A Computational and Electrochemical Study of Electropolymerised Indoles

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"Don’t you realise you’ll find next Monday or next Tuesday
Your golden shoes day”

Vivian Ellis

The spin density distribution of the asymmetric indole trimer radical cation.
Abstract

The electropolymerisation of a range of 5-substituted indoles results in the formation of redox active films. The redox species present in the films have been characterised as the asymmetric trimer. These films are observed to be extremely photoluminescent and the chief fluorophore has been identified as the trimer. Initial studies have involved electrochemical and photophysical investigation with a view to potential application as fast response potentiometric sensors or as materials for light emitting devices. This thesis extends this work by presenting a computational and electrochemical study of a range of electropolymerised 4-, 5-, 6-, and 7-substituted indoles.

This research has employed the powerful combination of computational quantum chemical methods with electrochemical techniques to explore the electronic structure of the 5-substituted indoles. Density Functional Theory and semi-empirical calculations have shown that it is possible to predict oxidation potentials to within ±0.1 eV of the experimental values. Calculation of the electronic structure of the monomer radical cation, the species involved in trimer formation, has shown a difference in the calculated π-spin density distribution between indoles with electron withdrawing substituents and indoles with electron donating substituents. For those with electron withdrawing groups the unpaired electron is located at the 3-position which is consistent with the formation of a dimer via 3,3'-linkage in the initial stages of polymerisation. For indoles with electron withdrawing substituents the chief location of the unpaired electron in the radical cation is near the substituent consistent with previous experimental observation that trimerisation of these indoles will only occur on a surface of a preformed trimer film.

The electronic structure of the indole radical cation has been probed by studying the effect of the substituent nature and position. The electrooxidation of a various 4-, 6- and 7-substituted indoles result in redox films consisting of novel indole trimers. The monomers and electropolymerised films are photoluminescent and the common fluorophore observed infers that the chief fluorophore in the films are indole trimers. Quantum chemical methods predict oxidation potentials of these indoles in good agreement to experimental values. The transmission of substituent electronic effects through the aromatic system of the indole radical cations is again different for electron withdrawing and electron donating substituents.
A computational study of the polymerisation process by consideration of the \( \pi \)-spin densities of the radical cation species reveals that a 3,3'-linkage is most likely for 5-substituted indoles with electron withdrawing groups and other indole radical cations with the spin density in the C3 position. In the dimer radical cation a redistribution of the location of the unpaired electron to the C3-C2 bond is consistent with the formation of the asymmetric trimer. For indole radical cations with the spin density at the C2 position an alternative mechanism to the asymmetric is likely \textit{via} the 2,2'-dimer. This method can be used to screen indoles monomers for potential candidates for polymerisation.

The rate of coupling of the 5-substituted indole radical cations during the polymerisation reaction at a 5-cyanoindole trimer modified electrode was investigated using Koutecky-Levich analysis. A correlation can be drawn between the radical cation coupling rate and the monomer oxidation potential, implying that the coupling rate depends on the reactivity of the radical cation. Two exceptions are noted and these are 5-aminoindole and 5-nitroindole.

A detailed study of the electrooxidation of 5-carboxaldehydeindole concentrated on the influence of the substituent on the electrochemical and photophysical properties. The electron withdrawing nature of the substituent gives rise to relatively high indole monomer oxidation potentials and upon electrooxidation trimers are formed with high half wave potentials. The carbonyl chromophore is responsible for the observed extreme sensitivity of monomer and trimer emission properties to the solvent environment. Low temperature studies revealed that both monomer and trimer are phosphorescent allowing the position of the triplet to be located and the phosphorescent lifetime to be measured.

Polymer Electrochemiluminescence (ECL) studies of the 5-cyanoindole trimer with benzophenone have been observed to give rise to ECL emission. This originates from the indole trimer, most probably \textit{via} triplet - triplet annihilation. These experiments can be used to screen novel conducting polymers for their potential application in light emitting devices.
Declaration

I hereby declare that the work presented in this thesis is my own unless otherwise stated by reference.
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Chapter 1
Introduction

1.1 Introduction

Conducting polymers are an exciting class of electronic materials which have attracted increasing interest since their discovery in 1977\(^1\). They are beginning to find application in battery materials, electrochromic displays, sensor technology, light emitting devices and molecular electronics. The electrical and optical behavior of these materials originate in their geometrical and electronic structures and much understanding has been gained by using electrochemical and spectroscopic methods to synthesise and characterise them. However commercial applications, to date, are not as numerous as one would expect based on the considerable amount of work in this area. This lies in the fact that electropolymerised conducting polymer films often have irreproducible structures. Ideally for commercially attractive films a high degree of reproducibility is required and it is for this reason that research on electropolymerised indoles is extremely interesting. During the electropolymerisation of indole mass transport kinetics are obeyed and a high degree of control can be achieved over the growth process. Furthermore a comprehensive photophysical study has been carried out and the electrooxidation products have been observed to be extremely fluorescent. These properties make electropolymerised indole films interesting candidates for commercial sensor and light emitting applications and further understanding is the motivation for the research presented in this thesis.

Electropolymerised indole was first produced by Tourillon et al\(^2\) in 1982 and since then considerable work has focused on its electrochemical and spectroscopic properties. However little attention has been given to the study of the electronic structure of indole, electropolymerised indole and its derivatives. Computational quantum chemical methods are beginning to have many applications in chemistry and are becoming more accessible to the experimental chemist. They can be used to interpret experimental results, provide supplementary information and perhaps may even be used as a predictive tool. Consequently, these techniques can be used to calculate the molecular and electronic properties of novel electronic materials such as electropolymerised indole. Computational methods should not be seen as a replacement for conventional experiments but instead the two approaches may complement one another.
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It is a combination of quantum chemical methods and electrochemical techniques that has been applied in the course of this research. This chapter introduces the subject of conducting polymers and reviews their synthesis and applications. Previous research on indole conducting polymers is then reviewed. The last section of this chapter discusses computational studies of conducting polymers and describes previous quantum chemical studies of indole and electropolymerised indole.

1.2 Conducting polymers

1.2.1 Advances in conducting polymers

In 1977 Heeger et al found that poly(acetylene) (PA) (Figure 1.1), an intrinsically insulating polymer, becomes highly conducting upon treatment with oxidising (electron accepting) or reducing agents (electron donating). The oxidation and reduction reactions which induce high conductivity are also referred to, in the language of semiconductor physics, as p-doping and n-doping respectively.

![Figure 1.1 The structure of poly(acetylene).](image)

Upon oxidative treatment the conductivity of PA can reach levels comparable with metals ($10^6 \text{Scm}^{-1}$). This discovery sparked much interest due to the possibility of combining the useful physical properties of synthetic polymers, (strength, elasticity, plasticity) with the electrical conductivity of a metal. However PA was observed to be unstable in air and this motivated research to find a more stable conducting polymer (CP). In 1980 Shacklette et al discovered that poly(p-phenylene) (PPP) could be doped to conductivity levels comparable to those in PA. This discovery paved the way for the development of a wide range of CPs. Some of the most widely studied types of conducting polymer are shown in Figure 1.2. The term conducting polymer is now often extended to include a wide range of organic aromatic polymers and oligomers even though most are only conducting in their oxidised form and in some, charge transfer occurs by means of redox hopping. CPs can be based on heterocycles, benzoid and non benzoid hydrocarbons. The essential characteristic being that the monomers must link together to form a polymeric species with a delocalised $\pi$-electronic system which allows efficient conductance of charge.
The most widely studied area is that of polyheterocycles, produced from monomers which have a five membered ring structure. Studies of polypyrrole and polythiophene (Figure 1.2) have dominated this area. Although the actual mechanism of charge conduction has been the subject of considerable debate, these polyheterocycles exhibit a conjugated $\pi$-electron system along which conduction of charge can occur. Their popularity stems from their high environmental stability, high conductivities and structural versatility. Manipulation of the monomer structure and judicious substitution allows modulation of the electronic and electrochemical properties of these polymers. There is also a large amount of research into conjugated polymers of poly($p$-phenylenevinylene) (PPV) as they are beginning to find commercial applications in light emitting devices. Consequently, at present, there is considerable drive to engineer novel conducting polymers in order to tailor the electronic and optical properties.

1.2.2 Synthesis of conducting polymers

Considerable research has been dedicated to the synthesis of conjugated polymers. There are four general polymerisation methods cited in the literature. These are electrochemical synthesis, Lewis acid induced polymerisation, ring opening methathesis and transition metal catalysed coupling. The latter three chemical methods have been used to produce poly(thiophenes), poly(acetylene) and poly(quinoxaline), (such as poly(2,3-quinoxaline-5,8-diphenyl) used in Chapter 9) respectively and have been reviewed elsewhere. The following section will focus on electropolymerisation as this method has been employed to produce the poly(indole) films described in this thesis.
The electrochemical synthesis of CPs, first explored with polypyrrole, has proven important in the development of novel polymeric materials. This method uses the ability of a monomer to self-couple upon electrooxidation (anodic polymerisation) or reduction (cathodic polymerisation). During an anodic polymerisation the monomer is dissolved in a solution containing a supporting electrolyte and is directly oxidised at an electrode. Using this method CPs have been obtained from a wide range of monomers which include thiophene, furan, carbazole, and polyaromatic monomers such as azulene, pyrene and fluoroanthrene. The growth of the polymer film at an electrode is believed to initiate via a nucleation process at specific sites on the electrode surface and is thought to be similar to the process observed for the deposition of metals on an electrode. Inert electrode materials such as platinum, gold or an indium tin oxide (ITO) film on a glass slide are commonly used, although a platinum surface appears to provide a larger number of active nucleation sites. This leads to a more compact and homogeneous film.

It is undisputed that anodic polymerisation begins with monomer oxidation to form a radical cation. However there remains significant discussion as to the ensuing steps that lead to the polymer formation. The mechanism widely accepted for the electropolymerisation of heterocycles such as pyrrole or thiophene by anodic coupling proceeds via the coupling of radical cations. A schematic of this general mechanism is shown in Figure 1.3.

The first step of the process is a one electron electrooxidation of the monomer which forms a very reactive radical cation at the electrode. The second step involves the coupling of two radical cations to produce a dihydrodimer dication which leads to a neutral dimer after loss of two protons and rearomatisation. Due to the applied potential the dimer, which is more easily oxidised than the monomer, is oxidised to its radical form by the electrode and undergoes a further coupling with a monomeric radical cation. The polymer is generated by a succession of these coupling reactions which occur at sites on the radical cation species with the largest radical electron density.
Figure 1.3 A schematic of the anodic polymerisation mechanism of aromatic five
membered heterocycles, (X represents NH, S or O).

This is often termed an E(CE)n process as the first step is electrochemical (monomer
oxidation) which is then followed by a series of chemical (radical cation linking, proton
loss and rearomatisation) and electrochemical steps (oxidation of the neutral oligomer
formed). The long chain polymers generated are often insoluble so the polymer is deposited
onto the electrode surface as a film. Due to the conductivity of the film further monomer
arriving at the electrode will become oxidised, continuing the growth of the polymer film.

Evidence for the E(CE)n mechanism has been obtained from ultrafast cyclic voltammetry,19
rotating disc studies20 and pH measurements.21 These have shown the presence of radical
cations, radical oligomers and protons during the electropolymerisation process. However
conflicting mechanisms have been proposed. One such alternative involves electrophilic
addition of the oxidised monomer to the neutral monomer.22 Another mechanism proposed
that the radical cation, once formed during electrooxidation, undergoes proton elimination
which is assisted by the solvent to give rise to a neutral monomer radical.23 Subsequent
coupling reactions between two neutral radicals will then afford a neutral dimer. Continued
research of the polymerisation process is necessary to elucidate the mechanism of
electropolymerisation.
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Figure 1.4 The reversible uptake of counterions during redox cycling of a conducting polymer film reproduced from reference 60.

The adsorbed polymer films are formed in their oxidised state with counterions from the supporting electrolyte incorporated into the film to maintain electroneutrality. These films can be reversibly cycled between the oxidised state, where anions are present in the film and a neutral reduced state, where anions are expelled back into the solution. This process of reversible uptake of counterions is summarised in Figure 1.4.

There are inherent advantages of the electrochemical synthesis over chemical routes. The polymer is produced in an oxidised and electrically conducting state where it is charge balanced by the incorporation of anions from the electrolyte. In conventional chemical methods first polymer synthesis is carried out which is subsequently followed by doping
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and processing in order to produce the polymer in its conducting form. Electrochemical synthesis is cleaner than chemical routes as there are no by-products or catalyst material to remove from the reaction. It is also much easier to control the rate of reaction (by the current) and/or the energetics of the reaction (by the potential) of an electropolymerisation reaction with electrochemical techniques. Also by controlling the monomer radical cation concentration generated at the electrode it should be possible to produce homogenous and reproducible polymer films.

1.2.3 Applications of conducting polymers

Potential applications of conducting polymers are numerous. They can be divided into three main categories. The first group of applications utilises the conjugated polymer in the neutral state and are often based around their semi-conducting properties such as the active material in a light emitting diode (LED). The second group includes uses of conducting films for electron transport, or electrostatic charge dissipation. Both of these two types of applications can be viewed as static applications as the polymers do not change their electronic state during operation. The final area of application is based on the ability of the polymers to undergo redox reactions and switch between charged states. These applications include battery materials, electrochromic devices, and biosensors. A further example of this last category, polymer electrochemiluminescence, shall now be discussed in greater detail.

1.2.3.1 Polymer electrochemiluminescence

Electroluminescence from electrochemical cells, known as electrochemiluminescence (ECL), has been known for many years. ECL involves the production of light at or near an electrode surface by electrochemically generating species capable of forming an excited state. The first ECL reactions involved electron transfer between electrogenerated radical cations (oxidised) and radical anions (reduced) with subsequent ion-annihilation reactions generating excited states that are capable of luminescence. The simplest scheme of this process is shown in Figure 1.5. Most of the ECL reactions studied involve organic molecular aromatic species (especially polyaromatic hydrocarbons (PAHs)) and certain transition-metal complexes.
Figure 1.5 The simplest scheme for the ECL reaction where $R^-$ symbolises electrogenerated radical anion and $R^+$ symbolises a radical cation of a PAH system. $R^*$ symbolises an excited state which then relaxes to give rise to ECL.

Recently there has been renewed interest in ECL production driven by the development of electrochemically based display devices. These are known as Light Emitting Electrochemical Cells (LECs). They are formed from a solid state sandwich structure, presented in Figure 1.6, which consists of a blend of luminescent conjugated polymer with solid polymer electrolyte (polyethylene oxide) complexed with a lithium salt (PEO:Li⁺) between two electrodes. The operating mechanism of the polymer LEC is shown schematically in Figure 1.6. Under an external bias the semi-conducting polymer is electrochemically doped p-type (oxidised) on one side and n-type (reduced) on the other side. Light is emitted from the compensated insulating region in the centre.

**Figure 1.6** The process that occurs in a LEC device. a) Injection of charge carriers from electrodes into the polymer/solid electrolyte mix and b) recombination of these oppositely charged species creating an excited state (★) which then radiatively decays. This schematic is reproduced from reference 27.
According to Pei et al.\(^\text{20}\) unlike polymer light-emitting diodes (LEDs), which utilise the semiconductor properties of non-doped conjugated polymers and conventional electrochemical cells, which utilise the redox properties of these polymers, LECs utilise both the semiconductor properties and the redox properties. LEC devices differ from conventional polymer LEDs as the former type of device have no ionic species to compensate for charges on the polymer chains. In many respects light generation from LECs appears to follow the classical pathways identified for ECL generation in solution.\(^\text{30}\) These pathways are discussed in detail in Chapter 9. The LEC devices exhibit delays in light production, have limiting currents consistent with diffusional mass transport and emit light with potential biases sufficient to generate the appropriate redox species in solution.\(^\text{30}\) Consequently an ECL approach can be used to investigate the potential application of polyindoles in light emitting devices and this study is described in Chapter 9. This simple electrochemical approach avoids the more complex fabrication of LECs involving solid polymer electrolytes.

Bard et al.\(^\text{31}\) have investigated electron transfer reactions and charge transfer in polymers by utilising ECL techniques. This group has carried out ECL experiments on one such polymer, a vinylpolymer of 9,10-diphenylanthracene (PVDPA), shown in Figure 1.7.\(^\text{31}\) This utilises electroactive and emitting moieties attached to a nonconjugated polymer backbone. The electrochemical behaviour of the polymer film is very similar to that for 9,10-diphenylanthracene (DPA) indicating that multiple electroactive groups on the polyvinyl chain do not interact strongly. Emission occurs upon stepping the potential between +1.6V, where the electroactive DPA groups are oxidised to radical cations and -2.0V, where radical anions are formed. Charge movement probably involves hopping between DPA groups with excitation involving anion / cation (or electron / hole) annihilation reactions in the polymer film.

ECL studies have also been carried out on conjugated polymers. In 1984 Bard et al.\(^\text{22}\) reported ECL from the reaction between reduced and oxidised centres of 4-methoxy-(2-ethylhexoxy)-2,5-poly(phenylenevinylene) (MEH-PPV), shown in Figure 1.8(c). This compound is a member of a broad class of light emitting conjugated polymers based on the poly(p-phenylenevinylene) backbone which has been studied in great detail as they can be made into solid state LEDs. Pei et al have carried out other solution ECL studies involving films of poly(3-hexylthiophene) (6-PAT)\(^\text{33}\) and poly(2-methoxy-5-dodecyloxy-p-
phenylenevinylene (MDOPPV). All three polymers are capable of undergoing both reversible electrochemical oxidation and reduction. The ECL emission is essentially the same as thephotoluminescence spectrum and can be assigned to an excited state formed as a result of an annihilation reaction between electrogenerated oxidised and reduced centres in the polymer film. The ECL mechanism for MEH-PPV at the electrode / polymer interface is illustrated by Figure 1.9. Bard proposed that continual anodic / cathodic pulsing of the electrode produces orange ECL from MEH-PPV, resulting from the annihilation of electrogenerated oxidised and reduced centres.

\[
\text{PVDPA} \quad -e^- \rightarrow \text{PVDPA}^{**} \\
\text{PVDPA}^{**} + 2e^- \rightarrow \text{PVDPA}^- \\
\text{PVDPA}^{**} + \text{PVDPA}^- \rightarrow \text{PVDPA}^* + \text{PVDPA}
\]

Figure 1.7 The structure of 9,10-diphenylanthracene (PVDPA) vinylpolymer and the mechanism of ECL during a double potential step experiment. (*) Indicates an excited state.

![Polymer Structures](image)

Figure 1.8 Polymer ECL studies have been carried out on a) poly(3-hexylthiophene) (6-PAT) b) poly(2-methoxy-5-dodecyloxy p-phenylenevinylene) (MDOPPV) and c) poly(4-methoxy-(2-ethylhexoxy)-2,5-p-pheneylenevinylene) (MEH -PPV).
The latest developments in this field have progressed towards device fabrication. Two electrode ECL experiments with MDOPPV have shown that ECL can be observed for a polymer film on an electrode immersed in an electrolyte solution and also for a dry composite film with a solid polymer electrolyte (polyethylene oxide). Solution ECL studies have also been conducted of the lumophores of aluminium-quinolate (Alq₃) based organic light emitting diodes. These ECL studies give the researcher the ability to estimate the amount of energy (ΔE) required by a polymer light emitting system to electrically (or electrochemically) generate an emitting species. This information can be exploited in the optimisation of polymer based light emitting devices.

