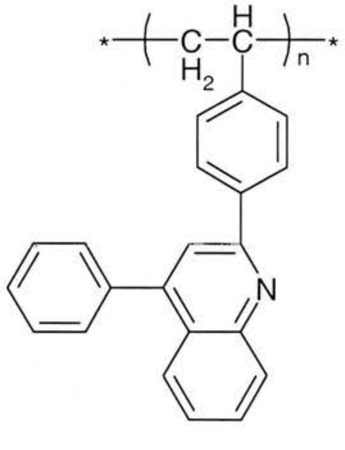
76

Ling has prepared a copolymer combining carbazole units with pendant units coordinated to a europium complex **77**. This polymer emits photoluminescent light in three bands in the red region of the electromagnetic spectrum, characteristic of complexes prepared from europium. Single layer devices were prepared from this polymer and were found to be relatively inefficient in comparison to conjugated polymers. These devices also had high turn-on voltages of 24 V. The insulating nature of this polymer is likely to be caused by the non-conjugated backbone of the polymer; however, this demonstrates that non-conjugated polymers may be utilised in light emitting diodes.[5]



77

Polystyrene-based polymers also exhibit photoluminescent properties. Poly(vinyl diphenylquinoline) **78** for example, emits blue light with an emission maximum of 413 nm in dichloromethane. The quantum efficiency of this polymer is very low at 2% in DCM and the charge transport properties of this polymer were not reported so it is unclear whether this material would be suitable for LED applications.[6]



78

The aim for this section was to prepare a non-conjugated polymer with pendant aluminium quinolate chromophores. Polystyrene was chosen as the polymer for this study for several reasons. Firstly, the synthesis of polystyrene is well developed and a considerable amount of work has been carried out into reactions on polystyrene. Secondly, polystyrene can be synthesized by a living polymerisation reaction, which yields high molecular weight polymers with low polydispersities. This is an important consideration as it allows the synthesis of polymers with reproducible mechanical properties.

Several methods of living polymerisations are known for polystyrene. Atom transfer radical polymerisation (ATRP) was selected in this case since it produces high molecular weight, low polydispersity polymers in relatively mild conditions. ATRP requires the use of both an initiator (a small organic halide with a reactive carbon - halide bond) and a catalyst which is typically a transition metal compound such as Cu(I)Br and a bidentate ligand. The carbon - halogen bond of the initiator is homolytically cleaved to generate a radical and the catalyst is oxidised to Cu(II)X_2. This radical can then attack the alkene and the propagation step of the polymerisation takes place. This process exists as an equilibrium, which is heavily weighted towards the initial state of initiator and non-oxidised catalyst, and therefore there is only ever a low steady state concentration of the radical chain ends. The rate of propagation is then significantly greater than the rate of termination reactions and polymers of very low polydispersities (typically less than 1.3) are generated.[7]

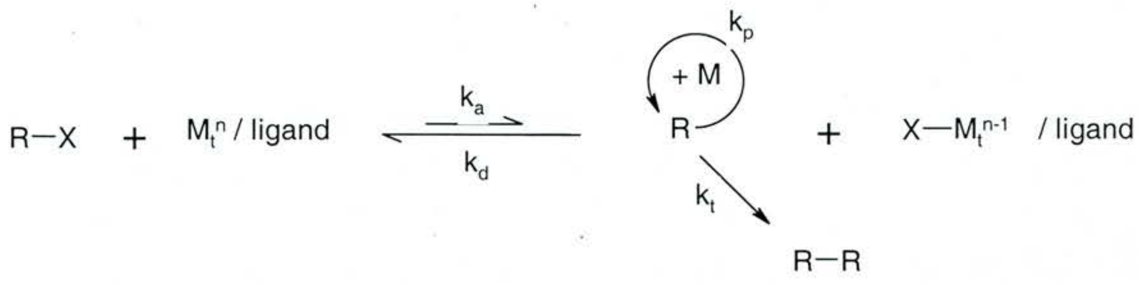
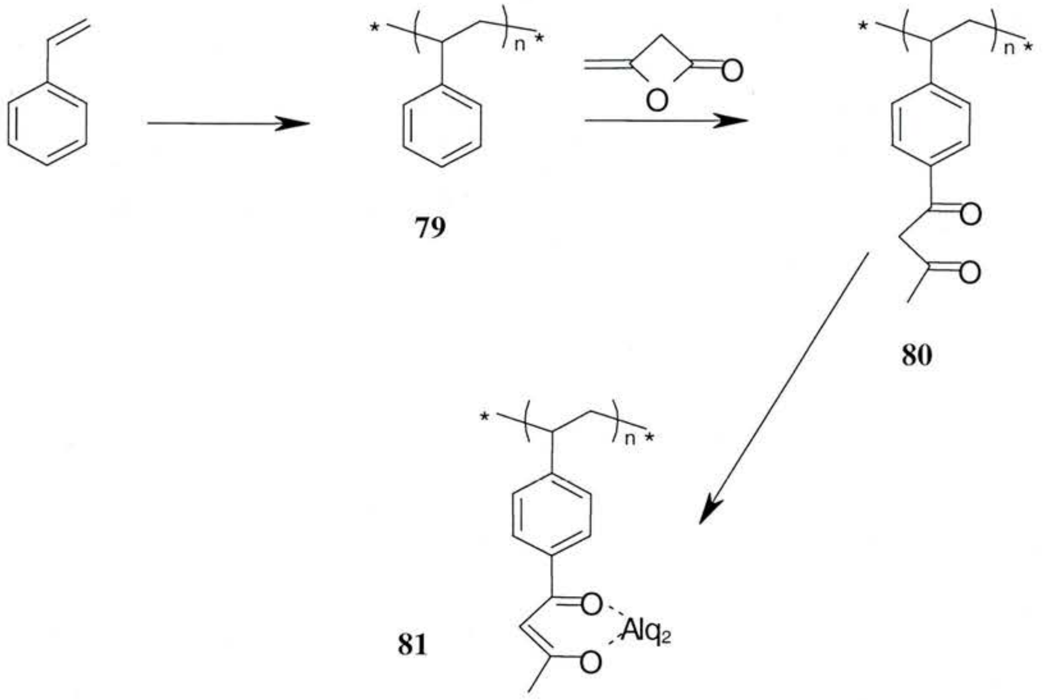