1.3 Indole conducting polymers

Conducting polymers can be produced from electrooxidation of the heterocycle indole. Indole (Figure 1.10), also termed benzopyrrole, can be thought of a pyrrole ring fused to a benzene ring. This section gives an overview of the previous research carried out on indole conducting polymers.

Figure 1.9 The proposed mechanism of an ECL reaction at the polymer/electrode interface. a) Oxidation of the polymer at the polymer / electrode interface occurs during an anodic pulse, this accompanied by the insertion of anions. b) Reduction of the polymer occurs during a cathodic pulse and electrolyte cations are inserted. c) Luminescence results from electron / hole annihilation. This schematic is reproduced from reference 32.

Figure 1.10 The structure of indole with the substituent positions.
1.3.1 Overview of indole electropolymerisation

Tourillon et al. first observed the formation of conducting polymer films upon the electropolymerisation of indole in 1982. These researchers proposed that polyindole contained dimeric units with N-N bonds between the monomer units, as shown in Figure 1.12(a). They did not, however, suggest a specific second linkage site to describe the linear polymer. Evidence for this was based on the observation that attempted electropolymerisation of N-methylindole did not result in a conducting polymer film and that the N-H band in the IR spectrum was not observed for a polyindole sample. Since then a range of possible structures and polymerisation mechanisms have been proposed by different research groups and these are shown in Figure 1.12. It was initially assumed that indole polymerised in a similar manner to other heterocycles such as pyrrole and thiophene and numerous theories concerning the polymerisation mechanism have tried to clarify the inconsistent behavior of polyindole to other heterocycles.

Waltman et al. proposed a possible 1,3'-linkage for polyindole, (Figure 1.12 (b)), based on the observation that conducting polymer films were obtained upon electrooxidation of indole and some 5-substituted indoles, however no films were obtained from 1-, 2-, or 3-substituted indoles. The 1,3'-coupling sites were proposed as a result of a semi-empirical INDO study of the radical cation spin density distribution. These are discussed further in Section 1.4. Bartlett et al. and Kim et al. agreed with the 1,3'-linkage, based on the results of experiments on polyindole and poly(5-carboxylic) acid indole using electron spin resonance (ESR), Fourier Transform Infra-red spectroscopy (FTIR), UV measurements and Scanning Electron Microscope studies (SEM).

In contrast Buckowska et al. proposed a 1,6'-linkage as presented in Figure 1.12(c). This challenged the structure proposed by Tourillon et al. on the basis of results from Raman and IR spectra of oxidized and reduced films on a platinum electrode. Their arguments were that stretching vibrations due to the N-N bond, which are usually strong in Raman spectra (approximately 1111 cm⁻¹ for hydrazine), were not observed. Also a broad absorption was observed in the N-H stretching (~3200 cm⁻¹) region in the IR spectrum of the oxidized sample. This also disagrees with the structure proposed by Waltman.
Figure 1.12 The proposed structures of polyindole. The a) 1,1'-linkage (Tourillon et al.) b) 1,3'-linkage (Waltman et al.)\textsuperscript{37} c) 1,6'-linkage (Buckoskwa et al.),\textsuperscript{42} d) 3,3'-2,2'-linkage (Zotti et al.),\textsuperscript{43} e) 1,1'-3,3'-linkage (Billaud et al.)\textsuperscript{45} and also proposed by Billaud et al.\textsuperscript{f)} the regular 3,2'-3,2'-linkage.

Zotti et al.\textsuperscript{43,44} challenged these proposed structures as a result of experiments on polyindole, poly(5-cyanoindole) and poly(5-carboxylic acid indole). In situ IR spectroelectrochemical experiments were used by this group to determine the structure of the polymer. They concluded the polymer was linear and contained C2 and C3 linkages, most likely via a regular alternating 2,2'-3,3'-linkage (Figure 1.12(d)) (assuming no rearrangement or bond breaking occurs on oxidation). An identical product was also produced from the anodic coupling of 3,3'-bi-indole, thus confirming that 3,3'-linkages exist in polyindole.

One of the most prolific research groups in this area are Billaud et al. During the past 6 years this research group has used a variety of electrochemical and spectroscopic techniques to investigate polyindole. These include investigations by scanning electron microscope, parallel detection electron energy loss (PEELS), X-ray photo electron XPS and FTIR spectrosopies.\textsuperscript{45} In a preliminary study, Billaud et al. excluded benzene ring linkages and they proposed instead a regular alternating linear polymer containing 1,1',-3,3'-linkages.\textsuperscript{45} FTIR, Raman and PEELS studies were later carried out by this research group\textsuperscript{46} and in contradiction to their previous spectroscopic paper, C2 and C3 sites were
proposed as the coupling positions of electropolymerisation. However they could not determine if these were a regular sequence, statistical or random. In their following papers, polyindole,\textsuperscript{47,48,49,50} poly(5-cyanoindole)\textsuperscript{47,48} and poly(5-nitroindole)\textsuperscript{51} were investigated by electrochemical methods and FTIR spectroscopy in acetonitrile and aqueous media (HCl, HClO\textsubscript{4}). These authors suggested that a regular 2,3'-linear polyindole polymer was most likely (Figure 1.12(f)). In an attempt to confirm this structure this Billaud et al carried out a semi-empirical study on the polymerisation mechanism. This is discussed further in Section 1.4.4. Recently this structure was also assumed by Bagheri et al\textsuperscript{52} and so controversy over the structure of electropolymerised indole and its derivatives still continues to the present day.

1.3.2 The asymmetric indole trimer

Mount and co-workers, at the University of Edinburgh, have carried out considerable work since 1992 in the area of electropolymerised indoles. Contrary to the linear structures proposed by other research groups, described in Section 1.3, Mount et al have shown that polymerisation of certain 5-substituted indoles gives rise to the formation of redox active films. The redox active species present in the films have been characterized as the asymmetric indole trimers (Figure 1.13).\textsuperscript{53}

![Figure 1.13 The structure of a 5-substituted asymmetric indole trimer.](image)

Initially work was concentrated on the polymerisation of indole, 5-carboxylic acid indole and 5-cyanoindole.\textsuperscript{54,55,56,57} It was observed that two different chemical species were present in the film which could be separated by their differential solubility in DMF. Characterization was achieved using UV-Visible spectroscopy, Time of Flight Laser Desorption / Ionisation mass spectrometry (L\textsuperscript{2}TOFMS), fluorescence spectroscopy, $^1$H NMR and IR spectroscopy. It was proposed that the DMF soluble product was the
asymmetric trimer and the DMF insoluble fraction was a polymer consisting of linked trimers. The trimer consists of 3 indole units linked through the C2 and C3 positions which is consistent with the observations of Zotti et al.\textsuperscript{43} and Billaud et al.\textsuperscript{47} The evidence for linked trimer units stems from the decrease in intensity of the N-H stretch in the IR spectrum which was first reported by Waltman et al.\textsuperscript{37} Mount et al.\textsuperscript{57} suggested that the formation of the trimer is achieved via initial coupling of the monomer radical cations to form a 3,3'-dimer. Further oxidation and coupling of the dimer with a monomer radical cation would yield the asymmetric trimer rather than a symmetric trimer. The process can be summarised by Schemes 1.1 and 1.2.

\[
3\text{In}_{(aq)} \rightarrow \text{In}_3^{+} + 7e^- + 6H^+ \quad \text{Scheme 1.1}
\]

\[
n\text{In}_3^{+} \rightarrow -\left(\text{In}_3^{+}\right)_n(s) + 2ne^- + 2nH^+ \quad \text{Scheme 1.2}
\]

The first step is the initial monomer oxidation and linking which occurs in the diffusion layer near to the electrode surface; this results in the deposition of a film of the asymmetric trimer on the electrode surface. Subsequent oxidation and adsorption of monomer occurs on top of this initial layer followed by radical cation adsorption and coupling to form more cyclic trimers. This is the mechanism that generates film growth. Trimers in the film can then undergo further oxidation to react with a neighboring trimer unit to form a conducting polymer chain. Controlling the mass transport of monomer to the electrode surface can give some degree of control over the composition of the film with respect to the trimer to polymer ratio. As trimer formation occurs at a faster rate than the linking reaction, at a high monomer concentration and high rotation speed, this gives rise to films with a higher trimer to polymer ratio.

The electrochemical results in acetonitrile presented by Billaud et al are consistent with those of Mount et al. However Billaud et al choose to interpret these results in terms of a linear polymer structure and have refrained from discussing or comparing research from the two laboratories. Due to the continued controversy over the polymerisation process further studies are required. In this thesis two studies of the polymerisation of indoles are presented. The first, discussed in Chapter 6, is a quantum chemical study and the second
(Chapter 7) is an electrochemical investigation of the radical cation coupling reaction at an electrode modified with a preformed poly(5-cyanoindole) film.

Although controversy over the structure of electropolymerised indole continues there are some workers who have agreed with the asymmetric trimer structure as proposed by Mount et al. Kokkindis et al. in 1996 examined the electropolymerisation of 4- and 5-nitroindole at a gold rotating disc electrode. Using electrochemical techniques they observed that asymmetric trimers can be obtained from both monomers. In the same year Bocchi et al. electropolymerised indole using I₂ as a counterion to obtain a crystalline product. From partial X-ray diffraction data they proposed an asymmetric trimer which they suggested formed as a result of radical cation coupling to form a 3,3'-dimer followed by reaction with a third monomer radical cation. The symmetric trimer was not observed.

1.3.3 Substituent effects

Waltman et al. and Mount et al. have both investigated substituent effects on the electrochemical properties of 5-substituted indole and the polymerisation process. Waltman observed that film formation could be achieved using 5-cyanoindole, 5-carboxylic acid indole, 5-bromoindole, 5-chloroindole and indole. Further research by Mount et al. showed that electroactive films could also be obtained for 5-nitroindole and thin films for 5-methylindole and 5-methoxyindole. For these last two, polymerisation was characterised by nonsteady state currents and accompanied by a large fraction of soluble product. It was suggested by Waltman et al. that polymer formation depends on the stability of the monomer radical cation which in turn depends on the electronic influence of the substituent. An electron withdrawing substituent, such as the cyano group, destabilises the radical cation which encourages linking to form a polymeric species. Conversely a strongly electron donating substituent, such as the amino group, stabilises the cation allowing them to diffuse away from the electrode before linking can occur. The research by Mount et al. has confirmed that the proposed electrooxidation structure and mechanism is consistent for all 5-substituted monomers that form a film. Furthermore, whilst 5-aminooindole and 5-hydroxyindole do not form films upon electrooxidation at a platinum electrode the use of a preformed 5-cyanoindole or 5-nitroindole film, as a template, promotes polymerisation. Film formation of these indoles occurs on top of this template layer. Due to the influence of the template film, polymerisation of these indoles follows a similar pathway to other film
Chapter 1 Introduction

forming indoles. This has been confirmed using ring disc and fluorescence studies. This was an important step as it allows polymer films to be produced from a much wider range of substituted indoles.

Variation of the substituent position has not been studied to any great extent. Waltman et al observed that films can be produced by electropolymerisation of 4-, 6- and 7-methylindoles, though the composition of these films were not further characterised. 37 Kokkindis et al have reported films electropolymerised from 4-nitroindole. 58 Mount et al reported that a trimer could be formed upon the electrooxidation of N-methyl indole which confirms that the N(1) position is not involved in the initial electrooxidation reaction. The products were mainly soluble and contained small amounts of linear oligomers which were shown to be redox inactive. The fluorescence spectrum showed that there is little further π-delocalisation in these linear oligomers than the trimer species. N-methylation removed the linking ability of these trimers which supports the proposed linking of 5-substituted trimers via the indole nitrogen atoms.

These previous studies suggest that there is huge scope for investigation into the effect of substituent position and type. This is studied in detail in this thesis by means of electrochemical, computational methods and fluorescence spectroscopy to give insight into the electronic effects of the substituent. This is the motivation for the research discussed in Chapters 4, 5 and 8 which will lead to further understanding of the indole electronic structure.

1.3.4 Photophysical properties of indole and electropolymerised indole

Indole and its derivatives are known to be highly photoluminescent. These molecules are of particular interest since they are the fluorescent chromophore of the amino acid tryptophan and have been used to probe the structure of various proteins. 62 The high quantum yield of indole has been attributed to promotion of an electron from a π molecular orbital to a π* orbital on exposure to electromagnetic radiation and the subsequent radiative relaxation to the ground state. Much research has concerned the sensitivity of the emission of indole to solvent polarity. In a polar solvent a large bathochromic shift of the emission is observed (causing a large Stokes shift), whilst the absorption is relatively unaffected. Various mechanisms have been proposed to account for this and the most popular concerns the inversion of two low lying excited states denoted \( 1L_a \) and \( 1L_b \). 63,64,65 These excited states are
close in energy and in the free molecule the $^1L_a$ state lies above the $^1L_b$ state. In a polar solvent, solvent relaxation occurs. The solvent molecules reorientate themselves around the excited state molecule before emission occurs to produce a system with a lower energy. The $^1L_a$ state in this case, lies below the $^1L_b$ state. In a non polar solvent the $^1L_b$ lies below the $^1L_a$ state even after this process has occurred and therefore emission is proposed to originate from the $^1L_b$ state. In polar solvents it is thought that solvent relaxation has a greater effect on the $^1L_a$ state which has been proposed to have a greater dipole moment. Consequently the $^1L_a$ state is lowered in energy below the $^1L_b$ state which gives rise to the bathochromic shift in emission. This theory was first suggested by Mataga et al in 1964 and since then considerable research has been aimed at understanding the response of the $^1L_a$ and $^1L_b$ states to the environment and there continues debate in this area. Mount et al have characterised the fluorescence spectroscopic properties of indole and its 5-substituted derivatives at room temperature and also at 77K. These results are consistent with $^1L_a$ / $^1L_b$ state inversion mechanism.

The observation of fluorescence from an electropolymerised indole was first made by Mackintosh and Mount in 1994. Since then a comprehensive photophysical investigation of indole monomer, trimer and ‘polymer’ species has been carried out by Jennings and Mount. The excitation and emission of the trimer chromophore occurs at a longer wavelength than those of the monomer, consistent with an increase in the delocalisation of π-molecular orbitals which extend over the entire trimer system. This is also reflected in the shorter fluorescent lifetime values. The emission of the trimer has less dependence on substitution than the monomer, implying a lower excited state dipole for the trimer than the monomer. Polymer species have been identified which have a broad emission band at longer wavelengths than the trimer. This suggests the presence of longer chains of linked trimers units with energy delocalisation over the chain. The observed intense photoluminescence of the trimers makes these materials extremely attractive for application in electroluminescent devices. Preliminary studies are reported in this thesis (Chapter 9) concerning the use of poly(5-cyanoindole) as the light emitting species in an ECL system.
1.3.5 Recent studies by Mount and co-workers

Recently the redox reaction and structural changes that are induced by redox cycling of electropolymerised films of poly(5-indole carboxylic acid) (5CAI) and poly(5-cyanoindole) (5CI) have been investigated by two methods. These are AC impedance\(^6^9\) and *in situ* fluorescence studies.\(^7^0\)

The AC impedance studies have shown that films of electropolymerised 5CAI and 5CI are deposited as highly conducting films with low electronic resistances.\(^6^9\) The steady state currents suggest good \(\pi\)-electronic communication through the film probably as a result of a high degree of stacking of trimer units. The 5CI films differ from 5CAI films by having a large barrier to counterion insertion and over prolonged redox cycling show little change in behavior. In contrast, 5CAI films exhibit a major change in behavior. Initially, these films show behavior similar to a porous metal electrode which alters over several days to behavior more like a redox hopping film. This was attributed to the presence of the three carboxylic acid groups on the 5CAI trimer which aid solvation, (a process not available to 5CI). It has been proposed that changes in the redox reaction and film structure are due to perchlorate anions moving in and out of the film and a second process for maintaining electroneutrality. The carboxylic acid indole trimers can lose a proton from the COOH substituent and so the charge on the polymer can be balanced by COO\(^-\). As the proton is lost to the bulk solution Li\(^+\) can be injected to maintain electroneutrality. This is supported by the sensitivity of the redox reaction to the nature of the cation. These structure changes in the film perhaps occur by reorientation of trimers which would affect interactions such as electron transport. If these changes result in a reduction of delocalisation then electron transport kinetics may change and therefore give rise to the changes observed in the redox behavior.

*In situ* fluorescence measurements have been reported by Jennings and Mount.\(^7^0\) They have given insight into the variation of the observed fluorescence quantum yield as a function of redox composition and electrode potential. The kinetics of the structural changes in the films have also been investigated by observing fluorescence with potential sweep rate. At high sweep rate the fluorescence / charge response indicates structural changes within the film, the extent of which can be reduced by linking the trimer redox centers.
1.3.6 Proposed applications of electropolymerised indoles.

Polymeric indoles films have been proposed as potential candidates for application as sensors and for the direct oxidation and reduction of biomolecules. Bartlett et al. observed that electropolymerised 5-carboxylic acid indole films were pH sensitive over the range of pH 1 to 7, and are therefore potential materials for pH sensors. These films exhibited a rapid response to changes in solution pH however were limited by the pH range. More recently, Mount and co-workers observed that films of poly(5-cyanoindole) have a rapid response to pH in the range pH 2 to 12. This wider range suggests that these films may be more suitable for application in a pH sensor.

Bartlett described the use of poly(5-indolecarboxylic acid) coated electrodes for the direct oxidation and reduction of horse heart Cytochrome C. The polymer is able to bind via the carboxylic acid substituent to lysine residues on the protein and electron transfer can then occur between the redox protein and the polymer modified electrode.

Pandey et al. have described the use of polyindole films in the fabrication of Cu$^{2+}$ and K$^+$ sensors. These researchers found that neutral films display a selective response for Cu$^{2+}$ ions in aqueous solutions with no response observed for Hg$^{2+}$, Ni$^{2+}$, Co$^{2+}$ and Zn$^{2+}$. It was assumed that Cu$^{2+}$ is of the correct size and geometry to enter interstices in the neutral polymer films. A Cu$^{2+}$ sensor has also been previously been described by Thomson and Mount. The electrode surface was modified with a layer of a 5-aminoindole / 5-cyanoindole copolymer in its oxidised form. The selectivity of the polymer was attributed to the complexation of Cu$^{2+}$ ions with the amino substituents. Pandey et al. proposed a K$^+$ sensor fabricated from a crown ether impregnated PVC matrix laid down on a polyindole film. The polymer film was observed to reduce the interfacial potentials.

Poly(indole) has also been evaluated for application in rechargeable battery technology. The cells appeared to show high efficiency over 50 charge / discharge cycles. The authors interestingly proposed that the polymerisation mechanism is solvent dependent and that when using dichloromethane solutions of the monomer, poly(indole) films are produced containing 1,3'-linkages as proposed by Zotti et al.
1.3.7 Other relevant studies

Polymerised indole can also be obtained via chemical methods using oxidising agents such as FeCl_3, CuCl_2 and KIO_3 in a range of solvents. In the first reported study the products were investigated by scanning tunneling microscopy and conductivity measurements by Billaud et al.\textsuperscript{76} Recently chemically polymerised indole derivatives were investigated by fluorescence spectroscopy and the major fluorophore observed were identical to those produced electrochemically. These species were inferred to be asymmetric cyclic trimers (Figure 1.13).\textsuperscript{67} Robertson \textit{et al}\textsuperscript{77} have generated the symmetric hexabrominated cyclic trimer by using bromine as an oxidising agent which they propose forms via 2,3-indole dimer (Figure 1.14).

![Figure 1.14 Structure of the symmetric indole cyclic trimer where R = Br (Robertson \textit{et al}) or R = OH or H (Prota \textit{et al})](image)

Considerable research has been carried out by Prota \textit{et al}\textsuperscript{78,79} on the acid induced polymerisation of various hydroxyindoles. This has been motivated by research into melanin, the pigments found in the skin and hair of mammals. The oxidising agent used was ammonium persulfate and both symmetric (Figure 1.14) and asymmetric cyclic hydroxyindole trimers have been isolated from the reaction mixtures involving indoles such as 5,6-hydroxyindole.
1.4 Computational Studies.

Computational methods can be used to calculate the electronic structures of atoms and molecules. From these calculations it is possible to determine many physical and chemical properties such as bond stretching frequencies, electron densities and dipole moments. With a quantum chemical approach to these studies the energy and properties of a system may be obtained from solution of the Schrödinger equation for that system. The full Schrödinger equation (equation 1.1) for a molecule involves a Hamiltonian operator (\(\hat{H}\)) and the total molecular energy (\(E\)).

\[
\hat{H}\Psi = E\Psi
\]  

[1.1]

The total molecular wavefunction, denoted as \(\Psi\), is a function of the positions of nuclei and electrons. The full Schrödinger equation however has never been solved exactly for any but the simplest of model problems (no more than two electron systems) and so approximations have to be introduced with even the most rigorous theoretical methods.

The first major simplification to be made is based on the Born-Oppenhiemer approximation which takes into account the large mass of the nuclei relative to electrons.\(^8\) This allows the nuclear and electronic motions of the system to be decoupled and treated separately. The nuclear motion, described by the nuclear Schrödinger equation is solved using molecular mechanics or force field methods whilst quantum mechanical methods aim to solve the electronic Schrödinger equation for describing the motion of electrons in field of fixed nuclei. A full mathematical description of quantum mechanical theory is beyond the scope of this thesis however the relevant aspects of these calculations are discussed in greater detail in Chapter 2 (Section 2.3).

1.4.2 Quantum chemistry methods

There are two main approaches to the solution of the electronic Schrödinger equation and these are \textit{ab initio} (first-principles) methods, and semi-empirical methods.\(^8\) \textit{Ab initio} methods require only the values of fundamental constants, atomic numbers and positions of atoms within a system. The accuracy of these methods depends chiefly upon the quality of model chosen for the wavefunction. In contrast, semi-empirical methods employ a simplified form of the Hamiltonian and fitted parameters obtained from experimental data.
They also require a model to describe the interactions between the atoms. These models and parameters simplify the calculation but may do so at the expense of accuracy.

For a large system *ab initio* calculations are computationally expensive. This is a major disadvantage however the heavy computational effort can be avoided by employing semi-empirical methods for simulation on a larger scale. Semi-empirical quantum mechanical calculations are a cheap alternative which provide a rapid means of generating results and are applicable to a wide range of systems. However with the availability of increasing computational power coupled with continual refinement of theory and its implementation, *ab initio* calculations are having a much larger impact in all areas of quantum chemistry.

The quantum chemical calculations in this thesis employ both semi-empirical and the more rigorous Density Functional Theory (DFT) methods to study the electronic structure of various substituted indoles. DFT methods are not strictly 'first principle' methods but can be viewed as of *ab initio* quality. They are however significantly more accurate than semi-empirical methods.

### 1.4.3 Computational studies of electroactive polymers

Quantum mechanical calculations are extremely useful in describing the properties of π-conjugated oligomers and polymers. The electrical and optical behavior of these materials originate in their geometric and electronic structures. Quantum chemistry is therefore a valuable complementary tool in predicting the nature of products from an electropolymerisation reaction and depicting their strong dependence on subtle effects such as those induced by chemical substitution.

Computational structural studies on conducting polymers and oligomers are numerous. Different methods have been used and include semi-empirical, Hartree-Fock methods and Density Functional theory. The use of these methods in relation to conducting polymers is reviewed elsewhere. The majority of these studies have concentrated on structure and conformation analysis and the types of polymers studied include thiophene oligomers (AM1, DFT, HF), pyrrole oligomers (AM1, DFT, HF, MP2), and furan derivatives (HF).
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The first theoretical studies on the growth of conducting polymers based on thiophene or pyrrole predicted the molecular geometry and reactivity of the monomer unit using semi-empirical methods such as Intermediate Neglect of Differential Overlap (INDO). A strong correlation was shown for pyrrole monomers and oligomers between the spin distribution and sites of polymerisation. High spin populations at the $\alpha$-positions of the monomer radical cations were calculated and $\alpha, \alpha'$-linkages were predicted to be prevalent in polypyrrole (Figure 1.15). When applied to oligomers the spin density became more delocalised and linkages involving the $\beta$-position were observed to be just as likely. Recent studies have used the more rigorous ab initio (Hartree-Fock) and DFT methods to calculate the $\pi$-spin densities for pyrrole and pyrrole-thiophene oligomers. Good correlation of the DFT spin density calculations has been observed with experimentally measured values (using EPR) for pyrrole oligomers, (E)-stilbene and thiophene oligomers and furan derivatives.

![Figure 1.15 The structure proposed for polypyrrole. The linkage sites are indicated by either $\alpha$ or $\beta$.](image)

Alternative approaches to studying the growth of conducting polymers during electrooxidation include transition state calculations. The growth of polypyrrole has been studied with this approach however due to the size of the species involved semi-empirical methods (AM1) were used. In order to include correlation energy these researchers combined AM1 optimised geometries with MP2 and DFT single point calculations. This procedure does not allow accurate calculation of absolute activation energies which would require huge calculation times. Computational methods have also been employed to study substituent effects on thiophene based tricyclic polymers (DFT, AM1) and pyrimidine functionalised thiophenes. The effect of the substituent on properties such as energy, dipole moment and molecular orbitals were determined. The structure and optical properties of various oligomers such as PPP (HF), polyaniline (DFT), thienylenevinylene oligomers (DFT) and PPV oligomers (HF / CI) have also been calculated. The vibrational structure of oligothiophenes and PPV have been investigated at the ab initio level.
Ab initio calculations have also been used to screen thiophene monomer derivatives in order to optimise the thermochromic properties of the polymer. These type of calculations are useful predictive tools to screen potential monomers in the design of novel conducting polymers.

1.4.4 Computational studies of indole and indole conducting polymers

Quantum chemical studies of indole have investigated the structure of indole at the ab initio and DFT level. The effect of small substituents on the properties of indole has also been studied at the ab initio level. The motivation for these studies stems from novel drug design where indole is treated as a fragment of a peptide based drug. The presence of a specific substituent on the aromatic ring can enhance or depress specific features of the system such as geometry, charge distribution and dipole moments which have to be considered in drug design. Vibrational frequencies of indole and various substituted indoles have been calculated using DFT methods.

The indole radical cation was first studied using semi-empirical INDO molecular orbital calculations by Waltman et al. The electronic withdrawing / donating nature of the substituent was characterised by spin density calculations. In this study all molecular geometries were rigid, a direct consequence of the relative computational expense of performing geometry optimisations fifteen years ago. These calculations predicted high spin density at N1 and C3 positions in the heterocyclic ring with little delocalisation of the unpaired spin into the benzene ring. Consequently these positions were identified as the reactive sites in an electropolymerisation reaction and a possible 1,3'-linkage in polyindole was proposed. The spin density of the indole radical cation has also been investigated using HF and Hybrid HF /DFT methods. These calculated spin densities were compared to experimentally measured values using Photochemically Induced Dynamic Nuclear Polarisation (p-CINDP) and EPR experiments and a good correlation was observed.

Investigation of the tryptophan radical has triggered many studies of suitable tryptophan fragments such as 3-methylindole with DFT and Hybrid methods. It has been established for biological in vivo radicals the unpaired electron resides in a π-orbital
extending over the whole aromatic system of tryptophan radical cation. DFT calculations revealed a similar distribution of the spin density which was dominated by the singly occupied π-orbital (SOMO). The calculated SOMO revealed significant π-bonding overlap of the SOMO between the C2 and C3 with the major concentration of the unpaired electron between these positions.

Few quantum chemical studies have concentrated on the oxidative polymerisation process of substituted indoles and those that have been published are of a solely semi-empirical nature. The two most recent theoretical studies of indole polymerisation have used a semi-empirical (AM1) method. These authors have discounted radical cation - radical cation coupling in favor of reaction between an indole radical cation and a neutral indole. The chain propagation of linear polymers has been considered, driven by electrical charges carried by the atoms. According to Billaud et al. the linking reactions take place between the most positively charged atom on the radical cation (C2) and the most negatively charged atom on the neutral molecule (C3) to preferentially form a 2,3'-linkage. The charges calculated in this study were determined using Mulliken charge analysis which has well documented shortcomings. These studies are discussed further in Chapter 6.

1.4.5 Solvation Models

Solvation effects in chemistry are of huge importance. Many biochemical and electrochemical processes occur in solution where the chemical properties are often very different from the gas phase. It is therefore important to simulate the effect of solvation in theoretical studies. The effect of the solvent may be divided into two major parts; specific solvation or 'short range effects', e.g. hydrogen bonding, and long range effects involving screening of charges (solvent polarisation). The specific solvation is mainly concentrated in the first solvation sphere whereas long range effects are responsible for generating a macroscopic dielectric constant and requires a large number of solvent molecules.

Methods for modeling solvation effects may be broadly divided into two types. Explicit solvent models that describe individual solvent molecules and implicit models which treat the solvent as a continuous medium. Combination of the two are also possible by explicitly considering the first solvation sphere and treating the rest of the medium by the continuum model.
The are two principal advantages of continuum models. The first is they are less computationally demanding due to a reduction in the number of degrees of freedom.\textsuperscript{111} Modeling the effect of, for example water, explicitly requires a sophisticated method to give an adequate description of the non-bonded interactions between the solvent and solute and also between the water molecules. This would involve several hundred water molecules and a realistic model would clearly be computationally expensive. To reduce computational effort implicit solvation models must be considered. If the solvent is treated as a continuous medium the averaging becomes implicit in the properties of the continuum. The second advantage is that explicit solvent models may not be any more accurate than continuum models.\textsuperscript{111} Considerable refinement of these explicit models is required before they can successfully simulate the solvent electric polarisation as well as continuum models. In most explicit models this is neglected due to computational cost. Consequently, continuum solvent models provide an accurate way to treat the long range electrostatic forces that are observed in many solvation phenomena without explicitly considering the individual solvent molecules.

1.4.5.1 Continuum solvation models

The idea of modeling the electrostatic solvation by placing the solute in a cavity immersed in a dielectric continuum was proposed by Born\textsuperscript{111} (the Born model for ionic solvation) and developed by Onsager\textsuperscript{112} and Kirkwood\textsuperscript{113} However it was soon recognised that the success of the model was limited by specific interactions between solvent and solute, known as first solvation shell effects. Since then various approaches to account for first solvation shell effects in the continuum model have been developed. Continuum model calculations are now implemented into several semi-empirical\textsuperscript{114} \textit{ab initio} and DFT\textsuperscript{115,116} codes which have been made possible by the enormous increase in computational power over the last five years. In these models the solute molecule is embedded in a dielectric continuum of permittivity $\varepsilon$, (Figure 1.16).
Figure 1.16 A schematic of the continuum solvation model, (CSM) with the solute M in a spherical cavity in the solvent continuum of permittivity $\varepsilon$.

The simplest of models uses spherical cavities and considers the coupling of the molecular dipole to the dielectric medium. This gives the advantage that electrostatic interactions between solute and solvent can be calculated analytically. This method fails however with symmetric molecules which have two dipoles as the total dipole moment is effectively zero. An expansion of this model uses electric multipole moments but these are restricted to compact systems and have been observed to converge slowly. This simple model also has obvious limitations for systems that are not very spherical.

One of the most successful continuum models is the polarisable continuum model, (PCM) developed by Tomasi and co-workers. This employs a solute shaped cavity, generated by a union of overlapping spheres centered on the atoms which have approximately a Van der Waals radii. The dielectric continuum is polarised by the charge distribution of the solute which results in a charge distribution on the cavity surface. A coupled iterative procedure is then required. For a given charge distribution within the cavity, the surface screening charges are calculated and used as a perturbation included in the Hamiltonian for electronic structure calculations of the solute. The new perturbed density of the solute is then used to calculate a new charge distribution and the procedure is repeated until self consistency is achieved. There are several applications of this model for calculating the solvation energy for cavities of arbitrary shape at the $ab\text{ }initio$ DFT and semi-empirical level of theory.

Klammt and Shuurmann developed the ConductorLike Screening Model (COSMO) which is very similar to the PCM. This model assumes that the surrounding medium is well modeled as a conductor which simplifies the electrostatic computations. This method is
described in greater detail in Section 2.4.3. The COSMO model has been implemented at the semi-empirical level and also with DFT (DMol) methods and has been used to provide solvation in the theoretical calculations presented in this thesis. The most recent development is the ConductorLike Screening Model for Real Solvents (COSMO-RS). This is an extension of the COSMO model where the solvent and solute are treated at the same level and the method no longer depends on experimental data or any parametisation for the solvent. COSMO-RS can describe mixed solvents as well as pure ones.

1.5 Aim of this research

In this thesis a range of electrochemical, spectroscopic and computational studies have been carried out. The primary aim of this research has been to investigate the electronic structure of substituted indoles and how this affects polymerisation and the properties of the resultant products. This has been achieved by a combination of electrochemical and computational methods. A second aim concerns the testing of indole conducting polymers as potential candidates for light emitting devices by means of ECL experiments.

The structure of this thesis is summarised below. Chapter 2 provides a summary of the theoretical aspects related to this work and Chapter 3 gives a brief summary of experimental details. In Chapter 4 the electronic structure and energies of indole and 5-substituted indoles are investigated using semi-empirical and DFT methods. Calculated theoretical oxidation potentials are calculation and compared to experimental results. The electronic distribution of monomer radical cations are calculated and discussed. In Chapter 5 some novel electropolymerised indoles are investigated, with characterisation by electrochemistry and fluorescence spectroscopy. Theoretical oxidation potentials are calculated and the electronic structure of the indole radical cation is probed by studying the effect of substituent type and position. Chapter 6 provides the first reported DFT investigation into the polymerisation process of indole. Chapter 7 investigates the coupling reaction of 5-substituted indole radical cations at a preformed poly(5-cyanoindole film). Chapter 8 illustrates how the photophysical properties of indole monomers and electropolymerised indole can be altered by the influence of the substituent. Chapter 9 describes the testing of poly(5-cyanoindole) for application in light emitting devices by ECL experiments which involves the construction of a novel ECL system. In Chapter 10 the conclusions of this research are discussed.
1.6 References


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Chapter 2
Theory

2.1 Introduction
The research presented in this thesis covers a range of electrochemical, spectroscopic and computational methods. For each of the techniques there exists a plethora of theoretical literature. This chapter contains a summary of the most important theoretical aspects on which the research has been based.

2.2 Electrochemical studies
2.2.1 Experiments at the Rotating Disc Electrode
The rotating disc electrode (RDE) can be used to obtain precise quantitative information regarding the kinetics of an electrode reaction. This is possible as it provides a forced convective-diffusion method of controlling mass transport of electroactive species to the electrode surface. The RDE consists of a platinum disc electrode surrounded by an insulating material such as PTFE (Figure 2.1). The RDE is suspended in a solution containing the electroactive species of interest and a supporting electrolyte. When the electrode is rotated at a controlled rate it acts as a hydrodynamic pump. The rotation of the disc drags the solution nearest to it up towards the electrode and throws it out radially across the disc. As a result, the solution flows parallel to the electrode and is replaced by solution moving in from the bulk in a direction perpendicular to the surface. The hydrodynamic flow of solution is shown in Figure 2.1.

The transport of electroactive species to the electrode surface can be described by a combination of forced convection due to the rotation of the electrode and diffusion. The convective component perpendicular to the electrode becomes less important as the distance to the electrode surface decreases and has no influence at the electrode surface. Consequently a boundary layer can be defined near the electrode in which the significant form of mass transport perpendicular to the electrode is due to diffusion. This is called the Nernst diffusion layer with a concentration profile as illustrated in Figure 2.2, with thickness defined by \( \delta \) and the bulk concentration is \( C_\infty \).
Figure 2.1 The rotating disc electrode construction and the hydrodynamic flow of solution (a) perpendicular to the RDE and (b) across the surface.

Figure 2.2 Variation of the concentration of active species normal to the electrode.

Outside the diffusion layer convection maintains the concentration of all species at their bulk values. Inside the diffusion layer the concentration of electroactive species varies approximately linearly with distance effectively producing a uniform concentration gradient. When the concentration of species R, [R], is zero at the surface the rate of the electrochemical reaction is limited by the rate of mass transport to the electrode and the corresponding current passed is called the diffusion limited current. Mass transport by diffusion is directly proportional to the concentration gradient which can be varied by decreasing or increasing the Nernst diffusion layer thickness. Solution of the convection-diffusion equations gives the thickness of this diffusion layer (equation 2.1) where $v$ is the
kinematic viscosity (in cm²s⁻¹) of the solvent, D is the diffusion coefficient (cm²s⁻¹) and W is the rotation speed (in Hz).

\[
\frac{1}{\delta} = 0.63 \nu^6 D^3 W^{-2}
\]  

[2.1]

The thickness depends upon the force of convection and therefore mass transport can be precisely controlled by the rotation speed of the RDE. If this is varied at a given potential the current data can be related to kinetic parameters of the electrode reaction.

Where the reaction is limited by mass transport and [R] at the surface is zero, the equation relating the limiting current density \( i_L \) and the rotation rate \( W \) (in Hz) is the Levich equation (equation 2.2) where \( F \) is Faraday’s constant, \( A \) is the area of electrode (cm²), \( n \) is the number of electrons and \( C_\infty \) is the bulk concentration (in cm³mol⁻¹). The sign of \( i_L \) is positive for an electrochemical oxidation and negative for a reduction.

\[
i_L = nFA \frac{DC_\infty}{\delta} = 1.554nFAD^3 \nu^{-1} C_\infty W^2
\]  

[2.2]

In a mass transport controlled system, with no mass transport independent steps a plot of \( i \) versus \( W^{1/2} \) should be linear and pass through the origin and is a test of whether the current density is entirely mass transport controlled. The gradient can be used to give an estimate of the number of electrons involved in the reaction.