Figure 5.1: Atom Transfer Radical Polymerisation (ATRP)

5.2 Results and Discussion

5.2.1 Functionalisation of Polystyrene: Diketene Method

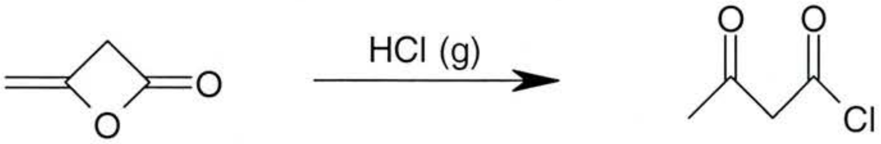
In order to coordinate metals to the polystyrene the polymer must first be functionalised with a chelating group. An acetylacetonate-type ligand (acac) was chosen for a number of reasons. Firstly, aluminium coordinates to only one acac ligand regardless of the molar ratios used in the reaction. Secondly, synthesis of this ligand appeared on first inspection to involve few steps in a relatively easy synthesis. The proposed synthetic procedure involves three steps and is shown in Scheme 5.1.



Scheme 5.1: Aluminium bound polystyrene (diketene method)

Polymerisation of styrene **79** was achieved in good yield by atom transfer radical polymerisation. The intended molecular weight is relatively modest; however, this is desirable as the molecular weight is expected to increase significantly on complexation of the aluminium.

It was attempted to introduce the 1,3-diketo functionality to the phenyl ring **80** by a method outlined by Hurd in which diketene was reacted with neat benzene in the presence of aluminium chloride.[8] Since the polystyrene is solid it was necessary to add a suitable solvent, carbon disulfide and tetrahydrofuran were both used. Unfortunately no evidence could be found that the diketene had reacted with the polymer in either case and proton NMR showed peaks only from the original polymer. In the original preparation using neat benzene only a 10% yield was obtained. However, the yield could be increased to 27% by first reacting the diketene with hydrogen chloride gas to form the acid chloride (Scheme 5.2). This is then reacted by the same method with aluminium chloride with the aromatic group.



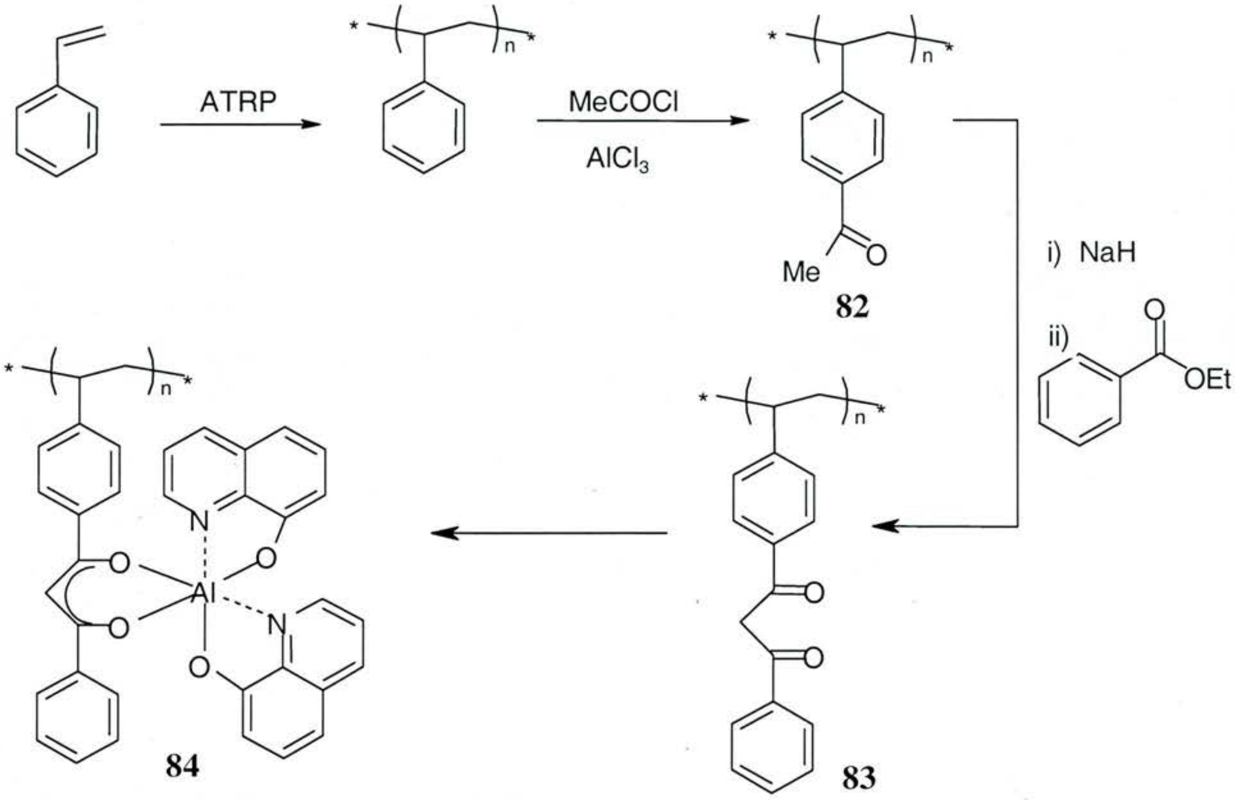
Scheme 5.2: Synthesis of acid chloride

The activated diketene method was again attempted on the polystyrene with the two different solvents, carbon disulfide and tetrahydrofuran. The heat generated in the reaction is as a result of the aluminium chloride being added to THF and not as a result of a reaction between the polymer and the diketene as no heat is given out when the aluminium chloride is added to carbon disulfide. Again no evidence of the formation of the diketone was found in either reaction. The reaction of the diketene directly onto an aromatic ring has been utilised by only one other group[9] and suggests that this is not the most efficient method of generating the diketo functionality. This coupled with the lack of evidence of the functional groups having been attached to the polymer led us to explore different methods of creating the diketone moiety.