If there is a mass transport independent step at the electrode, for example slow electron transfer, the rate constant for which is \( k' \), then the reaction mechanism can be described by Scheme 2.3, where \( C_\infty \) is the bulk concentration of species [R] and the concentration at the electrode surface is \( C_0 \), the product [O] has the concentration \( C \), \( k_d \) is the rate constant for mass transport. When \( k_d \gg k' \) the reaction at the electrode is limiting and the kinetics of the reaction can now be described as in equation 2.3 where \( i_{obs} \) is the observed current. If the number of electrons passed, \( n \), does not vary then a plot of \( 1/i_{obs} \) versus \( 1/W^{1/2} \) will show a linear relationship; the gradient of this will allow a measure of the number of electrons passed if the diffusion coefficient is known. The intercept, \( i_{in} \), can be used to calculate \( k' \) at a given potential. This is termed a Koutecky-Levich plot.³
2.2.2 Experiments at the rotating ring disc electrode

The rotating ring disc electrode, (RRDE) can be used to detect soluble products generated at the disc electrode\(^1\). With an RDE these products are continually swept away from the disc and out into the solution by the radial flow of solution across the electrode surface. However the products can intercepted (collected) by the ring electrode which is effectively placed down stream of the hydrodynamic flow. This is illustrated in Figure 2.3.

![Figure 2.3](image)

**Figure 2.3** The construction and hydrodynamic properties of the rotating ring disc electrode a) perpendicular to the electrode b) across the electrode surface.

The potentials of both the disc and the ring can be controlled independently to selectively study a specific process. The hydrodynamic operation of the RRDE is very similar to the RDE with an additional important parameter, the collection efficiency of the ring electrode, \(N_0\), which is calculated by equation 2.4.

\[
N_0 = |I_{\text{ring}}|/|I_{\text{disc}}| \quad [2.4]
\]

For a electrochemically reversible reaction producing an electroactive product with 100% efficiency with the same number of electrons passed in the disc and ring reaction and mass transport limited detection of the ring products, \(i_{\text{ring}}\) indicates the mass transport limited current expected for any disc current \(i_{\text{disc}}\).
2.2.3 Potential sweep voltammetry

Potential sweep voltammetry techniques are invaluable to the electrochemist. These experiments provide useful information on a number of processes such as the occurrence of oxidation or reduction reactions of electroactive species in solution, the adsorption of species at the electrode, kinetic information and the detection of soluble species generated at an electrode. In linear sweep voltammetry (LSV) the experiment is conducted in a stagnant solution and so transport of material to the electrode occurs by diffusion and uncontrolled thermal convection. These studies can be described as dynamic techniques i.e. non steady state. They involve the application of a continuously time-varying potential to the working electrode which is a function of the sweep rate $v_s$ and the time of sweep, $(t)$ . The potential of the electrode is swept in one direction at a constant rate between two potential limits, $E_1$ and $E_2$ stopping at the chosen value $E_2$. The sweep direction is inverted on reaching $E_2$ and the potential is swept back to the original value $E_1$. Figure 2.4a) illustrates the potential time profile. This Scheme can be repeated a number of times and changes in the current response is measured and plotted against the applied potential, this is known as cyclic voltammetry (CV). A typical LSV response curve is shown in Figure 2.4b).

If the scan is begun at a potential negative relative to the potential ($E^0$) where $O$ and $R$ are at equilibrium concentrations no current is passed since the applied potential is not great enough to induce electron transfer. $E^0$ is related to the standard potential for the reaction by equation 2.5.

$$E^0 = E^9 + \frac{RT}{nF} \ln \left[ \frac{[O]}{[R]} \right]$$

[2.5]
Consider the oxidation $R \leftrightarrow O + ne^-$. As the electrode reaches $E^0$ the oxidation begins and current begins to increase. As the potential moves past $E^0$ the mass transport of species $R$ reaches a maximum rate and the surface concentration begins to drop to zero as depletion effects set in. This results in the peaked current potential curve as depicted in Figure 2.4a) where $E_{p/2}$ is the potential at the half peak height. For a Nernstian reversible system is related to the half wave potential ($E_{1/2}$) by equation 2.6.

$$E_p - E_{1/2} = 1.09 \frac{RT}{nF} = 28.2 \text{ mV at 25°C} \quad [2.6]$$

$E_{1/2}$ is approximately halfway between $E_p$ and $E_{p/2}$ for a Nernstian wave and so

$$|E_p - E_{p/2}| = 2.2 \frac{RT}{nF} = 56.5/n \text{ mV at 25°C} \quad [2.7]$$

$E_{1/2}$ is related to the standard potential ($E^0$) for a one electron reversible electrode reaction by equation 2.8, where $D_R$ and $D_O$ are the diffusion coefficients for the reduced and oxidised species.

$$E_{1/2} = E^0 + \frac{RT}{F} \ln \frac{D_R^{1/2}}{D_O^{1/2}} \quad [2.8]$$

For an electrochemically reversible wave $E_p$ is independent of scan rate and $i_p$ is proportional to the square root of the scan rate. For an irreversible wave $i_p$ is also proportional to the square root of the scan rate and the concentration of the species at the electrode surface however $E_p$ is a function of scan rate, shifting in a positive direction for an oxidation.

For a surface adsorbed species which is capable of undergoing a reversible one electron transfer the CV shows a pair of peaks corresponding to the oxidation of the adsorbed species on the forward sweep and the reduction on the reverse sweep. The electrode reaction is controlled by electron transfer kinetics and not a coupled problem of diffusion and electron transfer. The ideal voltammetric peaks appear symmetric where the areas of the two peaks are identical. This provides a direct measure of the amount of charge required for the electrochemical reaction. Deviation from ideal behavior will occur if diffusion within the layer is important, if the surface adsorbed species either undergoes a reaction in its charged or uncharged forms or if it desorbs during potential cycling.
2.2.4 Potential step experiments

Indoles were electropolymerised using single potential step voltammetry with mass transport control provided by the RDE. In potential sweep experiments the voltage scan rate is the important parameter. A limiting case of this occurs when the potential is stepped instantaneously between values $E_1$ and $E_2$ corresponding to no reaction at $E_1$ whilst at $E_2$ the reaction does occur. This shown schematically in Figure 2.5. In a stagnant solution the currents are initially large but as the diffusion layer becomes depleted the current will decrease with time $^{1/2}$ according to the Cottrell equation (equation 2.9).

$$i = \frac{nFAD_R^{1/2}[R]_\infty}{\pi^{1/2}t^{1/2}}$$  \hspace{1cm} [2.9]

Figure 2.5 a) the potential time profile for a potential step experiment b) the current response for a potential step carried out in a stagnant solution.

Double potentials step experiments were used in the ECL experiments. These transient methods find frequent applications in this area as they allow sequential or simultaneous generation of the reactants and careful control of the potential allows selectivity in radical ion production. These experiments involve the alternate generation of reactants at a single electrode and rely on diffusion or thermal convection for transport or mixing (Figure 2.6). The electrode is suspended in a solution of the reactant precursors and at time $t_0$ the potential is stepped to a potential in the mass transfer controlled region for anion radical production.
This produces a layer of radical anions adjacent to the electrode. At time \( t_f \) the electrode is stepped to a value in the mass transfer region for the radical cation. Time into this step is represented by \( t_r \). The second step initially destroys some concentration of the radical anion (Scheme 2.2 where \( R^{*+} \) is the radical cation and \( R^{-} \) is the radical anion). \( R^{-} \) now faces an ion concentration gradient towards the electrode and will diffuse in that direction and meet \( R^{*+} \) diffusing towards the solution. Midway through the second step the two meet in a narrow zone near the electrode and the subsequent annihilation reaction produces a light pulse which decays with time (Scheme 2.3). When \( t_e = t_f \) the electrode potential is changed back to the intermediate rest potential at which both radicals are destroyed electrolytically and the solution returns to the original state. This experiment can be extended to involve the generation of a series of pulses which is very useful for spectral studies.

\[
\begin{align*}
R^{*-} & \rightarrow R^{*+} + 2e^{-} & \text{ Scheme 2.2} \\
R^{-} + R^{*+} & \rightarrow R^{*} + R & \text{ Scheme 2.3} \\
R^{*} & \rightarrow R + h\nu
\end{align*}
\]
2.3 Fluorescence spectroscopy

It has been observed that the indole monomers and the polymeric films produced from these monomers are highly fluorescent and therefore are suitable for study by fluorescence spectroscopy.

At room temperature most organic molecules occupy the lowest electronic state (the ground state) and have a Boltzmann population of vibrational levels. The ground electronic state is usually a singlet, labeled $S_0$, which refers to the total electron spin of the state or the spin multiplicity. Spin multiplicity is defined as $2S+1$, where $S$ is the total spin quantum number calculated as the vector sum of the individual contribution of all electrons. In a magnetic field the electron may be in two possible spin states defined by the magnetic spin quantum number, $m_s$ ($m_s = \pm \frac{1}{2}$). If the spins of two electrons are opposed then $S=0$ and $2S+1=1$ and is known as a singlet state. If the spins are parallel then $S=1$ ($2S+1=3$) hence this referred to as a triplet state, $T$. The molecule can absorb electromagnetic radiation, typically in the ultraviolet or visible region of the spectrum which induces a transition from the ground state to an electronically and vibrationally excited state. With very few exceptions, organic photochemistry is concerned with the lowest excited singlet state ($S_1$) or the lowest triplet state ($T_1$) in accordance with Kasha’s rules. This generalization stems from the observation that most photochemical reactions studied do not involve higher order electronic states ($S_2$, $T_2$ etc.) because rapid radiationless conversion to $S_1$ and or $T_1$ competes favorably with higher order processes. Triplet states tend to lie at lower energy than the corresponding singlet states as repulsion between the two electrons occupying different orbitals is minimised if their spins are parallel. This is the basis of Hund’s rule of maximum multiplicity and arises due to the spin correlation.

Associated with each electronic energy level there exists a set of vibrational and rotational energy levels. The energy differences between rotational energy levels are of two magnitudes smaller than for vibrational energy levels and so at room temperature in the solution phase rotational transitions are not resolved. These transitions involve a change in electronic and vibrational energy and so are referred to as vibronic transitions.
2.3.1 Excitation processes

Absorption of photons of equivalent energy to the separation between molecular vibronic energy levels will excite an electron from a lower to a higher energy level producing an excited state (Scheme 2.4).

\[ M + h\nu \rightarrow M^* \]  

Scheme 2.4

Different types of transition originate in the different types of molecular orbitals involved. The ground state of organic molecules can consist of σ, π or nonbonding, n orbitals and upon excitation a number of different transitions are possible. With most aromatic molecules \( \pi \rightarrow \pi^* \) transitions are important and result in intense fluorescence emission. Also possible are \( n \rightarrow \pi^* \) transitions which refers to the excitation of a nonbonding electron to an antibonding \( \pi^* \) orbital. These are commonly observed for compounds containing a carbonyl, imine, nitro or thiocarbonyl chromophore.
The absorbed energy and excitation of an electron to one of the higher vibrational levels of
an excited state results in a separation of the electronic charge within a molecule and this
gives rise to a transition dipole moment. The intensity of the vibronic transition is
proportional to the square of the transition moment for the interaction with the electric
component of the excitation radiation. The electronic transition which excites an electron
by absorption of electromagnetic radiation occurs rapidly compared to nuclear motion. The
nuclei remain essentially frozen at the equilibrium geometry of the ground state molecule
during the transition and any changes in nuclear geometry will take place after the
electronic transition has occurred. This is the Franck Condon principle. Due to the vertical
nature of the transition the excited state will be produced with some additional vibrational
excitation as the transition reaches the excited state potential energy curve at a position
above the lowest level. The transition dipole moment depends on the nuclear overlap
integral which is interpreted as a vibrational overlap integral \( \langle N_n | N_m \rangle \) which when squared is
known as the Franck Condon factor. This term predicts which of the vibrational levels of
the excited state will become populated. Where the ground state and the excited state
geometries are very similar then the largest vibrational overlap arises from transition with
\( \Delta v=0 \). Where the ground state and excited state have very different geometries then the
largest overlap will arise from \( \Delta v \neq 0 \). Polyatomic molecules have many vibrational motions
which may be involved in the transition. These may become overlapped to give a
featureless absorption profile.

2.3.2 De-excitation processes

The electronically excited molecule is energetically unstable with respect to the ground
state. The molecule will lose its excess of excitation energy to return to the ground state
and a number of de-excitation pathways may be involved. These include radiative
processes involving the emission of electromagnetic radiation by the excited molecule and
nonradiative processes in which the population in the initial excited state is transferred into
others without any accompanying emission. Quenching processes may also be involved in
which energy is transferred from the excited molecule to other species in collisional events.
The following discussion will concentrate on the radiative and nonradiative processes. The
different types of transition in these processes can be summarized by the Jablonski diagram
(Figure 2.7). Radiative transitions are indicated by straight arrows and nonradiative
processes are indicated by wavy arrows.
2.3.2.1 Radiative processes

There are two types of radiative transition and these are fluorescence and phosphorescence. Fluorescence is emission from an excited state of the same spin multiplicity as the lower state (usually the ground state). Excitation of the molecule to the \( S_1 \) state may be followed by an \( S_1 \rightarrow S_0 \) transition. This is spin-allowed as there is no change in multiplicity and as a result fluorescence is strongly allowed and occurs on a relatively fast time scale (\( 10^{-12} \) to \( 10^{-6} \) s).

The operation of the F-C principle means that if there is no change in geometry upon excitation the \( 0-0 \) (\( v''=0 \) to \( v'=0 \)) transition will be the most intense in the absorption of energy. For the emission process the \( 0-0 \) transition is accompanied by emission of radiation to lower energy due to transitions to \( v''=1, 2, 3, \) etc. Where the vibrational spacings are similar in both the \( S_1 \) and \( S_0 \) levels the emission spectrum will resemble a mirror image of the absorption spectrum. Therefore one may expect the absorption and emission spectra to overlap at the wavelength corresponding to the \( 0-0 \) transition. However, in practice, the emission and absorption spectra rarely coincide, reflecting the small loss in energy due to interaction of the excited state molecule with surrounding solvent molecules. The difference in the energy between the \( 0-0 \) transitions in the absorption and emission spectrum is called the Stokes shift which is often dependent on solvent polarity.

Mechanisms for interaction between solvent and the excited state molecule include hydrogen bonding, electrostatic interaction of solvent with the excited state dipole moment and also reorientation of the solvent cage. This last process is known as solvent relaxation. It is caused when a large dipole moment is generated upon excitation and the polar solvent molecules reorientate themselves accordingly. As a result, energy is lost from the excited state and emission occurs at longer wavelengths often with lower intensity and broadening of the peak shape. Consequently the energy of the emission spectra are often quite sensitive to the polarity of the solvent, whereas the absorption is relatively unaffected. This can be avoided by cooling the sample to 77K where the solvent molecules becomes frozen in a rigid matrix. This also prevents collisional deactivation and so the resulting fluorescence is more intense, occurs at shorter wavelengths and has better vibrational resolution.
If the spin multiplicity of the emitting state is different from the lower state the emission is known as phosphorescence. Thus if the $T_1$ state is populated by intersystem crossing from $S_1$, emission due to the $T_1 \rightarrow S_0$ transition may be observed if a mechanism for spin orbit coupling is provided, whereby this otherwise forbidden transition becomes weakly allowed. As a result phosphorescence is expected to be less intense and occurs less rapidly ($10^{-3}$s to 1s).

2.3.2.2 Nonradiative processes

Internal conversion, IC, involves the transfer of population between electronic states of the same multiplicity and intersystem crossing involves the transfer of population between states of different multiplicity.

Upon excitation of a molecule to a vibronic level of an electronic state higher than $S_1$, e.g. $S_2$, the molecule will first lose its excess of vibrational energy by collisional processes and fall to the lowest vibrational level of $S_2$. The molecule will then undergo IC and pass from $v'=0$ of $S_2$ to a higher vibration level of $S_1$. IC occurs with the rapid vibrational relaxation on a fast time scale and this ensures that emission is from the lowest vibrational energy level of the $S_1$, because of this the emission spectrum is independent of the excitation wavelength.

The process of conversion of energy from an excited singlet state to the triplet manifold is known as intersystem crossing. This transition is spin forbidden but will be enhanced by spin-orbit coupling. An electron has two sources of angular momentum from its intrinsic spin and orbital motion and in specific circumstances some angular momentum can be exchanged between them. This results in spin-orbit coupling which allows the singlet and triplet states to mix. The triplet takes on some singlet character and the singlet takes on some triplet character. The degree to which this occurs depends on the values of $n$ and $l$ quantum numbers and the fourth power of the atomic number, $z$. Spin-orbit coupling is therefore important where heavy atoms such as Br are present and so intersystem crossing is enhanced in these molecules. The presence of a $n \rightarrow \pi^*$ transition also enhances the intersystem crossing. ISC is allowed to occur by spin-orbit coupling between a $(n,\pi^*)$ state and $(\pi,\pi^*)$ state according to El-Sayed's selection rules.
2.4 Computational studies

As introduced in chapter 1 the Born Oppenheimer Approximation effectively decouples the nuclear and electronic motion and so we can focus on the electronic Schrödinger Equation\(^1\) for a system of electrons in a fixed field of nuclei (equation 2.10). This applies to a fixed set of locations of electronic positions \(r\), and the nuclei \(R\), where \(E\) is the electronic energy and \(\Psi_e(r;R)\) is the electronic wavefunction. The Hamiltonian for the electronic Schrödinger Equation is given by equation 2.11.

\[
\hat{H}_e \Psi_e (r;R) = E(R) \Psi_e (r;R) \quad [2.10] \\
\hat{H}_e = T_e + V_{ne} + V_{ee} + V_{nn} \quad [2.11]
\]

The first term of the Hamiltonian operator describes the kinetic energy of a system of noninteracting electrons and the second term describes the attractive nuclei-electron Coulombic potential energy. Conventionally the nucleus - nucleus repulsion energy, \(V_{nn}\), is added at the end of the calculation as a classical term. The third term represents the electron-electron repulsion and this term introduces many complications to the calculation of the electronic structure of systems involving more than one electron. Solving the Schrödinger Equation is indeed a challenging problem and has not been solved analytically for any but the most simple of model systems and so approximations must be employed.

At this point the computational chemist is faced with two decisions. These are: what level of theory should be used and what form and quality of functions (basis functions) should be used to represent the electron in the system of interest? These two concerns are addressed in the following sections.