5.2.2 Functionalisation of Polystyrene: Friedel Crafts Method

5.2.2.1 Synthesis

The second strategy employed to functionalise the polystyrene (Scheme 5.3) required a slightly longer four step synthesis and involved synthesis of a ketone and its reaction in the crossed Claisen reaction used in chapter 4.



Scheme 5.3: Synthesis of aluminium coordinated polystyrene

The polystyrene was again synthesized by atom transfer radical polymerisation. Acylation was carried out in high yield by a method given by Jenekhe,[6] producing a polymer with 50% of the repeat units converted to the ketone **82**. The acac functionality was formed by a crossed Claisen reaction **83**.[10] Several different bases were used in the reaction including sodium methoxide, sodium ethoxide and sodium hydride with sodium hydride proving to be the most successful. The ^{1}H NMR spectrum for such a flexible polymer produces peaks that are very broad. As a result it is difficult to accurately determine the degree of formation of the diketone; nevertheless we estimate that in this case approximately 8% functionalisation was obtained. This 1,3-dicarbonyl exists as a keto-enol tautomer as in the analogous small molecule dibenzoylmethane (Figure 5.2). For dibenzoylmethane the equilibrium lies heavily towards the enol tautomer.[11] Infra-red analysis provides key evidence that the third step in scheme 5.3 has been successful. Polyacetyl styrene **82** shows an intense band at 1684 cm^{-1} caused by the C=O stretching mode which is characteristic of a ketone. For the dicarbonyl polymer, an intense band does exist at 1683 cm^{-1}, however there is an additional band at 3447 cm^{-1} caused by the hydroxyl functionality in the enol.

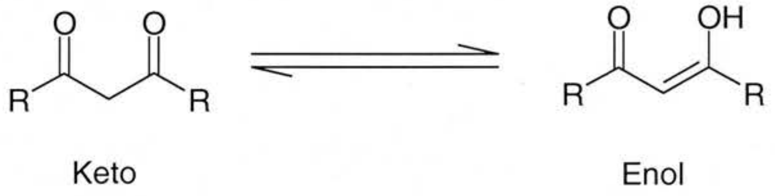


Figure 5.2: keto-enol equilibrium

Complexation of the polymer with aluminium was achieved by reaction of the polymer with aluminium trisisopropoxide and two equivalents of hydroxyquinolate **84**. Infra-red analysis shows that the hydroxyl band at 3447 cm^{-1} has decreased in intensity relative to **83**. Elemental analysis of **84** indicates 1.38% nitrogen which suggests one aluminium complex repeat unit to approximately 12 un-coordinated units and is consistent with the 8% acac functionalisation determined from the proton NMR of **83**. The GPC data (Table 5.1) show increasing molecular weights with each step of the reaction. This increase is greater than would be expected for 8% aluminium complex functionalisation. This may be accounted for by the polymer having reduced flexibility relative to polystyrene, which appears to give a higher molecular weight in GPC analysis.

Table 5.1: Molecular weights of functionalised polystyrenes

	Mn	Mw	P.D.
Polystyrene **79**	8300	9100	1.092
Acetyl Polystyrene **82**	11900	28300	2.389
Diketo Polystyrene **83**	17800	36700	2.063
Alq_2 Polystyrene **84**	27700	73500	2.657

5.2.2.2 Optical Properties

The absorption spectrum of the aluminium-containing polymer **84** consisted of two peaks at 256 and 363 nm (Figure 5.3). This is in accordance with the findings of Periasamy et al.,[12] who report two intense absorption peak for Alq_3 in DCM at 261 and 390 nm which are assigned to ligand centred electronic transitions. Note that large differences in absorption spectra for the heteroleptic Al complexes are not expected, since the aluminium acetylacetonate di-8-quinolate complex prepared in chapter 4 also displayed two peaks at 260 and 388 nm in the absorption spectrum. Additionally Weck observed that the optical properties of the aluminium complexed norbornene polymer were independent of the polymer backbone and are comparable to the pure Alq_3 properties.[3]

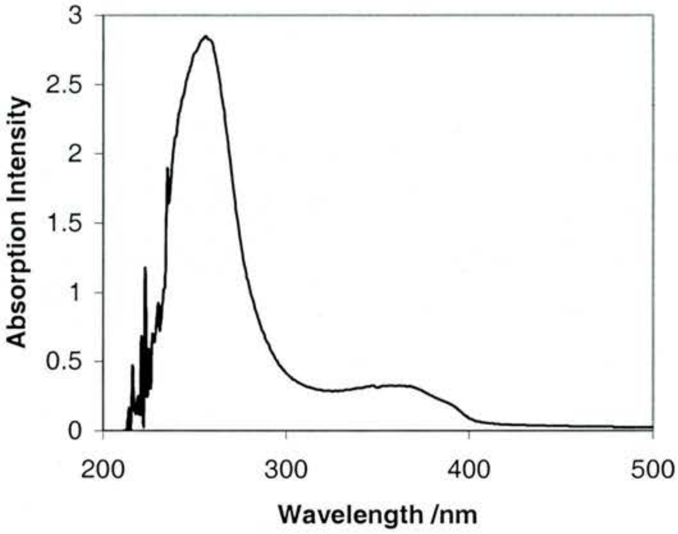


Figure 5.3: Absorption Spectrum of ***61*** *in* $CHCl_3$

Excitation into each intense absorption i.e. at 260 and 380 nm produces light emission at 516 nm (Figure 5.4). This indicates that the optical properties of aluminium trisquinolate have been retained and are unaffected by coordination to the polystyrene through the acac moiety.