2.4.1 Level of theory

As mentioned above the term representing electron - electron repulsion prevents an analytical solution to the electronic Schrödinger Equation for molecular systems. There are two effects which further lower the Coulombic energy of a system of electrons\(^2\). The first of these is based on the fact that electrons are indistinguishable, and this requires the wavefunction for a system of electrons to change its sign when any two electrons are interchanged. This is the origin of the Pauli Exclusion Principle which states that two electrons cannot be in the same quantum state; this is also known as exchange symmetry. Exchange symmetry acts as to lower the energy as it keeps the electrons with the same spin...
away from each other and so they experience less repulsive energy. This energy reduction is called the exchange energy, $E_x$. Exchange symmetry is included in Hartree-Fock theory (HF) by making the assumption that the electron moves in an average field generated by all other electrons and nuclei. The energy of a system calculated by HF (HF energy) is always greater than the 'true' energy of the system. This deviation decreases as the number of basis functions used to describe the system is increased in accordance with the Variational Principle and the energy calculated by HF methods improves (see Section 2.4.2). However even with an infinite number of basis functions an exact solution to the Schrödinger Equation is still not obtained and the existing deviation (HF limit) lies in the premise central to HF theory that the electron under consideration moves in an average field generated by all other electrons and nuclei.

The motion of electrons in a system are correlated. This means that movement of one electron affects the motion of other electrons in the system. This also causes electrons to avoid each other and so provides a second mechanism for the lowering of Coulombic energy by the correlation energy ($E_c$). The deviation between the HF limit and the exact energy is often referred to as the correlation energy. The HF model is a branching point where either additional approximations may be invoked leading to semi-empirical methods or improved by introducing correlation to the theory. There are various methods to treat correlation in calculations and the two most widely used are based upon a linear combination of individual electron configurations known as configuration interaction (CI) and Møller - Plesset perturbation (MP) theory. However these tend to involve a large increase in computational expense. The cost of performing an HF calculation scales formally as $N^4$, or more if correlation is included (where $N$ is the number of basis functions used). This is due to the number of two electron integrals which need to be included. In this thesis Density Functional theory (DFT) (Section 2.4.1.2) has been used which, in contrast to HF, provides an explicit consideration of correlation energy whilst being computationally cheaper (DFT problems scale as approximately $N^{2.7}$).

2.3.1.1 Semi-empirical methods

Semi-empirical methods were developed as an alternative to the computationally demanding *ab initio* methods. Semi-empirical methods reduce computational cost by reducing the number of the two electron integrals. Many are replaced by parameters
determined by empirical fitting. Only valence electrons are considered explicitly, the core electrons are accounted for by introducing functions to model the combined repulsion due to the nuclei and core electron. A minimal basis set is used to describe the valence electrons. The three most commonly used are Modified Neglect of Differential Overlap (MINDO), the Austin Method I (AM), and the Parameterisation Method 3 (PM3). These are derived from the same basic approximation, Neglect of Diatomic Differential Overlap (NDDO), which neglects all 3 and 4 center two electron integrals. The PM3 method was used for most of the semi-empirical work carried out in the course of this research. These semi-empirical methods are limited due their parametisation however they are still quantum mechanical based methods which have the advantage of being less expensive than equivalent ab initio methods and so make it possible to treat larger systems.

2.4.1.2 Density Functional Theory
In contrast to the Hartree-Fock picture which begins with a description of individual electrons interacting with nuclei and other electrons in the system, DFT starts with consideration of the entire electron system. The first theorem of DFT, developed by Hohenberg and Kohn is that the total electronic ground state energy of a system of electrons \( E_T \) is a function of the electron density, \( \rho \), at position \( r \). The electron density can now be viewed as the basic variable on which the total energy depends i.e. \( E_T[\rho(r)] \). The total electronic energy is then decomposed into three main contributions in the form of functions of the electron density (2.12).

\[
E_T[\rho(r)] = V_{\text{en}}[\rho] + T + V_{\text{ee}}[\rho] \tag{2.12}
\]

The first term, \( V_{\text{en}} \), is the potential due to the nuclei - electron attraction energy and the second term \( T \), represents the kinetic energy of a system of non-interacting electrons. The third term \( V_{\text{ee}} \) is the electron electron repulsion energy.

The second theorem of density functional theory is that the ground state total energy can be found by varying the density until a minimum total energy is found. The resultant electron density distribution is then the ground state density. Kohn and Sham introduced an orbital expression for \( \rho \) such that for a system of \( n \) electrons the exact ground state charge density, \( E[\rho(r)] \), at a location \( r \) can be written in terms of one electron densities which are constructed from one electron wavefunctions, \( (\Psi_i) \).
The one electron spatial orbitals $\Psi_i$ ($i=1, 2, 3, ..., n$) are the Kohn-Sham orbitals and the electron density is given by equation (2.13).

$$\rho(r) = \sum_{i=1}^{n} |\Psi_i(r)|^2$$ [2.13]

This allowed Kohn and Sham to write the solution of the Schrödinger Equation in the form of a set of self consistent one electron (Kohn-Sham) equations and to reformulate the expression of total energy as:


In this relationship the first three terms are of an uncorrelated electron model. The first term is the potential due to nuclei-electron interaction, the second term, $T[p]$, is the kinetic energy term of all noninteracting particles and the third defines the classical Coulombic electron-electron repulsion energy. The last term $E_{xc}[p]$ contains all the exchange and correlation terms which contains the remaining portion of the real system kinetic energy. The exact analytical form for the $E_{xc}[p]$ term is not known and so approximate forms are required. The simplest form is known as the Local Density Approximation, LDA and defines $E_{xc}[p]$ as equation (2.15).

$$E_{xc}[p] = \int \rho(r) e_{xc}(\rho(r)) dr$$ [2.15]

The term $e_{xc}(\rho(r))$ is the exchange correlation energy per electron in a homogeneous electron gas of constant density. In a homogeneous electron gas an infinite number of electrons travel through a space of infinite volume where there is a uniform and controlled distribution of positive charge to retain electroneutrality. However neither positive charge nor electronic charge are uniformly distributed in actual molecules and in general the LDA underestimates the exchange energy by approximately 10% and therefore probably creates errors larger than the correlation energy. The electron correlation is overestimated often by a factor of two and as a consequence bond strengths are also overestimated, nevertheless, the LDA has been found to give good results over a wide range of solid state systems.

To account for the inhomogeneity of electron density a non-local correlation involving gradients of electron density is added to the parameterisation of $E_{xc}$. These are known as
Generalised Gradient Approximations (GGA), and they have shown improved accuracy in the calculation of molecular structures. A number of functionals for implementing gradient corrections have been developed and some of the most popular are those of Perdue and Wang (PW91)\(^9\) and Becke (B88)\(^{10}\). The DFT work in this thesis has made use of the PW91 method.

### 2.4.2 Basis functions

The number and form of functions used to describe the electrons in the system has influence over the accuracy of the calculation. In quantum chemical calculations the molecular orbitals (\(\Psi_i\)) are formed from a linear combination of a set of \(N\) known one-electron functions; \(\psi_1(x,y,z)\), \(\psi_2(x,y,z)\), \(\ldots\), \(\psi_N(x,y,z)\).

\[
\Psi_i = \sum_{\mu=1}^{N} c_{\mu i} \phi_\mu 
\]  

[2.16]

The functions \(\phi_1, \phi_2, \ldots, \phi_N\) are one-electron basis functions and \(c_{\mu i}\) are coefficients. A set of these basis functions form a basis set. If the basis functions used are atomic orbitals then equation 2.16 is called the Linear Combination of Atomic Orbitals or LCAO method.

The mathematical form of the basis functions used also has influence over the accuracy. The better a single function is able to reproduce the unknown function, (the molecular orbital) the fewer basis functions are necessary for achieving a given level of accuracy. One choice of basis function are Slater type orbitals (STO)s. However the calculation of 3 or 4 center two electron integrals cannot easily be performed analytically with this type of function and so SCF calculations on molecules with three or more atoms are impractical. The introduction of Gaussian type orbital (GTO) by Boys\(^1\) made calculations on larger systems computationally feasible. These are of the general mathematical form \(e^{-\alpha r^2}\) and are easy to integrate and differentiate, however they give a poor representation of atomic radial functions. GTOs have problems representing the proper behavior near the nucleus as at the nucleus the GTO has zero slope in contrast to the STO which has a cusp (a discontinuous derivative). The GTO also falls off too rapidly and therefore the tail of the wavefunction is also poorly represented. This can be overcome by choosing linear combinations of Gaussian functions, this is termed as a contracted Gaussian type function (CGTF). The
CGTF mimics the behavior of an STO. With the DFT package DMol³ the atomic basis sets are generated numerically. The basis functions are given numerically as values on an atomic centered spherical polar mesh rather than analytical (Gaussian) functions. As a result numerical basis sets are more accurate but are limited by the number of grid points used to construct the spherical mesh.

Ideally basis sets composed of an infinite number of functions would provide the maximum accuracy for describing the motion of electrons. However this is not possible so in practice a finite truncated series is used instead. A minimal basis set is the simplest level of molecular orbital theory as only the minimal number of functions are employed to describe the electrons of the neutral atom, as a result it may inadequately describe the electrons in the system of interest and consequently large errors may be introduced due to the truncation.

Extension of a basis set is required for a more accurate description of the electronic structure and the simplest method of doing this is by multiplying the basis functions describing the valence regions. For example, using two (or three) contracted Gaussian functions to describe each occupied orbital gives rise to a double zeta (or triple zeta) basis set. The importance of a DZ basis set over a minimum basis set is that it allows a much better description of systems where the bonding is different in different directions, for example for the C atom in H-C=N.

The common feature of atom centered basis sets is that all basis functions are centered on the nucleus. However this is not an ideal description where highly polar molecules are involved. A solution to this is to allow for slight displacements of the center of electronic charge by including a function of higher angular momentum quantum number than those required, for example, using p functions on H atoms and d functions on heavy atoms. These are known as polarisation functions. Another method for extending the basis set is to include diffuse or larger versions of the atomic orbitals to the atoms. These are especially useful where the calculations involve species such as anions and electronegative atoms where the electron is density removed from near the nucleus or loosely bound electrons are present.
2.4.3 The Conductorlike Screening Model

The Conductor-like Screening Model (COSMO) (Klammt and Schuurmann 1993) is a continuum solvation model (CSM), where the solute molecule forms a cavity within the dielectric continuum of permittivity, $\varepsilon_r$, that represents the solvent. Figure 2.8 illustrates the basis of this model. The solute forms a cavity within the dielectric and this is constructed by superimposition of spheres centered on the atoms, discarding all parts lying on the interior part of the surface. The radii of spheres are approximately van der Waals radii of the atoms of the molecule. The interface between the cavity and the dielectric is represented by the cavity surface, which is usually referred to as the solvent accessible surface, (SAS).

The creation of a cavity causes destabilization whilst dispersion interactions between the solvent and solute adds stabilization (roughly van der Waals energy between the solvent and solute). The electric charge distribution of the solutes, represented by partial atomic charges, will polarise the dielectric medium which in turn produces electrostatic stabilisation. The surface charges are calculated directly from the electrostatic potential of the charge distribution within the cavity. The continuum is modeled as a conductor and in the ideal case the solvent has freely moving charges which can offer the opposite ideal surface charge densities for all faces of the solute and therefore can screen the solute as well as a conductor. Due to this simplification the deviation from a real situation of COSMO for strong dielectrics is approximately less than 1% while for nonpolar solvents ($\varepsilon_r < 2$) may reach up to 10% of the total screening effects. However for these nonpolar solvents the screening effects will be small and therefore the absolute error will also be small.
The response of the dielectric medium is described by the generation of screening or polarisation charges, \( V_{\text{POL}} \), on the cavity surface. These screening charges are calculated using the boundary condition for a conductor of a vanishing potential on the surface of the conductor and this avoids the complicated boundary conditions for a dielectric, (equation 2.17).

\[
V_{\text{TOT}} = V_{\text{SOL}} + V_{\text{POL}} = 0
\]

for a conductor \( V_{\text{TOT}} = 0 \) must hold. \[2.17\]

Due to this considerable simplification of the CSM approach without significant loss of accuracy, COSMO allows for a more efficient implementation of the CSM into quantum chemical programs. A DMO13 / COSMO calculation begins with the construction of the cavity surface. The screening charges and the initial solute charges are then evaluated. This allows calculation of the electrostatic COSMO potential which is present in every SCF cycle. This process is continued until the SCF is converged. During geometry optimisation a new geometry is calculated and the next optimisation cycle begins with the reconstruction of the cavity surface and the process continues until convergence is achieved.
2.5 References

Electrochemistry

Fluorescence Spectroscopy

Computational Quantum Chemistry
Chapter 3
Experimental

3.1 Introduction
In this chapter the reagents and experimental and computational methods used during the course of this research are outlined.

3.2 Chemicals

3.2.1 Purification
5-Indole carboxylic acid (Aldrich 99%), 5-cyanoindole (Aldrich 99%), 5-nitroindole (Aldrich 99%) 5-bromoindole (Aldrich 99%) and 6-indole carboxylic acid (Acros 98%) were recrystallised from deionised water and dried in a vacuum oven at 90°C for two days. Tetrabutylammonium tetrafluoroborate (Acros 99%) was recrystallised twice from an ethylacetate/n-pentane mixture (50:50 v/v) and dried in a vacuum oven for 24 hours prior to use. Lithium perchlorate (Acros 99%) was also dried in this way.

3.2.2 Other Chemicals
5-chloroindole (Aldrich 98%), 5-methylindole (Aldrich 99%), 5-methoxyindole (Aldrich 99%), 5-hydroxyindole (Aldrich 97%), 5-aminoindole (Aldrich 97%), indole (Aldrich 99%), 4-nitroindole (Acros 98%), 4-carboxylic acid indole (Aldrich 99%), 4-chloroindole (Acros 99%), 4-methylindole (Acros 99%), 4-methoxyindole (Acros 99%), 4-hydroxyindole (Acros 99%), 6-indole carboxylic acid (Acros 98%), 6-methylindole (Acros 99%), 7-methylindole (Acros 99%), thianthrene (Aldrich 98%), benzophenone (Aldrich 99%), silver perchlorate (Aldrich 99%), Raney Nickel (50% slurry in water, Acros), iron(III) chloride, (Fisher) were all used as received.

3.2.3 Solvents
Acetonitrile (MeCN, Fisons) was dried over CaH₂ then distilled and stored under nitrogen. Ethanol (EtOH, Acros spectrophotometric grade), isopentane (Aldrich, spectrophotometric grade), N,N-dimethylformamide (DMF, Aldrich spectrophotometric grade) were all used as received. All water was of doubly deionised quality by means of a Millipore water system.
3.2.4 Synthesis

3.2.4.1 Synthesis of 5-carboxaldehyde indole
The synthesis involved the reduction of 5-cyanoindole using a Raney nickel catalyst and the details are reported elsewhere. The crude product was recrystallised from cyclohexane to give pink crystals. The product was then characterised by electron impact mass spectrometry (EIMS), m/z at 145. $^1$H NMR (DMSO-d); 6.6(s 1H), 7.55(m 1H), 7.61(m 1H), 7.65(m 1H), 8.179(s 1H), 9.96(s 1H), 11.67(br s 1H). IR (CHCl₃) spectra of the pink crystals were obtained which showed clearly the presence of a carbonyl group 1659, 3270 cm⁻¹. The melting point (98-100°C) of the product agrees with reported literature values (99-101°C) for 5-carboxaldehydeindole.

3.2.4.2 Synthesis of poly(5,8-diphenyl-2,3-quinoxaline)
The dibromo derivative of the monomer was synthesised in a three step procedure reported elsewhere using benzo-(2,3,1)-thiadiazole as the starting material. The monomer was converted into the π-conjugated polymer by dehalogenation polycondensation using a zero valent nickel (Ni(0)) complex. The electrochemical and fluorescent properties of the polymer were in agreement with those reported previously.

3.2.4.3 Synthesis of 1-indole carboxylic acid
The procedure for the synthesis of 1-indole carboxylic acid is described elsewhere. The crude product was recrystallised from water to afford white crystals: mp105-106 °C [lit 107-108 °C (water)]; EIMS, m/z 161(M⁺), 117; L2MS m/z 161, 117; IR (nujol) 3401, 3492, 2360, 2340, 1639 cm⁻¹.

3.3 Electrochemistry

3.3.1 Circuitry
Electrochemical studies were carried out using a modular potentiostat / galvanostat with combined waveform generator and voltage sources (Oxford Electrodes Ltd.). The rotating disc electrode was controlled using a rotator and a motor controller (Oxford Electrodes Ltd.). This system is described elsewhere. Data was collected on a PC with tailored programs compiled using Visual Designer software (Intelligent Instruments).
3.3.2 Electrodes

The working electrode was a Pt rotating disc electrode, RDE, (Oxford Electrodes Ltd.), disc area 0.387cm². This electrode was polished by hand with a 3μm alpha-alumina polish (Buehler Ltd.) in a water slurry, then washed in doubly deionised water. A 2cm² platinum gauze was used as the counter electrode which was cleaned by washing in acetone and heating in a bunsen burner flame. The reference electrode was made in house and consisted of a silver wire dipping into a solution of silver perchlorate (0.01 mol dm⁻³) in background electrolyte solution of anhydrous lithium perchlorate in acetonitrile. This electrode has a potential of +0.437V with respect to a saturated calomel reference electrode and a potential of +0.681V with respect to a normal hydrogen electrode. In the ring disc experiments a Pt-Pt rotating ring disc electrode (RRDE) was used (disc area of 0.387cm²) with a measured collection efficiency of Nₑ=0.21 as measured by the ferrocene / ferrocenium couple.¹⁰

3.3.3 Experimental details

3.3.3.1 Experiments at the RIDE

Monomer peak oxidation potential were measured using linear sweep voltammetry, LSV. This techniques is detailed in Chapter 2 and elsewhere.¹¹ Polymerisation of indoles at the RDE was achieved using the technique of potential step chronoamperometry. The potential at the electrode was stepped instaneously from 0V to a potential 400mV higher than the monomer oxidation peak potential whilst rotating the RDE at rotation speeds from 0Hz to 16Hz. For a larger ratio of trimer to polymer species, concentrations from 30 to 100mmol dm⁻³ were used and for polymer rich oxidation products concentrations of 10-20mmol dm⁻³ were used.¹²

Where electrochemical experiments involved polymerisation on top of a preformed polymer film, 'template' films of poly(5-cyanoindole) (5Cl) were used, (50mmol dm⁻³ monomer solution, 4Hz rotation speed). The template film and the counter and reference electrodes were then washed in background electrolyte and all three electrodes were placed in the new monomer solution. Electropolymerised films of 5-nitroindole (50mmol dm⁻³, 4Hz) were employed as templates where the oxidation products were to be analysed by fluorescence spectroscopy as the template does not fluoresce appreciably.¹⁰ Films were dissolved from the electrode with the appropriate spectroscopic grade solvent.
Koutecky-Levich analysis of the polymerisation process also used templates of 5Cl. Polymerisation was carried out from monomer solutions of 30mmol dm\(^{-3}\) (or 50mmol dm\(^{-3}\)) with a range of rotation speeds. In these studies experimental parameters such as cell dimensions, the monomer solution volumes (20ml) and most importantly the thickness of template were kept constant, the latter by controlling the charge passed. Cyclic voltammograms were obtained for films with the electrode placed in a fresh electrolyte solution.