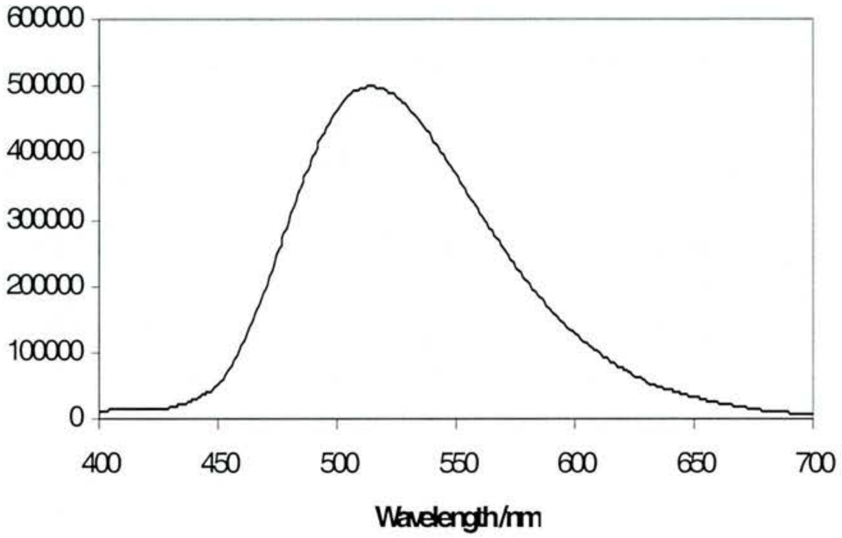


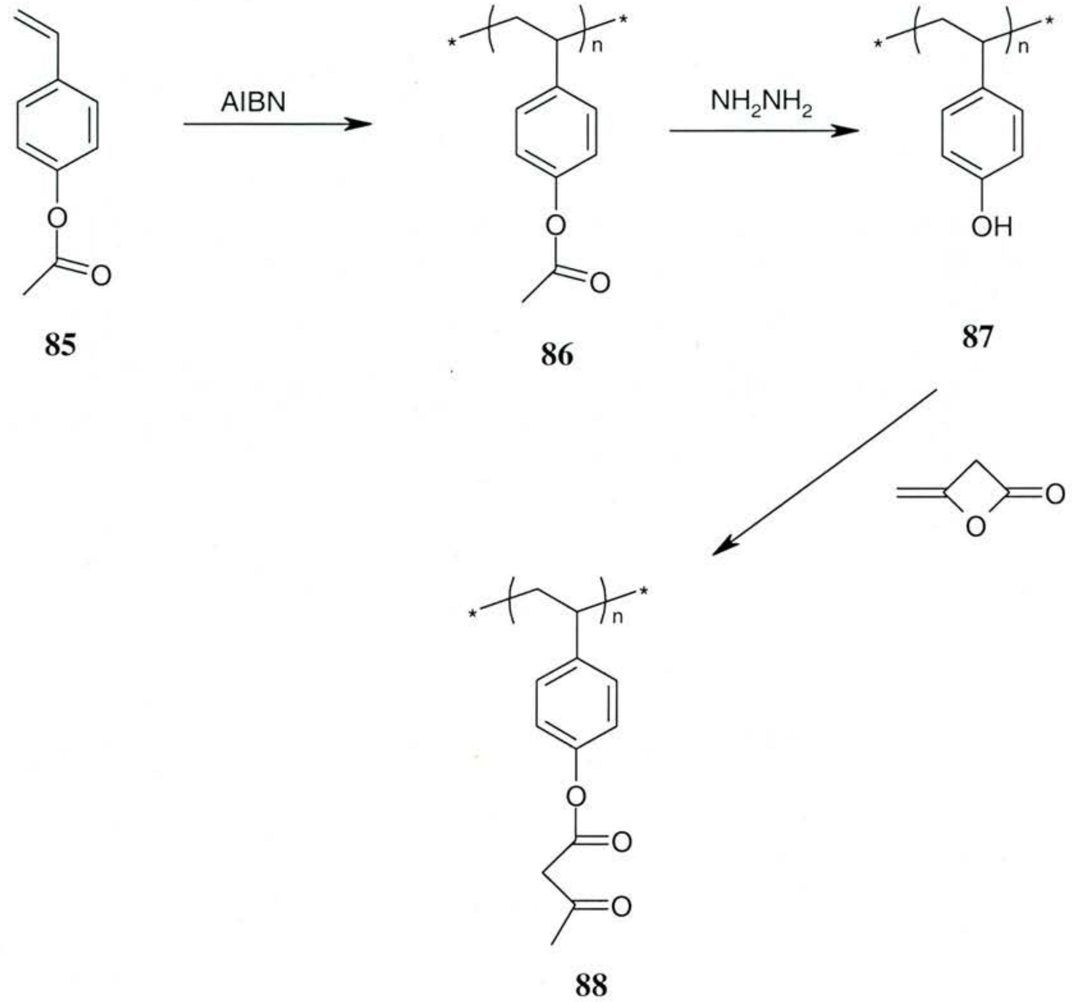
*Figure 5.4: Solution photoluminescence of **61** in THF (λ_{ex} = 360 nm)*

Only a small quantity of this polymer was produced so it was desirable to repeat the procedure and also increase the fraction of repeat units attached to the chromophore. Polyacetylstyrene was prepared with near quantitative yield of repeat units substituted with acetyl groups. However, conversion to the acac moiety **83** produced a material insoluble in common organic solvents. To determine whether this insolubility was as a result of the higher degree of functionality polyacetystyrene with approximately 50% functionalisation was produced. However, this also produced insoluble material when reacted in the crossed Claisen step. One possible explanation of this behaviour lies in the presence of metal ions (copper) from the synthesis of polystyrene which may coordinate to the acac units being formed causing the polymer to cross-link and become insoluble. Extensive purification was carried out on the polystyrene including repeat precipitation into methanol and hexane, washing with acid and washing with EDTA to remove any metal ions. The polyacetylstyrene produced form this rigorously-purified polystyrene precursor was itself precipitated many times into methanol. Frustratingly, after these extended purifications reaction with ethyl benzoate gave only the polyacetylstyrene starting material, underlining the unreliability of our synthetic route. Clearly, it would be desirable to design a reliable synthetic route for the properties of this polymer to be optimised or different metals to be coordinated to the polymer.

5.2.3 Functionalisation of Polyhydroxystyrene

Reaction of the diketene directly onto aromatic rings is a little used reaction due to low yields. However, several papers have been published in which diketene is successfully reacted with an alcohol or amine group.[13] It was hoped that by preparing poly(4-hydroxystyrene) that this could react with the diketene to synthesize the acetylacetonate moiety in a more reproducible way (Scheme 5.4).

For the polymerisation stage a protected hydroxyl functionalised monomer is required and acetoxystyrene **85** was chosen for this purpose. To remove the inhibitors, it was attempted to filter the monomer through a short alumina column. Unfortunately, this could not be achieved, as the monomer is very viscous and could not be flushed through the column. Atom transfer radical polymerisation (ATRP) was attempted on the monomer with the inhibitors present however no polymer was obtained. In order to determine the feasibility of the reaction scheme a free radical polymerisation was carried out. Using this method a polymer **86** of Mn 10400 (P.D. = 1.28) could be obtained even in the presence of the inhibitor. The polymer was then deprotected with hydrazine hydrate following a method used by Dadmun.[14] The resulting product **87** was soluble in methanol and was precipitated in water. Infrared analysis showed the formation of a hydroxyl peak not present in the original polymer. Proton NMR still displayed a peak at δ2.0 ppm which is at the same shift as the acetoxy group in **86**. The difference in solubility is a clear indication that the deprotection reaction has been successful and the peak at δ2.0 ppm must be due to the amide by-product, acetylhydrazine, $CH_3CONHNH_2$. Several attempts to remove this amide impurity by repeated washing with water were tried but this was unsuccessful. Washing with dilute sodium hydroxide solution was also unsuccessful as the polymer dissolved in the basic solution. The reaction with the diketene was not attempted on the crude product and there was insufficient time to purify the polyhydroxystyrene and react this with diketene.



Scheme 5.4: Synthesis of ***acac moiety*** *via hydroxyl functional polystyrene*

5.3 Conclusions / Future Work

An aluminium complexed polystyrene has been prepared, combining the solution processing properties of a polymer with the light emission characteristics of Alq_3. Unfortunately, the synthetic route from poly(acetylstyrene) **82** to the acac functionalised polystyrene **83** was not reliable due to the vagaries of the Claisen condensation step.

Accordingly, a new route was developed from acetoxy polystyrene **86**. However, the chosen deprotection method gave rise to an amide by-product, acetylhydrazine, which could not easily be removed. An alternative method is required in which the troublesome side product is not formed. There are several different methods of deprotecting an acetoxy group. Potassium carbonate / methanol is one possible method of deprotection.[15] With this system polyhydroxylstyrene and methanoic acid are generated. The methanoic acid by-product will remain in solution when the polymer is precipitated from water and any traces that remain should be easy to wash away.

A second method of generating a hydroxyl functionalised polystyrene involves reducing polyacetylstyrene **82** to a secondary alcohol using lithium aluminium hydride.[16] The only conceivable flaw in this strategy, is that references in the literature only detail reactions of the diketene with primary alcohols. The secondary alcohol generated by this method may prove to be too unreactive for this reaction to be feasible.

In the future polystyrenes with varying percentages of coordinated aluminium complexes could be prepared in order to optimise the polymers properties such as solubility and charge transport with the light emission. It would also be interesting to synthesize other metal complexed polystyrenes such as the phosphorescent iridium complexes or rare earth complexes.

5.4 Experimental

All starting materials were obtained from Aldrich or Lancaster, were reagent grade and used without further drying or purification except where stated otherwise. Tetrahydrofuran was distilled over sodium and benzophenone in a continuous still prior to use. ^1H and ^{13}C NMR spectra were recorded on a Bruker Av-300 in deuterated chloroform solutions, operating at 299.998 MHz for ^1H and 75.45 MHz for ^{13}C.

Molecular weights were recorded on a Polymer Laboratories Gel Permeation Chromatography 120 Integrated GPC system with Polymer Laboratories gel 5 μm mixed column relative to polystyrene standards.

Infra-red spectra were recorded as KBr discs on either a Perkin Elmer Paragon 1000 or a Nicolet Avatar 360 FTIR spectrometer. Absorption Spectra were recorded in THF unless stated otherwise or as a thin film on a quartz substrate using a Varian Cary 300 Bio uv-vis machine Photoluminescence spectra were recorded either as a dilute solution in THF or as a thin film on quartz substrates.

Polystyrene 79

Styrene (9 ml, 95.4 mmol) was first purified by passing the styrene through a short column of alumina, stirring over calcium hydride overnight and then vacuum distilling from calcium hydride. Copper (I) bromide (0.2009 g, 1.40mmol) and 2,2'-dipyridyl (0.4848 g, 2.83 mmol) were placed in a Schlenk flask which was then evacuated and filled with nitrogen three times. To this was added the styrene by syringe and finally phenylethyl bromide (0.195 ml, 1.43 mmol) which had been degassed for 30 mins. by bubbling nitrogen through it. Residual oxygen was then removed by two freeze-thaw cycles and the mixture was heated to 110°C for 5 hours. Once cool the mixture was dissolved in THF and filtered on a Bűchner funnel to remove catalyst residues. The filtrate was then poured into methanol (150 ml) to precipitate the product as a fine white powder (5.65 g, 56.9%)

^{1}H NMR δ (ppm) 6.8 - 7.2 (br s, 3H), 6.2 - 6.8 (br s, 2 H), 1.6 - 2.0 (br s, 1H), 1.2 - 1.6 (br s, 2H)

Mn = 8305 Mw = 9066 P.D. = 1.09

Attempted Reaction of Diketene with Polystyrene Aimed at Preparing polymer 80

Polystyrene (1.04 g, 9.99 mmol) was placed under an atmosphere of nitrogen and dissolved in dry THF (20 ml). Diketene (1 ml, 13 mmol) was distilled under vacuum (50 °C / 10 mmHg) prior to use and added to the reaction. Aluminium chloride (2.9 g, 20 mmol) was added in portions and the reaction controlled by cooling in an ice bath when necessary. The reaction was then allowed to warm to room temperature and stirred for 2 hours. Dilute hydrochloric acid was added to quench the reaction and the aqueous layer was extracted with ethyl acetate. The solvent was reduced to a minimum under evaporation and this was then poured into methanol. A white precipitate was collected (1.09 g) which was determined to consist of unreacted polystyrene by ^{1}H NMR.