3.3.3.2 Experiments with the RRDE
The detection of soluble trimers was carried out using a Pt-Pt RRDE with a bipotentiostat. This allowed the potential of both the ring and the disc electrode to be controlled independently. Using a N\(_2\) degassed solution ring polarograms were obtained at 10mVs\(^{-1}\) at 2Hz with the disc potential at 0V and at a potential required to induce polymerisation.

3.3.4 Electrochemiluminescence
3.3.4.1 Equipment
Double step electrochemiluminescence experiments employed a conventional three electrode cell. The schematics of the experimental setup is shown in Figure 3.1. based on a fluorescence cuvette the cell was built in house and was designed to attach to a vacuum line and also fit into the sample compartment of the fluorescence spectrometer. A platinum flag electrode (1.17cm\(^2\)) was used as the working electrode with a platinum gauze (0.8cm\(^2\)) as the counter electrode. The pseudoreference electrode was a platinum wire, and the potential of this was determined by the positions of the redox couples on the voltammogram axis.

Care was taken to position the reference away from the counter and working electrode to minimise contamination at the working electrode from products generated in the counter electrode reaction. Pulsed potentials were applied to the potentiostat via a waveform generator (HI-TEK Instruments). The ECL emission was detected with a photomultiplier tube (Spex Industries inc.) operated at -950V. The experimental setup was tested with well characterised ECL reaction involving diphenylanthracene,\(^{13}\) DPA. In this reaction DPA serves as the parent molecule for both the electron donor (radical anion) and the electron acceptor (radical cation).
Figure 3.1 A schematic diagram of the ECL experimental setup.

3.3.4.2 Experimental details

The cell was soaked in a bath of isopropanol to remove vacuum grease and the electrodes were rinsed in acetone and heated in a bunsen flame. Both cell and electrodes were then dried in an oven prior to immediate use. The electrolyte salt employed in these ECL experiments was TBABF₄ 0.1 moldm⁻³ in acetonitrile, as it can be recrystallised and dried easily. Solution preparation and transfer of the solution to the bulb section of the cell was carried out in the minimum time possible to avoid the intrusion of water. The ECL cell was then connected to a vacuum line for degassing via four freeze pump thaw cycles with backfilling of nitrogen. The tap was then closed and the cell inverted to transfer the solution into the cuvette section of the ECL cell. The photomultiplier was placed facing the working electrode and the entire setup was blacked out. A CV of the ECL solution was obtained to determine the redox potentials of the species present and therefore the potentials required to apply in order to generate the reactants at the electrode. An overpotential of 200mV was usually added to ensure mass transport control of the reaction. A background PMT response was recorded then the pulses of alternating potential applied to the working electrode and the current and PMT response monitored with time.
3.4 Data Acquisition

3.4.1 Cyclic Voltammetry

The voltage and current outputs from the potentiostat were sent to the inputs of a data acquisition card (Intelligent Instruments), with data processing carried out by Visual Designer software (Intelligent Instruments). The custom application is displayed as a flow chart in Figure 3.2. There are two analogue inputs; one is the potentiostat voltage and the other a voltage given by passing the electrode current through a suitable measuring resistor. These signals can be averaged over a variable number of points and written to an ASCII file controlled by a data acquisition on/off switch.

3.4.2 Double step electrochemiluminescence

The application designed for collection of data from a double potential step ECL experiment is shown in Figure 3.3. The current outputs from the potentiostat and the potential applied via the waveform generator were sent to the inputs of a data acquisition card and recorded on a chart against time. The PMT response was also recorded with time and displayed on a separate chart. Averaging of data points could be altered for reduction of noise. All sets of data were then packed into a single ACSII output file for data analysis in Microcal Origin.

Figure 3.2 A Schematic diagram of the data acquisition program for recording cyclic voltammograms constructed using Designer software.
3.5 Laser time of flight mass spectroscopy

Laser time of flight mass spectroscopy, was carried out in collaboration with Angela Mudge of Dr P. P. R. Langridge-Smith’s research group within the Department of Chemistry, University of Edinburgh. The mass spectrometer system used in these studies has been described elsewhere\textsuperscript{14}. The mass spectra of monomers and electrooxidation products were recorded using two step desorption laser photoionisation time of flight mass spectroscopy, L\textsuperscript2TOFMS. The sample was deposited by drop coating onto the sample probe from a concentrated solution in ethanol. After solvent evaporation a pulsed CO\textsubscript{2} laser (wavelength 10.6\textmu m) was used to desorb intact neutral molecules from the sample probe. A second laser was employed to photoionise these neutral molecules by multiphoton absorption using a laser radiation wavelength of 266nm (0.4\text{MWcm}^{-2}) obtained from a Nd:YAG. The product photoions were mass analysed using a reflectron time of flight mass spectrometer and were detected by a multichannel plate detector.
3.6 Fluorescence spectroscopy

All steady state fluorescence and phosphorescence measurements were carried out on a Jobin Yvon Spex Fluoromax spectrofluorimeter (Instruments S.A. Group). A schematic diagram of the instrument components of the spectrometer is shown in Figure 3.4. The excitation source is a 150W continuous ozone-free xenon lamp, with modified Czerny-Turner spectrometers in both emission and excitation positions. The gratings in both the excitation and emission allow both emission and excitation spectra to be obtained. The data was acquired and manipulated using Instruments S.A. Datamax software.

3.6.1 Steady state fluorescence

All room temperature fluorescence measurements were carried out using a fused silica cuvette (Starna 3/Q/10) which has a pathlength of 10mm. Low temperature analysis was carried out using fused silica sample tubes, constructed in house. Samples were cooled to 77K with liquid nitrogen contained in a fused silica dewar (Instruments S.A.). Ethanol and methylbutane were used as solvents as they form a clear glass without fracturing.

3.6.2 Phosphorescence emission and lifetime measurement

The fluorescence lifetimes of indoles are generally on the nanosecond time scale whereas the phosphorescent lifetimes are nearer the millisecond (or greater) time scale. It is for this reason we can differentiate between fluorescence and phosphorescence emission at 77K. The fluorescence emission can be successfully gated out using a shutter (Oriel Instruments model 76994). This set up is shown in Figure 3.5. The shutter operation was achieved with a controller and a digital delay/pulse generator (Stanford Research Systems) provided timing control. The excitation shutter was opened for 15ms, followed by at least a 15ms delay, gating out the fluorescence before opening the emission shutter which was left open for up to 100ms to collect the phosphorescence emission. The shutters were operated at repetition rates from 20 to 40Hz and the emission or excitation monochromators scanned to build up a spectrum. To measure phosphorescence lifetimes the spectrometer was run in a time acquisition mode with constant excitation and emission wavelengths. The excitation shutter was opened for 10ms, followed by a 15ms delay and the emission shutter remained open for the length of the phosphorescence decay. The resulting decay curves were fitted to a single exponential function to obtain the phosphorescent lifetime.
Chapter 3 Experimental

Figure 3.4 A schematic diagram of the components of the fluorescence spectrometer.

1. Excitation Source
2. Excitation spectrometer
3. Sample compartment coupling optics
4. Sample compartment
5. Emission spectrometer
6. Electron components

1. 150W ozone free lamp
2. Collection mirror (excitation spectrometer)
3. Entrance slit (excitation spectrometer)
4. Collection mirror (excitation spectrometer)
5. Grating
6. Focusing mirror (excitation spectrometer)
7. Excitation slit (emission spectrometer)
8. Excitation shutter
9. Collection mirror (excitation spectrometer)
10. Beam splitter
11. Deflection mirror
12. Photodiode reference collector
13. Sample position
14. Window
15. Sample collection mirror
16. Emission shutter
17. Entrance slit
18. Collection mirror
19. Grating (1200 gr./mm)
20. Focusing mirror
21. Exit slit (emission spectrometer)
22. Emission detector
Figure 3.5 The fluorescence spectrometer adapted for the measurement of phosphorescence spectra and lifetimes. The operation of the shutters are summarised (with a excitation pulse of 10ms, a delay of 15ms and the emission collected over 100ms).

3.6.4 Time Resolved Emission

The experiments were carried out at the Central Laser Facility of the Rutherford Appleton Laboratories. The experiment consists of three main components, a picosecond pulsed laser, a single photon counting / time resolved emission system and the sample. A full description of the experimental set up is described elsewhere. The sample was an ethanol solution of the species of interest in a 3.5mm, 1cm path length fused silica cuvette. The output from the time to amplitude converter (TAC) in the single photon counting experiment was connected to a PC card (Oxford Instruments Inc. PCA3). A full fluorescence decay was first obtained then a section of the decay was selected using an upper and lower limit discriminator. As the monochromator was scanned a time gated emission spectrum was obtained corresponding to the selected decay section.
3.7 Computational details

The computational studies were carried out in conjunction with Dr. Simon Bates, of the Department of Physics and Astronomy, University of Edinburgh. Two computational methodologies, semi-empirical and density functional theory (DFT) were used.

3.7.1 Semi-empirical computational methods

The CAChe 3.11 program suite, (Oxford Molecular)\textsuperscript{16} was used to carry out the semi-empirical calculations. This a MOPAC\textsuperscript{17} based package which gives the choice of either the PM3 or AM1 Hamiltonians for various types of calculation including geometry optimisations and frequency calculations. This method is ideal for larger systems, for example, indole trimers as it is allows a reduction in CPU hours. The energy gradients were optimised using the non-linear least squares method, NLLSQ, and the geometry was optimised by the Broyden, Fletcher, Goldfarb and Shanno, BFGS method. The SCF convergence criterion was $0.00001 \text{H/Å}$. SCF convergence was achieved if the root mean square difference in the elements of the density matrix is below this value for any two successive cycles. For a tighter convergence by a factor of 10, the Keyword ‘precise’ was specified.

3.7.2 DFT computational methods

All DFT calculations were run on Silicon Graphics work stations. For small systems such as the gas phase and solvated indole molecules either an Indy\textsuperscript{®} or Indigo\textsuperscript{2TM} workstation was used. A Silicon Graphics O₂ visual workstation was used for larger systems such as dimers and trimer. The DMol\textsuperscript{3} and Amsterdam Density Functional (ADF) packages were used for DFT calculations under license from Molecular Simulations Inc.\textsuperscript{20} Both these packages are based on a density functional theory (DFT) approach for the solution of the electronic structure of atoms and molecules as described in Section 2.3. The DMol\textsuperscript{3} program uses a double-numeric basis set augmented by polarisation functions on all atoms. ADF uses a basis set comprising Slater-type orbitals of double zeta quality with polarisation functions on all atoms (DZ+P). The core 1s electrons of all non-hydrogen atoms were frozen in the ADF calculations.

For all DFT calculations, generalised gradient corrections (GGA) to the local density approximation were used via the PW91 functionals.\textsuperscript{21} Gradient corrections generally
provide improved predictions of bonding energies and electronic spectra compared to the local density approximation.

3.7.2.4 Calculations
Medium convergence criteria were used for geometry optimisations in all cases except where specified. With ADF the optimisations were continued until the energy gradients were less than 0.01H/Å for medium and 0.001Ha/Å for fine convergence. DMol³ convergence criteria is a factor of ten times more rigorous than that of ADF and so for medium convergence criteria to be met the SCF calculation were continued until the energy gradient was below 0.001H/Å. For larger systems, which demand a large increase in CPU hours, maximum gradients between iterations of less than 0.001H/Å were accepted.

Frequency analysis of the stationary point geometry was carried out on previously optimised structures. DMol³ evaluates frequencies by finite differences of analytical gradients and a complete set of frequency calculations would be computationally demanding. As an estimate it would take approximately 1000 CPU hours on a silicon Graphics O₂ (R5000) workstation. Instead, semi-empirical calculations were employed. This took around 2CPU hours per molecule on a PC with the accuracy of these checked by repeating one of these frequency calculations using the DFT method. DMol³ calculates harmonic frequencies. For DFT methods, calculated vibrational frequencies are, in general, quite close to the "true" values (hence the scale factor to account for anharmonicity is close to 1). For semi-empirical calculations the frequencies were unscaled and are typically overestimated by 11-14% (hence a scale factor of 0.89 is required).

3.7.3 COSMO
The MOPAC and DMol³ programs have the facility to include the effects of solvation in the calculations, clearly important in trying to predict the experimentally observed oxidation potentials. The COSMO solvation model of Klamt and Schuurmann is used, which treats the solvent as a polarisable continuum of relative permittivity, ε; this is discussed in Section 2.3. Relative permittivities of 78.5 and 37.5 were used for water and acetonitrile respectively. Default values for the description of the COSMO shell were used. These included the grid size, the number of segments in the grid, the solvent radius, and the solvent cutoff value around the solute.
3.8 References

Chapter 4
Computational Studies of 5-Substituted Indoles

4.1 Introduction

There are numerous experimental studies focusing on the polymerisation of indole and its 5-substituted derivatives. These have explored the electrochemical and spectroscopic characteristics and have tried to establish how the nature of the substituent affects these properties. The electrical and optical behavior of these materials arise from their geometrical and electronic structures, which can be adequately described by quantum chemical calculations. A computational investigation using quantum chemical techniques would therefore be a valuable complementary tool in interpreting the existing experimental data.

In this chapter the electronic structure and energy of 5-substituted indole neutral monomers and radical cations are calculated using two quantum chemical methodologies; semi-empirical and density functional theory, DFT. Although semi-empirical methods are less rigorous presenting results using this technique would serve as a direct comparison between the theoretical work in this thesis and other published data that have used these methods. They also serve as an assessment of the reliability of this semi-empirical method compared to the more accurate DFT approaches. Most importantly, they form a reference point for calculations of larger, more complicated systems such as dimer and trimer species, which are discussed in Chapter 6. Theoretical studies on systems of this size (for example, the asymmetric indole trimer comprises 42 atoms and this number increases with the addition of various substituents) become computationally expensive using DFT methods. Semi-empirical methods provide a faster method of calculation, and are useful as long as accuracy is not compromised in the favour of speed.

In this chapter, some confidence tests of the software packages are examined. The electronic structure and the energy differences between the neutral and radical cation indole molecules are then calculated in the gas phase and the trends due to the electronic effect of the substituent is discussed. The inclusion of solvation to these calculations is crucial if
comparison to electrochemical measurements are to be made and this is achieved using the COSMO model, with solvation by acetonitrile and water being investigated. The effect of temperature on the calculated results is then considered and this information is used to calculate theoretical oxidation potentials of 5-substituted indoles. These are compared to experimental data in order to test the accuracy of these calculations. Finally, the calculated electronic distribution in the monomer radical cations, and the effect this has on the observed redox potentials and the mechanism of radical cation coupling is discussed.

4.2 Confidence tests

The wide availability of quantum mechanical packages has made them easily accessible; however there may be a danger of misinterpreting the results from a theoretical calculation. Consequently it is important to be aware of the specific deficiencies of each quantum mechanical software package and sometimes it may even be advantageous to use a mix of various techniques in order to obtain a reliable answer. Using two different DFT calculation packages allows an assessment of their "off the shelf" performance to predict the structure and energetics of substituted indole monomers. Basic "confidence tests" using both packages, were performed to assess initially their accuracy in calculating structures and energetics. Both packages, ADF$^9$ and DMol$^3$, were able to predict the gas phase heterolytic bond dissociation energy (Scheme 4.1) of some small OH-containing molecules such as water, methanol and formic acid to within ±0.1 eV of the experimentally determined values.$^{11,12,13}$ The DMol$^3$ parameters are presented in Table 4.1.

$$A:B \rightarrow A^+ + B^-$$

<table>
<thead>
<tr>
<th>Molecule</th>
<th>DMol$^3$ Calculated bond dissociation energy / kJ mol$^{-1}$</th>
<th>Experimentally determined bond dissociation energy / kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$OH</td>
<td>1584.2</td>
<td>1592±8.8$^a$</td>
</tr>
<tr>
<td>HCO$_2$H</td>
<td>1447.0</td>
<td>1445.0±9.2$^b$</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>1631.7</td>
<td>1634.7±0.4$^c$</td>
</tr>
</tbody>
</table>

$^a$ref 11, $^b$ref 12, $^c$ref 13

Table 4.1 The gas phase heterolytic bond dissociation energies, DFT calculated and experimental values.

To assess the accuracy of these packages in calculating molecular structures the predicted optimised geometry of 5-hydroxyindole was compared with that determined from X-ray crystallography$^{14}$. This is the only simple 5-substituted indole crystal structure in the
Cambridge Crystallographic Data base and the structural parameters are presented in Table 4.2 and Figure 4.1 provides the atom numbering Scheme. The crystal structure of 5-hydroxyindole contains three independent molecular stacks with intermolecular O-H...O hydrogen bonding between molecules, which produces indole molecules in three different environments (These are denoted as A, B and C in Table 4.2). This is not uncommon for aromatic alcohol molecules however it does complicate the data to some extent. In absolute terms, bond lengths are generally predicted to within ±0.02Å and bond angles to within ±1 degree of the experimental values. These are typical of the general accuracy of gradient-corrected DFT calculations with basis sets of this quality (DNP). However, we cannot automatically assign discrepancies between calculated and experimental parameters to the inadequacy of the DFT method. The H-bonding interactions present in the crystal, together with the fact that the structure was determined at 210K will result in inherent structural differences compared to the calculation carried out at 0K.

In Table 4.2, the structural data for a semiempirical optimisation of 5-hydroxyindole is also included. Table 4.2 shows that this method predicts bond angles of similar quality to the DFT results. The maximum deviation is approximately 1.5° compared with the experimental data. However, the bond lengths show slightly larger deviations than their DFT counterparts, particularly around the N atom, where MOPAC calculations predict the N-C bonds to be 0.03Å longer. These structural discrepancies between theoretical and experimental structures can be attributed to vibrational averaging effects in the crystal phase. As the X-ray diffraction data was collected at a temperature of 210K, thermal vibration will lead to a blurring of the atomic positions in the molecule. This effect causes the apparent bond distances to shorten whilst angles remain unchanged with respect to the calculated values at 0K. When this contraction is taken into account these experimental bond lengths do not vary significantly from theoretical lengths.
Figure 4.1 Atom numbering Scheme for 5-hydroxyindole.

<table>
<thead>
<tr>
<th>Parametera</th>
<th>DMol PW91b</th>
<th>ADF PW91b</th>
<th>PM3</th>
<th>X-ray Crystallography</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Molecule A</td>
<td>Molecule B</td>
<td>Molecule C</td>
<td></td>
</tr>
<tr>
<td>r(N(1)-C(2))</td>
<td>1.381</td>
<td>1.362</td>
<td>1.407</td>
<td>1.357(6)</td>
</tr>
<tr>
<td>r(N(1)-C(9))</td>
<td>1.385</td>
<td>1.366</td>
<td>1.410</td>
<td>1.370(6)</td>
</tr>
<tr>
<td>r(C(2)-C(3))</td>
<td>1.378</td>
<td>1.366</td>
<td>1.381</td>
<td>1.349(8)</td>
</tr>
<tr>
<td>r(C(3)-C(8))</td>
<td>1.433</td>
<td>1.416</td>
<td>1.436</td>
<td>1.420(5)</td>
</tr>
<tr>
<td>r(C(4)-C(5))</td>
<td>1.392</td>
<td>1.375</td>
<td>1.388</td>
<td>1.368(4)</td>
</tr>
<tr>
<td>r(C(5)-C(6))</td>
<td>1.413</td>
<td>1.398</td>
<td>1.421</td>
<td>1.392(6)</td>
</tr>
<tr>
<td>r(C(5)-0(5))</td>
<td>1.380</td>
<td>1.357</td>
<td>1.372</td>
<td>1.395(5)</td>
</tr>
<tr>
<td>r(C(6)-C(7))</td>
<td>1.390</td>
<td>1.375</td>
<td>1.377</td>
<td>1.373(7)</td>
</tr>
<tr>
<td>r(C(7)-C(9))</td>
<td>1.399</td>
<td>1.384</td>
<td>1.404</td>
<td>1.393(5)</td>
</tr>
<tr>
<td>r(C(8)-C(4))</td>
<td>1.409</td>
<td>1.394</td>
<td>1.402</td>
<td>1.403(6)</td>
</tr>
<tr>
<td>r(C(9)-C(4))</td>
<td>1.397</td>
<td>1.409</td>
<td>1.421</td>
<td>1.414(6)</td>
</tr>
<tr>
<td>r(C(2)-N(1)-C(9))</td>
<td>109.3</td>
<td>109.5</td>
<td>108.7</td>
<td>109.1(4)</td>
</tr>
<tr>
<td>r(N(1)-C(2)-C(3))</td>
<td>109.4</td>
<td>109.4</td>
<td>108.9</td>
<td>110.1(4)</td>
</tr>
<tr>
<td>r(C(2)-C(3)-C(8))</td>
<td>107.2</td>
<td>107.0</td>
<td>107.4</td>
<td>118.9(4)</td>
</tr>
<tr>
<td>r(C(4)-C(5)-C(6))</td>
<td>121.4</td>
<td>121.1</td>
<td>122.4</td>
<td>122.1(4)</td>
</tr>
<tr>
<td>r(C(4)-C(5)-O(5))</td>
<td>122.8</td>
<td>122.6</td>
<td>122.8</td>
<td>121.6(3)</td>
</tr>
<tr>
<td>r(C(5)-C(6)-C(7))</td>
<td>120.8</td>
<td>120.9</td>
<td>120.5</td>
<td>120.8(3)</td>
</tr>
<tr>
<td>r(C(6)-C(7)-C(9))</td>
<td>118.0</td>
<td>118.0</td>
<td>117.8</td>
<td>117.9(4)</td>
</tr>
<tr>
<td>r(C(3)-C(8)-C(9))</td>
<td>107.0</td>
<td>107.0</td>
<td>107.6</td>
<td>106.3(4)</td>
</tr>
<tr>
<td>r(C(4)-C(8)-C(9))</td>
<td>119.0</td>
<td>119.0</td>
<td>120.0</td>
<td>118.5(3)</td>
</tr>
<tr>
<td>r(N(1)-C(9)-C(8))</td>
<td>107.2</td>
<td>107.2</td>
<td>107.0</td>
<td>107.2(3)</td>
</tr>
<tr>
<td>r(0(N(1)-C(9)-C(7))</td>
<td>130.7</td>
<td>130.9</td>
<td>131.1</td>
<td>130.9(4)</td>
</tr>
<tr>
<td>r(C(7)-C(9)-C(8))</td>
<td>122.1</td>
<td>121.9</td>
<td>121.9</td>
<td>121.9(4)</td>
</tr>
</tbody>
</table>

*a* see figure 4.1 for atom numbering  
*b* Basis sets used were of DNP quality

Table 4.2 DFT (DMol³ and ADF) and semi-empirical (MOPAC, PM3) gas phase and X-ray crystallographic structural data¹⁴ (bond lengths, r in Å, bond angles, 0 in degrees. Labels A, B and C refer to the three different indole environments in the crystal).
4.3 Gas phase calculations

In electrochemical studies using a RDE, Mount et al. have shown that the observed peak oxidation potentials of 5-substituted indoles measured by linear sweep voltammetry (LSV) have a reasonably good correlation with the Hammett substituent constant ($\sigma^+$) as shown in Figure 4.2. All oxidation potentials lie on a regression line constructed from electron withdrawing substituted indoles only with the notable exception of hydroxy and methoxy substituents. The Hammett constant found to be the most appropriate is that for a para substituent efficiently conjugated into an aromatic system. The correlation suggests that there is good conjugation of the substituent into the indole aromatic system and consequently the Hammett constant can be used as a means of describing the substituent effect on the electronic structure of indole. A major component of these observed oxidation potentials is the energy difference between radical cation and neutral 5-substituted indoles, and this can be calculated using the computational methods. The results presented in this section are for the gas phase molecules at 0K and therefore neglect the effects of solvation and temperature. The calculated energy differences were plotted against the Hammett constant, as they were be expected to show a similar trend to the peak potentials and this is indeed the case (Figure 4.3). As for the experimental measured oxidation potentials the regression includes the electron withdrawing substituents only and the electron donating groups show a systematic deviation from the line similar to that observed experimentally.

The calculated ADF$^{16}$ and DMol$^3$ gas phase energy differences are similar. This is relatively unsurprising as they employ a common methodology and the same choice of functional to describe the non-local corrections to the local density approximation via the Perdue and Wang (PW91)$^{17}$ method. The basis sets used are of approximately the same quality with each DFT method however the basis functions are of different mathematical form and this will be expected to cause small energy differences. It can be seen in Figure 4.3 that the semi-empirical energy differences are consistently larger than the DFT values.
Figure 4.2 Electrochemically measured peak oxidation potentials of 5-substituted indoles versus the Hammett substituent parameter, $\sigma^+$. All potentials are quoted with respect to Fe/Fe$. The substituent, $R$, is shown for each point. The gradient of the line of best fit (calculated without the OH, OCH$_3$ and NH$_2$ data points) is 0.45V$^{-1}$.

Figure 4.3 Energy differences, $\Delta E$, between 5-substituted neutral and radical cation indoles in the gas phase versus the Hammett substituent parameter, $\sigma^+$, as calculated using different theoretical methodologies. The substituent, $R$, is shown for each point. The gradients of the lines of best fit (calculated without the OH, OCH$_3$ and NH$_2$ data points) are (■)0.642 ev$^{-1}$, (○)0.783 ev$^{-1}$, (▲)0.872 ev$^{-1}$. 
It is interesting to note that the calculations predict a similar departure of the 5-methoxy, 5-hydroxy, and 5-amino substituents from the regression line of the Hammett plot produced from the electron withdrawing substituents. When experimentally observed these anomalies were previously attributed to aggregation in solution possibly by hydrogen bonding or electrode surface interactions, specifically involving adsorption via the substituent to the platinum surface. However these calculations suggest that the cause is intrinsic to the electronic structure of the 5-hydroxyindole, 5-methoxyindole and 5-aminoindole molecules and not due to any experimental factor. These deviations are also observed in the calculations corrected for thermal and solvation effects which are discussed in the next section (Section 4.4 and 4.5).

4.4 The effect of solvation

In order to determine theoretical values for solution oxidation potentials, the inclusion of the stabilisation effect due to solvation in the calculations is necessary. Solvation has a dramatic effect on these calculated energy differences. Figures 4.4 and 4.5 show results for semi-empirical (PM3) and DFT (DMol³) calculations of the radical cation - neutral energy difference, performed using the Conductor-like Screening Model (COSMO) with acetonitrile and water as solvents. Corrections due to solvation are included in each iteration in the SCF calculation, allowing the geometry optimisation of the solute to continue inside the cavity in the dielectric continuum. The gas phase energy differences are added to these figures as a comparison. The inclusion of a solvent environment leads to a marked reduction in energy of the radical cation solution species relative to the neutral molecule. This is consistent with the screening charges which are set up in the solvent, which effectively stabilises the charge on the radical cation and produces the subsequent reduction in the energy between neutral and radical cation solvated species. It is interesting to note that the gradient and intercept of the plots for water and acetonitrile are very similar, even though their relative permittivities, $\varepsilon_r$, differ by nearly a factor of two (78.5 and 37.5 respectively).
In electrochemical studies a supporting electrolyte such as 0.1M LiClO₄ is added to a suitable solvent, in this case acetonitrile, and the introduction of this electrolyte will be expected to slightly change the relative permittivity of acetonitrile. Although there is no published value for the relative permittivity of this electrolyte, εᵣ for acetonitrile containing 0.1M tetrabutyl ammonium tetrafluoroborate, TBABF₄, has been measured as 38.8 at 25°C and 0.1M LiClO₄ would not be expected to be very different. These results suggest that such a relatively small change in permittivity will cause little change in the measured difference in the energies of the radical cation and neutral species, and hence that the value of relative permittivity of acetonitrile can be used as a suitable approximation of the dielectric continuum.

Interestingly the effect of solvation has brought the anomalous energy differences of 5-aminoindole, 5-methoxyindole and 5-hydroxyindole all closer to the regression when compared to the gas phase data. In fact the value for the 5-aminoindole actually now lies on the regression as a result of including solvation. This was previously observed experimentally and lead to the conclusion that departure from the Hammett correlation was found for only OR substituents. In fact this result suggests that an electronic effect is exactly offset by solvation effects in the case of 5-aminoindole and that electronic effects are observed for all three electron donating groups. At this point it should be remembered that COSMO, like any other continuum solvation model is an approximation and with this specific model there is an inherent error of the order of ±0.1eV and so no great importance can be put on this specific effect.

To follow the effect of solvation as the nature of the dielectric continuum changes the energy differences between the neutral and radical cation form of indole were calculated with a series of solvents. The results are shown in Table 4.3 and from these it can be seen that with solvents of decreasing relative permittivity the energy differences increases. This is consistent with a reduction in stabilisation of the radical cation suggesting less effective screening charges set up at the cavity interface around the solute.
Figure 4.4 Energy differences, $\Delta E$, (PM3) between 5-substituted neutral and radical cation indoles versus Hammett substituent parameter, $\sigma^+$, in the (■) gas phase, (●) with acetonitrile solvation, (▲) with water solvation. The gradients of the lines of best fit (calculated without the OH, OCH$_3$ and NH$_2$ data points) are (■)0.642 eV$^{-1}$, (●)0.246 eV$^{-1}$, (▲)0.220 eV$^{-1}$.

Figure 4.5 Energy differences, $\Delta E$, (DMol$^3$) between 5-substituted neutral and radical cation indoles versus Hammett substituent parameters, $\sigma^+$, (■) gas phase and (●) acetonitrile solvation. The gradients of the lines of best fit (calculated without the OH, OCH$_3$ and NH$_2$ data points) are (■)0.872 eV$^{-1}$, (●) 0.509 eV$^{-1}$.
The polarisation response of the solvent continuum induced by the electronic charge distribution in the solute molecule can be displayed graphically. The COSMO surface for the neutral molecules 5-cyanoindole and indole are shown in Figure 4.6. The colour scale is as follows; negative screening charges are blue, positive screening charges are red with green representing approximately zero solvent polarisation. Note that in both molecules the heterocyclic nitrogen induces negative screening charges. Also in 5-cyanoindole the substituent induces positive screening charges. Thus solvation of both the aromatic ring and the substituent are important in determining solvation, which accounts for the variation in the solvated energy calculated by COSMO.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Relative permittivity, $\varepsilon_r$</th>
<th>$\Delta E /eV$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>DMol³</td>
</tr>
<tr>
<td>water</td>
<td>75.3</td>
<td>5.62</td>
</tr>
<tr>
<td>acetonitrile</td>
<td>37.5</td>
<td>5.65</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>2.01</td>
<td>6.81</td>
</tr>
<tr>
<td>gas phase</td>
<td>-</td>
<td>7.54</td>
</tr>
</tbody>
</table>

Table 4.3 The effect of solvation on the energy difference, $\Delta E$ between the indole neutral molecule and indole radical cation.

Figure 4.6 The COSMO surface for a) 5-nitroindole and b) indole generated at 5Å around the atoms in acetonitrile. The colour scale is explained in the text.
4.5 The effect of temperature

The calculations discussed so far relate to total energies calculated at 0K. To obtain room-temperature, solution-phase free energy differences ($\Delta G_{300,K}^0$), with which theoretical oxidation potentials ($E_{300,K}^0$) can be calculated, temperature effects must be included. These include corrections for the zero point energies and the differences in enthalpy and entropy of the neutral and radical cation species between 0K and 300K. Such thermodynamic terms are readily obtained from a semi-empirical frequency analysis of the stationary point geometry having first carried out a geometry optimisation on the structure. All structures were confirmed as true minima on the potential energy surface (with zero negative vibrational frequencies). Semi-empirical correction terms were then calculated and used to convert the DFT energy differences at 0K into values of free energy differences at 300K ($\Delta G_{300,K}^0$).

The oxidation reaction for indole (In) is shown in Scheme 4.1 where In$^{**}$ is the radical cation. In order to calculate the standard free energy, $\Delta G_{(T)}^0$, at temperature, T, for this reaction we need first to consider the standard enthalpy at this temperature, $\Delta H_{(T)}^0$ (equation 4.1).

$$\text{In} \rightarrow \text{In}^{**} + e^- \quad \text{Scheme 4.2}$$

$$\Delta H_{(T)}^0 = \Delta E_{(T)}^0 + \Delta pV \quad [4.1]$$

The calculation of $\Delta H_{(T)}^0$ involves a work term, $pV$, and this is equal to $RT$ since we gain one mole of electrons. $\Delta E_{(T)}^0$ is the electronic energy difference between 0K and T and involves several terms (equation 4.2);

$$\Delta E_{(T)}^0 = \Delta E_{(0 \text{electronic})} + \Delta E_{(0 \text{vibrational})} + \Delta E_{(0 \text{rotational})} + \Delta E_{(0 \text{translational})}$$

$$+ \Delta (\Delta E_{(T \text{electronic})}) + \Delta (\Delta E_{(T \text{vibrational})}) + \Delta (\Delta E_{(T \text{rotational})}) \quad [4.2]$$

$\Delta E_{(0 \text{ electronic})}$ is the energy difference between the neutral and radical cation at 0K, $\Delta E_{(0 \text{ vibrational})}$ is the difference in the zero point vibrational energy for products and reactants, $\Delta E_{(0 \text{ rotational})}$ is the difference in rotational energy for products and reactants at 0K, $\Delta E_{(0 \text{ translational})}$ is the difference in translational energy for products and reactants, $\Delta (\Delta E_{(T \text{ electronic})})$ is the change in electronic energy difference from 0K to T, $\Delta (\Delta E_{(T \text{ vibrational})})$ is the change in vibrational energy difference between 0K and T, and $\Delta (\Delta E_{(T \text{ rotational})})$ is the change in
rotational energy difference from 0K to T. The $\Delta(\Delta E_{\text{rot}})$ terms are negligible and so can be disregarded. DMol$^3$ calculates most of these terms such as $\Delta E_{\text{vibrational}}$, $\Delta E_{\text{rotational}}$, $\Delta E_{\text{translational}}$ and $\Delta(pV)$ in a total enthalpy, H, term and so $\Delta H^0(T)$ can be calculated (equation 4.3) where $H_{T, R}$ and $H_{T, N}$ are the total enthalpies of the radical cation and neutral with ZPE included at temperature T. $3/2RT$ represents the translational energy for a mole of electrons. And hence:

$$\Delta H^0(T) = \Delta E_{\text{vibrational}} + H_{T, R} - H_{T, N} + \Delta(pV) + \frac{3}{2}RT$$  \hspace{1cm} [4.3]

Once $\Delta H(T)$ has been obtained then calculation of $\Delta G^0(T, 0)$ is possible (equation 4.4)

$$\Delta G^0(T, 0) = \Delta H^0(T, 0) - T\Delta S^0(T, 0)$$  \hspace{1cm} [4.4]

where $\Delta S(T, 0)$ is the predicted change in entropy between radical cation and neutral molecule at temperature T.