Reaction of Diketene / HCl with Polystyrene; Attempted Preparation of Polymer 80

Diketene (1 ml) was distilled under vacuum (50 °C / 10 mmHg) and was placed in a schlenk tube under an argon atmosphere. Hydrogen chloride gas was generated by dropping concentrated sulphuric acid onto sodium chloride and bubbling this through the diketene. The diketene was then cooled to -78°C in a dry ice / acetone bath and evacuated with a water pump. During this period the diketene solution turned pale yellow and the weight of the schlenk increased., Polystyrene (1.01 g, 9.70 mmol) was dissolved in dry THF (10 ml) and added dropwise to the diketene. Aluminiuim chloride (2.88 g, 21.6 mmol) was added in portions. Cooling in an ice bath when necessary controlled the reaction. This was then allowed to warm to room temperature and stirred overnight. Dilute hydrochloric acid was added to quench the reaction. The organic components were extracted with ethyl acetate. The volume of solvent was reduced under vacuum and then precipitated into methanol. A white powder was obtained which proved to be polystyrene by NMR analysis.

Poly(4-acetylstyrene) 82

Polystyrene (2.03 g, 19.5 mmol) was placed in a 3 necked round bottom flask and flushed with argon to this was added the aluminium chloride (5.82 g, 43.6 mmol) and carbon disulfide (50 ml). Acetyl chloride (3.5 ml. 49.2 mmol) was then added dropwise to the mixture, which was then heated to 45 °C overnight. Once cool the mixture was poured into a beaker of water and stirred at 30 – 40 °C for 1 hour to remove the carbon disulfide. After extracting with dichloromethane, the solution was concentrated under vacuum and then precipitated by pouring into methanol. The white powder was collected by filtration. (1.27 g)

^{1}H NMR δ (ppm) 7.3 - 7.8 (br s), 6.8 - 7.1 (br s), 6.2 - 6.6 (br s), 2.5 (s), 1.2 (s)

IR (cm^{-1}) 3025, 2924, 1684 (C=O), 1602, 1493, 1452, 758, 698

Mn = 11850 Mw = 28300 P.D. = 2.389

Dibenzoylmethane Functionalised Polystyrene 83

4-polyacetylstyrene (0.30 g, 1.20 mmol) was placed in a round bottomed flask under an argon atmosphere. Ethyl benzoate (2 ml) was added and the mixture heated to 110 °C. Sodium hydride (0.0623 g, 1.56 mmol) as a dispersion in mineral oil was added to the reaction and this was heated for a further hour, during which time the temperature of the reaction reached 150 °C. Once cool, water was added to the reaction mixture and the aqueous layer was extracted with ethyl acetate. The excess solvent of the combined organic extracts was removed under reduced pressure. The crude product was then precipitated into methanol and the polymer collected by filtration. A white powder was obtained (0.256 g)

^{1}H NMR δ (ppm) 7.8 – 8.0 (br s), 7.3 – 7.7 (br s), 6.8 – 7.1 (br s), 6.2 – 6.5 (br s), 2.3 – 2.5 (br s), 1.20- 1.8 (br s)

IR (cm^{-1}) 3447 (OH), 3027, 2925, 1683, 1605, 1270, 701

Mn = 17780   Mw = 36670   P.D. = 2.063

Al Complexed Polystyrene 84

Aluminium isopropoxide (0.0632 g, 0.309 mmol), acac polystyrene (0.22 g, 0.3107 mmol per acac repeat units) and 8-hydroxyquinoline (0.945 g, 0.651 mmol) were placed in a 3 necked round bottomed flask under an argon atmosphere. Dry toluene (15 ml) was added and the mixture heated to 40 °C for 1 hour. The mixture was allowed to cool to room temperature and stirred overnight. A yellow precipitate formed which was filtered. The filtrate was dissolved in the minimum amount of solvent and precipitated in hexane the pure product was collected by filtration (0.0474 g)

^{1}H NMR δ (ppm) 8.5 – 8.7(br s), 7.8 – 8.1 (br s), 6.5 – 7.5 (br m), 6.1 – 6.5 (br s), 2.0 – 2.5 (br s), 1.1 – 1.9 (br s)

IR (cm^{-1}) 3025, 2924, 1683

Mn = 27650   Mw = 73460   PD = 2.657

CHN analysis Found: C 79.73, H 6.78, N 1.38

Polyacetoxystyrene 86

Acetoxystyrene (2 ml, 13.1 mmol) and azobis(isobutyronitrile) (0.0052 g, 0.032 mmol) were placed under an inert atmosphere and dissolved in anhydrous toluene (15 ml). The reaction mixture was heated to 60 °C for 18 h. The solvent was reduced to a minimum on a rotary evaporator and the mixture was precipitated into methanol. A white powder was collected by filtration. (1.63 g, 76.9 %)

^{1}H NMR ($CDCl_3$) δ (ppm) 6.9 - 6.6 (br s, 2H), 6.6 - 6.2 (br s, 2H), 2.2 (s, 3H), 1.9 - 1.7 (br s 1H), 1.4 - 1.2 (br s, 2H)

IR (cm^{-1}) 1762 (C=O), 1507, 1370, 1218, 1016, 912, 847

Mn = 10400 Mw = 13300 PD = 1.28

Poly(hydroxylstyrene) 87

Polyacetoxystyrene (0.75 g, mmol) was placed in a round bottomed flask under an argon atmosphere and dissolved in dioxane (15 ml). Hydrazine hydrate (2.5 ml, mmol) was added dropwise. The reaction mixture was then stirred at room temperature for 40 hours. The solvent was reduced to a minimum on a rotary evaporator and the crude product was precipitated in water. A white powder was collected by filtration (0.18 g, 32.4%).

^{1}H NMR (CD_3OD) δ (ppm) 7.0 - 6.0 (br s, 4H), 2.0 - 1.7 (br s, 1H), 1.7 - 1.2 (br s, 2H)

IR (cm^{-1}) 3367 (OH), 1612, 1512, 1448, 1374, 1231, 828

Mn = 8079 Mw = 15360 PD = 1.902

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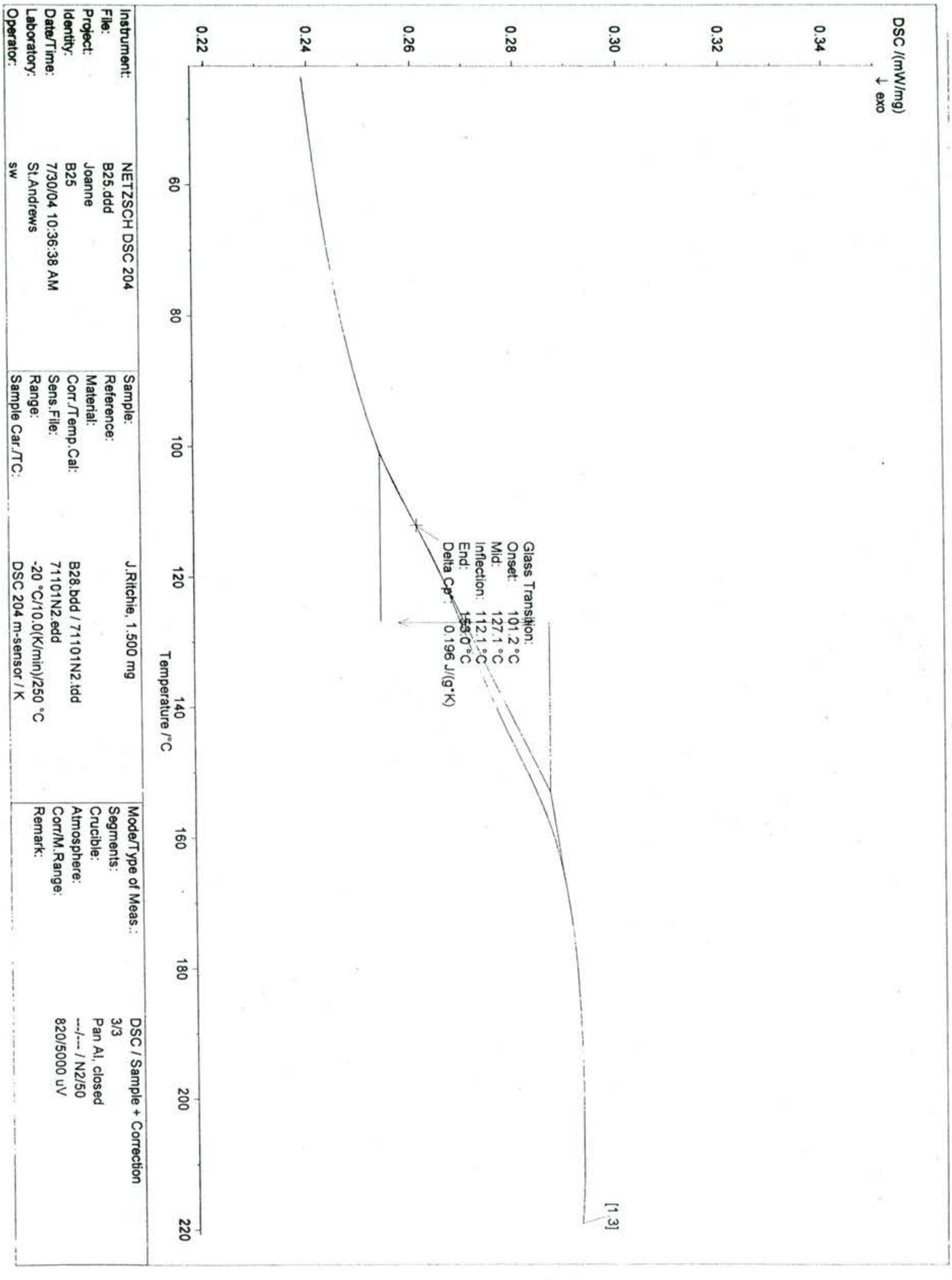
Appendix 1



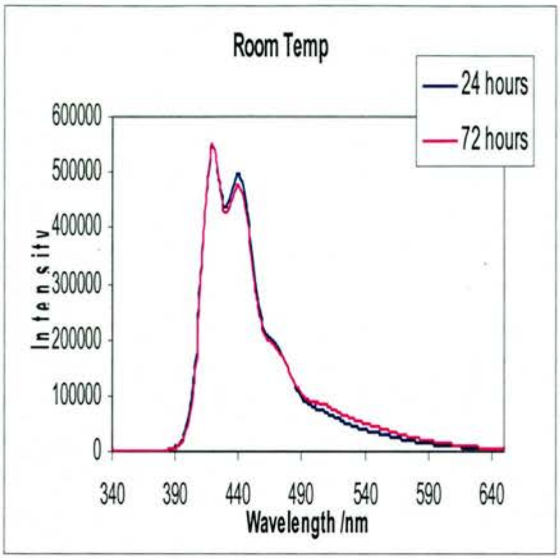
Glass Transition:
Onset: 101.2 °C
Mid: 127.1 °C
Inflection: 112.1 °C
End: 153.0 °C
Delta Cp*: 0.196 J/(g*K)

Instrument: NETZSCH DSC 204
File: B25.ddd
Project: Joanne
Identity: B25
Date/Time: 7/30/04 10:36:38 AM
Laboratory: St.Andrews
Operator: sw

Sample: J.Ritchie, 1.500 mg
Reference:
Material:
Corr./Temp.Cal: B28.bdd / 71101N2.tdd
Sens.File: 71101N2.edd
Range: -20 °C/10.0(K/min)/250 °C
Sample Car./TC: DSC 204 m-sensor / K

Mode/Type of Meas.: DSC / Sample + Correction
Segments: 3/3
Crucible: Pan Al, closed
Atmosphere: ---/--- / N2/50
Corr/M.Range: 820/5000 uV
Remark:

Appendix 2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24 hours
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400000
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200000
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0
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390
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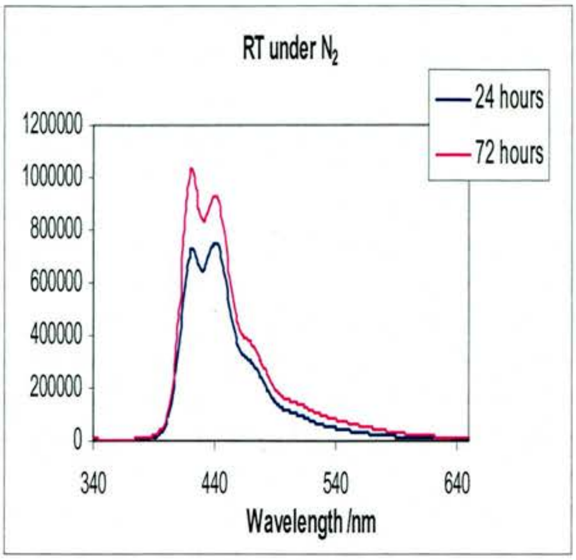
490
540
590
640
Wavelength /nm


RT under N_2
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72 hours
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1000000
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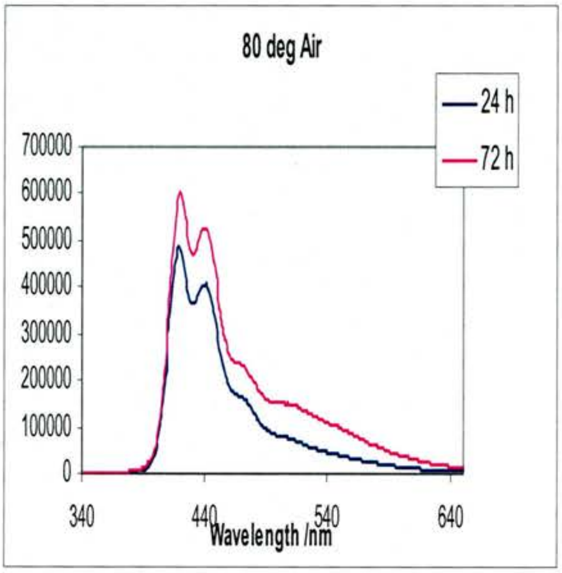
400000
200000
0
340
440
540
640
Wavelength /nm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24 h
72 h
700000
600000
500000
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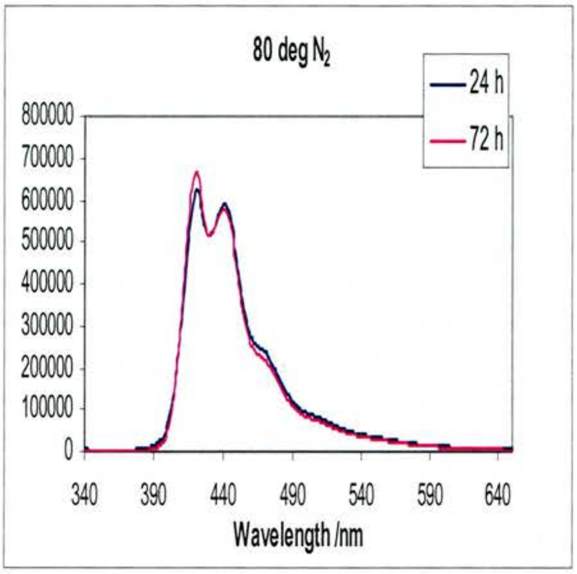
300000
200000
100000
0
340
440
540
640
Wavelength /nm


80 deg N_2
24 h
72 h
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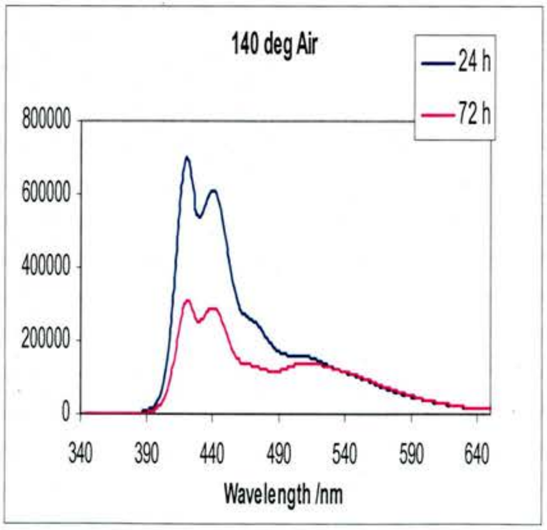
640
Wavelength /nm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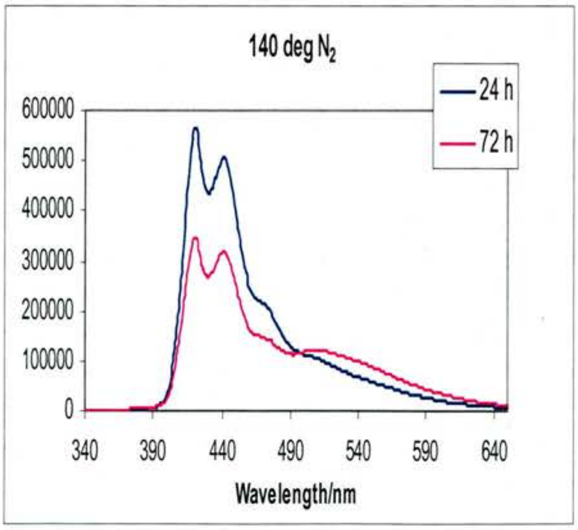
Wavelength /nm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72 h
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540
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640
Wavelength/nm