However to avoid the inclusion of work terms and the translational energy of electrons we can calculate the free energy of the one electron oxidation reaction of an indole, In with respect to another species such as the ferrocene, Fc, which also undergoes an one electron redox reaction to ferrocinium, Fc$^+$. The Fc/Fc$^+$ couple was used as a reference for the calculated oxidation potentials. The thermodynamic properties of this couple were calculated in a similar manner to the indole oxidation potentials, using DMol$^3$, COSMO and frequency analysis for zero point energy, enthalpy and entropy corrections. This data is shown in Table 4.4.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Fc</th>
<th>Fc$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_{0,c}$</td>
<td>4334.75x10$^3$</td>
<td>4334.27x10$^3$</td>
</tr>
<tr>
<td>$S_{300,c}$</td>
<td>393.66</td>
<td>393.72</td>
</tr>
<tr>
<td>$H_{300,c}$</td>
<td>461.49</td>
<td>462.49</td>
</tr>
</tbody>
</table>

Table 4.4 The thermodynamic parameters calculated for the acetonitrile solvated Fc / Fc$^+$ couple by DMol$^3$ where $H_{0,c}$ is the total molecular enthalpy, $S_{300,c}$ is the entropy at 300K, $H_{300,c}$ is the thermal enthalpy parameter at 300K. The enthalpy terms have the ZPE included.
Chapter 4 Computational Studies of 5-Substituted Indoles

The standard reduction potential of $\text{In}^- / \text{In}^+$ can be calculated by considering the cell reaction shown in Scheme 4.3.

\[
\text{RH half cell} \quad \text{In}^+ + e^- \rightarrow \text{In} \\
\text{LH half cell} \quad \text{Fc}^+ + e^- \rightarrow \text{Fc} \\
\text{Overall RH-LH} \quad \text{In}^+ + \text{Fc} \rightarrow \text{In} + \text{Fc}^+ 
\]

Scheme 4.3

To calculate the standard free energy, $\Delta G^{0}_{(300,c)}$ at 300K the ferrocene terms can be calculated and treated as a constant term for subtraction (equation 4.5).

\[
\Delta G^{0}_{(300,c)} = H^{0}_{\text{Fc}} - H^{0+}_{\text{Fc}} - T(S^{0}_{\text{Fc}} - S^{+}_{\text{Fc}}) \\
+ H^{0+}_{\text{In}} - H^{0}_{\text{In}} - T(S^{+}_{\text{In}} - S^{0}_{\text{In}}) 
\]

[4.5]

This can then be used to calculate a redox potential ($E^{0}_{(300,c)}$) from equation 4.6.

\[
\Delta G^{0}_{(300,c)} = -nF E^{0}_{(300,c)} 
\]

[4.6]

The degree of correction produced by zero point energy and thermal corrections can be calculated using equations (4.7 to 4.9). This procedure has been used to calculate values of $E^{0}_{\text{corr}}$ for a variety of 5-substituted indoles shown in Table 4.5.

\[
\Delta G^{0}_{(0,c)} = H^{0}_{\text{Fc}(0)} - H^{0+}_{\text{Fc}(0)} - T(S^{0}_{\text{Fc}} - S^{+}_{\text{Fc}}) \\
+ H^{0+}_{\text{In}(0)} - H^{0}_{\text{In}(0)} - T(S^{+}_{\text{In}} - S^{0}_{\text{In}}) \\
\Delta G^{0}_{(0,c)} = -nF E^{0}_{(0,c)} \\
E^{0}_{\text{corr}} = E^{0}_{(300,c)} - E^{0}_{(0,c)} 
\]

[4.7] [4.8] [4.9]

The semi empirical heat of formation values were used to represent $H_n$ and $H_{Fc}$ as they have the zero point energies included. The thermodynamic properties at this temperature and the calculated correction factors for temperature are displayed in Table 4.5 for 5-substituted indoles.
Chapter 4 Computational Studies of 5-Substituted Indoles

<table>
<thead>
<tr>
<th>Substituent</th>
<th>$H_{\text{of } F} / \text{kJmol}^{-1}$</th>
<th>$S_{300,\text{c}}^{\theta} / \text{kJmol}^{-1}\text{K}^{-1}$</th>
<th>$E_{300,\text{c}}^{\theta} / eV$</th>
<th>$E_{\text{corr}} / \text{meV}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_2$</td>
<td>30.451</td>
<td>627.89</td>
<td>0.397</td>
<td>0.394</td>
</tr>
<tr>
<td>CN</td>
<td>267.85</td>
<td>854.46</td>
<td>0.372</td>
<td>0.370</td>
</tr>
<tr>
<td>CHO</td>
<td>-22.82</td>
<td>560.13</td>
<td>0.381</td>
<td>0.380</td>
</tr>
<tr>
<td>COOH</td>
<td>-266.03</td>
<td>320.13</td>
<td>0.409</td>
<td>0.406</td>
</tr>
<tr>
<td>Br</td>
<td>173.09</td>
<td>756.14</td>
<td>0.376</td>
<td>0.375</td>
</tr>
<tr>
<td>Cl</td>
<td>28.357</td>
<td>167.17</td>
<td>0.365</td>
<td>0.363</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>112.17</td>
<td>683.28</td>
<td>0.335</td>
<td>0.332</td>
</tr>
<tr>
<td>OCH$_3$</td>
<td>-17.08</td>
<td>557.89</td>
<td>0.383</td>
<td>0.369</td>
</tr>
<tr>
<td>OH</td>
<td>-52.88</td>
<td>521.28</td>
<td>0.359</td>
<td>0.355</td>
</tr>
<tr>
<td>NH$_2$</td>
<td>129.07</td>
<td>652.18</td>
<td>0.363</td>
<td>0.357</td>
</tr>
</tbody>
</table>

*a* denotes the neutral molecule  
*b* denotes the radical cation

Table 4.5 Semi empirical (PM3) thermodynamic data. $S_{300,\text{c}}^{\theta}$ is the entropy at 300K  
$E_{300,\text{c}}^{\theta}$ is the calculated solvated redox potential at this temperature. $E_{\text{corr}}$ is the difference in the calculated redox potentials at 300K and 0K.

Although this procedure of using the frequency data calculated using the semiempirical package to correct the total energy derived from DFT calculations is not a strictly accurate method, reasonable accuracy can be achieved. This procedure was necessary due to the considerable computational expense involved in a full DFT frequency analysis of all the 5-substituted neutral and radical cation indoles. It is clear from these data that the corrections due to thermal enthalpy and entropy are in general very small. $E_{\text{corr}}$ is of the order 4-13meV, with the exception of the 5-methyl substituted indole which is slightly larger at 22meV. A "spot check", was performed to test the applicability of this approach by comparing the magnitude of the correction terms determined from semi-empirical and DFT calculations. The DFT frequency analyses of the neutral and radical cation of 5-cyanoindole were performed and from these the magnitude of the DFT correction terms was determined to be 11.4 meV. This is in comparison to the semi-empirical value of 11.2 meV. The similarity of these values suggests that the semi empirical approach gives a correct order of magnitude estimate of the corrections due to these effects, at a fraction of the computational cost.
The DFT temperature corrections for 5-cyanoindole were calculated over a range of temperatures and these are displayed in Table 4.5 where $E_{\text{corr}} = E_{T,C} - E_{0,C}$ at temperature $T$. It can be seen that the correction required at 275K is 9.1 meV and when compared to the value at 300K there is little difference. Although the magnitude of the correction factor is entirely dependent upon the substituent in general the corrections at room temperature are small. Consequently the slight error introduced when comparing experimental oxidation potentials measured at 298K and the predicted oxidation potential calculated at 300K would be expected to be negligible.

<table>
<thead>
<tr>
<th>Temperature /K</th>
<th>$\Delta E_{T,C}$/eV</th>
<th>$E_{\text{corr}}$/meV</th>
</tr>
</thead>
<tbody>
<tr>
<td>275</td>
<td>6.032</td>
<td>9.1</td>
</tr>
<tr>
<td>300</td>
<td>6.035</td>
<td>11.4</td>
</tr>
<tr>
<td>325</td>
<td>6.036</td>
<td>13.3</td>
</tr>
<tr>
<td>350</td>
<td>6.040</td>
<td>15.6</td>
</tr>
</tbody>
</table>

Table 4.6 Correction Factors due to temperature calculated from frequency analysis (DFT) of 5-cyanoindole neutral molecule and the radical cation.

### 4.6 Prediction of oxidation potentials

Using the procedure described in the previous section (Section 4.5) redox potentials were corrected for temperature from the semiempirical and DFT (DMol³) calculations at 300K and these data are presented in Table 4.7 In Figure 4.7 the corrected MOPAC (PM3) and DMol³ redox potentials were plotted against the Hammett parameters of the substituents. The correlation shows that both the semi-empirical and DFT redox potentials predict a good correlation between the Hammett parameters and the redox potential, with the exception of hydroxy, methoxy and amino substituents as observed with experimental peak oxidation potentials and the gas phase and solvated calculations. They also highlight differences between the semi-empirical and DFT calculations. The gradients of the semi-empirical and DFT lines are different and the semi-empirical calculations consistently produce $E_{0,300,c}$ values which are greater than those calculated by DMol³.
Table 4.7 The calculated and experimentally determined redox potentials for the 5-substituted indoles. Both sets of redox potentials are referenced with respect to the Fe / Fe$^\text{+}$$^\text{−}$

The obvious test of these calculations to determine which is more accurate, is by comparison with experimental data. To do this, it is necessary to obtain standard redox potentials from experimentally determined peak oxidation potentials. At high concentrations the shapes of these peaks are complicated by the coupling reaction of radical cations as the polymerisation reaction proceeds. However at low concentrations (less than 1mM) all monomer oxidation peaks appeared to show a shape characteristic of electrochemical reversibility. This was assessed by using the convenient diagnostic for a Nernstian linear sweep voltammetric (LSV) response at 25°C for a 1-electron redox reaction (equation 4.10)$^{21}$. In this expression, $E_p$ is the LSV peak potential, $E_{p/2}$ is the half peak potentials and as the polarographic half wave potential, $E_{1/2}$ is located at approximately midway between $E_p$ and $E_{p/2}$ a fairly accurate estimate of $E_{1/2}$ can be obtained (equation 4.11).

$$E_p - E_{p/2} = 2.2 \frac{RT}{F} = 56.5 / \text{nmV} \quad [4.10]$$

$$E_p - E_{1/2} = 1.09 \frac{RT}{F} = 28.2 \text{mV} \quad [4.11]$$
Concordance with this diagnostic indicates that the effect of coupling reactions of the radical cations at the electrode on the measurement of the standard redox potentials $E^0$ is small at these low concentrations. The assumption is made that the neutral and radical cation species have equal diffusion coefficients in solution, and so $E_1/2$ at 298K will be equal to the standard redox potential, $E^{0}_{298}$. $E_1/2$ is related to the standard redox potential by equation 4.12 where $D_{R}^{1/2}$ and $D_{O}^{1/2}$ are the diffusion coefficients of the reduced and oxidised species respectively.

$$E_1/2 = E^{0} + \frac{RT}{nF} \ln \frac{D_{R}^{1/2}}{D_{O}^{1/2}}$$  \hspace{1cm} [4.12]$$

These values are also presented in Table 4.7. Figure 4.8 shows these experimental values, $E^{0}_{298}$, plotted against the calculated values, $E^{0}_{300}$, for semi-empirical and DFT (Dmol$^3$) calculations. A good correlation between calculated and experimental data corresponds to a straight line of gradient unity and intercept zero. The small error introduced by the slight difference in temperature between the two data sets is neglected. It is clear that the DFT data in Figure 4.8 fits the experimental data more closely than the semi-empirical data. This is to be expected, as the DFT method is more rigorous. The DFT-calculated oxidation potentials for all 5-substituted indoles predict absolute values within ±0.1 V of the experimental values. This value is an approximate error for the DFT method and the notional value of ±0.1 V can be added as error bars to the calculated data on Figure 4.8. As discussed in Section 4.4 this is the approximate error associated with the COSMO solvation model and is considered to be the major involved in the calculation of oxidation potentials in this way. It is highly satisfying that (from Figure 4.8) this method of calculation is able to predict the oxidation potentials of hydroxy, methoxy and amino substituted indoles more accurately than the Hammett parameter.
Figure 4.6 Plot of calculated standard redox potentials, $E^{0}_{300,c}$, using (●) semi-empirical (MOPAC, PM3) and (▲) DFT (DMol$^3$) packages and (■) experimental redox potentials, $E^{0}_{298}$, versus the Hammett substituent parameter, $\sigma^+$. 

Figure 4.7 Plot of $E^{0}_{300,c}$ verses $E^{0}_{298}$ for (●) semi-empirical method (PM3) and (■) DFT (DMol$^3$) data. The dotted line shows the relationship expected if the calculated and experimental data were equal.
4.6 Electronic distribution calculations

Given the close fit of DMol³ calculation to experiment, it is informative to look at the calculated variation in electron density in these molecules. Since the coupling reaction of indoles involves radical cations, we have concentrated on the electron density of the indole radical cations. The variation in electron density can be displayed in the form of molecular orbital shapes, electron density isosurfaces and spin density maps. Previous work has considered charges derived from a Mulliken population analysis on each atom in the indole molecule.22,23 This method like other point charge models has well documented shortcomings, including the fact that electrons located in orbitals on different atoms are divided equally. This may be expected to be far from the actual electronic distribution in the molecule especially with heterocyclic atoms in the aromatic system and so is a very crude method of charge analysis.23

4.6.1 Electron density calculations

Both the DFT packages allow the calculation of the electron density and this can be graphically displayed as an isosurface (a surface of constant electron density). A slice can be taken through this isosurface to investigate the changes in electron density from neutral to radical cation. This shows a slice of the total electron density which includes both σ and π electrons and consequently it is difficult to determine the effect of the removal of one π electron to form a radical cation on the total electron density. In Figure 4.9 the total electron density slices (DMol³) of the neutral 5-cyanoindole and indole and their radical cations are shown.

There are no obvious changes in electron density distribution from neutral to radical cation and this is also the case for the other 5-substituted indoles. Consequently a more sensitive method of probing the π-electron density and determining the most likely location of the radical electron is required and these are discussed next.
Figure 4.8 A slice of the total electron density through the molecular plane for the a) neutral indole, b) indole radical cation, c) neutral 5-cyanoindole and d) 5-cyanoindole radical cation calculated using DFT methods. Red indicates high total electron density and blue indicates low total electron density.

4.7.2 Calculation of the HOMO

The HOMO shapes of the radical cations were calculated using DMol³ to determine the location of the radical electron. This is also known as the singly occupied molecular orbital (SOMO) as in the radical cation it is occupied by the single radical electron. In Figure 4.10 the HOMO shapes for indoles with electron withdrawing groups (NO₂, CN, Cl), 5-methylindole and two indoles with electron donating substituents (OCH₃, OH) are shown A major difference in HOMO shape and location was noted between the indoles with electron withdrawing groups (and indole) and those with electron donating groups.
Figure 4.10 The HOMO shapes calculated for the radical cations of a) 5-cyanoindole, b) 5-indole carboxylic acid, c) indole, d) 5-methylindole, e) 5-hydroxyindole and f) 5-aminindole. The HOMOs are plotted on a 60% isosurface value with the blue and yellow areas representing the \(-/+\) lobes of the HOMO orbital.

For both the electron withdrawing and electron donating substituted indoles the HOMO extends over the whole aromatic system. However it can be seen that the HOMOs of the electron withdrawing substituted radical cations are localised chiefly over the C3 and C2. These are representative for the all 5-substituted radical cations studied so far with electron withdrawing groups. This is in contrast to the electron donating substituted indoles which have HOMOs located much closer to the substituent, with lobes of this orbital concentrated on the C5 position and the substituent. Again the two chosen are representative of the other electron donating substituted indoles.
There is a definite correlation of the distribution of the HOMO and therefore the most likely location of the SOMO electron with the indoles that readily form a trimer upon electropolymerisation. This probably lies in the relation of the double character of the C2-C3 bond with the formation of a 3,3'-linkage in the initial stages of the polymerisation process. With indoles with electron donating groups the HOMO is not located over the C2-C3 bond and have only been observed to form trimers with the aid of a template film. To summarise if the chief location of the SOMO is over the C2-C3 bond then this favours trimerisation.

### 4.7.3 Calculation of the spin density

As coupling of the radical cations would be expected to occur by pairing of the radical spin from each radical cation to form a bond, a more sensitive picture of the position of the unpaired electron is achieved by calculating the spin density for the radical cation. This is equal to the difference in the densities of the \( \alpha \) and \( \beta \) spins in the molecule at any point, giving a measure of the amount of unpaired spin. Furthermore, mapping the spin density onto a 99% electron density isosurface of the radical cation gives a pictorial representation of the distribution of the spin density (the unpaired electron) in the radical cation on this isosurface. The larger the value of the spin density is at a given point, the more likely bond formation via radical pairing would be as it is at this point where the electronic orbitals of neighbouring radical cations would begin to overlap.

Figure 4.11 shows the spin density distributions for all 5-substituted indole radical cations studied with electron withdrawing substituents (Hammett parameter greater than zero), the unsubstituted indole radical cation (Hammett parameter equal to zero) and electron donating substituents (Hammett parameters less than zero). It is clear from these plots that all electron withdrawing substituents show similar spin density distribution around the aromatic system, with the greatest spin density being found in the 3-position. This indicates that the spin density distribution is insensitive to the nature of the electron withdrawing substituent and is dominated by the unpaired electron in the HOMO of the radical cation. Also, significant spin density is observed around the aromatic system, indicating good conjugation between the aromatic ring and the substituent.
Figure 4.11 The spin density mapped onto a 99% electron density isosurface for the radical cations of a) 5-nitroindole, b) 5-cyanoindole, c) 5-carboxylic acid indole, d) 5-bromoindole, e) 5-chloroindole, f) indole, g) 5-methylindole, h) 5-methoxyindole and i) 5-aminoindole. Red areas represent high spin density and blue areas represent low spin density.
This similar electronic distribution may explain the correlation of the energy of the radical cation (and hence the oxidation potential) with the Hammett parameter. In contrast, the electron donating groups show a very different distribution, with the most significant spin density located on the substituent and the carbon atom adjacent to it in the aromatic ring. This is the most likely origin of the deviation of these calculated energies (and the observed oxidation potentials) from the Hammett relationship. The fundamental arrangement of the $\pi$-electronic system for indoles with electron donating substituents appears to be very different to the unsubstituted indole and those with electron withdrawing substituents. In terms of the Hammett relationship, this will be expected to influence the transmission of electronic effects of benzene ring substitution through the aromatic system, consequently the simple Hammett relationship will break down for those indoles with electron donating substituents.

Table 4.8 presents a comparison of the locations of maximum spin density calculated for the indole radical cation and previous experimental and theoretical determinations. Experimental determination were achieved by using photochemical induced dynamic nuclear polarization spectra (p-CIDNP)$^{22}$, a specialised NMR technique. These experiments show the proton isotropic hyperfine coupling constants, and through the McConnell relation the spin densities on the heavy atoms. It is satisfying that in contrast to previous work the locations of maximum spin density predicted by the DFT calculations agree with experimentally measured trends in these atomic spin densities.$^{22,23}$ As mentioned above, the published theoretical studies rely on the Mulliken point charge model which even some of the authors of these studies have suggested that the results may be misleading. It is therefore interesting that the calculations in this work produce significant differences in the locations of maximum spin density from those calculated with the point charge model.$^5$ This indicates the sensitivity of these systems to the level of calculation and further illustrates the danger of using approximate computational methods.
Table 4.8 Comparison of method and location of spin density in order of decreasing spin density distribution for indole radical cation.

### 4.7 Conclusions

Theoretical calculations have been used to explore the energy differences between the neutral and radical cation of indole and some 5-substituted indoles in the gas phase. Correlation of the energy differences with the Hammett parameter was found to be similar to that of the experimentally measured oxidation potentials. This suggests that the anomalous oxidation potentials of 5-methoxyindole, 5-hydroxyindole and 5-aminindole actually have their origin in the fundamental electronic structure of these indoles and are not due to specific substituent / electrode surface interactions as previously proposed.

DFT (GGA) and semiempirical (PM3) calculations were used to determine theoretical values for the standard redox potentials for the oxidation of 5-substituted indoles. Correction for solvation by acetonitrile were included using COSMO and corrections for thermal effects were incorporated by calculation of zero point energy and temperature variations in enthalpy and entropy using frequency analysis at 300K. For the DFT calculations good agreement between these theoretical values and those observed experimentally were found. The less rigorous semiempirical calculations show a greater discrepancy between experiment and theory but however do produce a reasonable estimate of the redox potentials. This emphasises the sensitivity of these calculations to the level of accuracy. Prediction of redox potentials using DFT calculations reveals that the changing nature of the substituent does have an effect on the electronic structure and this can be
determined computationally. The calculation of theoretical oxidation potentials in this way appears to be successful and consequently this method may be used to predict the oxidation potentials of as yet unstudied substituted indoles before synthesis. This would be extremely useful in the development of novel indole conducting polymers as it would also make possible the screening of indole radical cation for their potential to form asymmetric trimers.

The electronic distribution of the radical cations were investigated using DFT calculations of the spin density and HOMO electron density. These calculations indicate that electron withdrawing 5-substituents show a different distribution of the unpaired radical electron in the aromatic system, when compared to those with electron donating substituents. This may explain the origins of observed differences in the redox potentials of electron withdrawing and electron donating substituents. Furthermore it may give an insight into the subsequent coupling reactions of the indole radical cations with electron donating and those with electron withdrawing 5-substituents. Significant differences are observed in the spin density distribution between these and previous DFT and semiempirical calculations. In this work and the most recent semi-empirical method gives an increased error in energies and spin density calculations over DFT methods. This further emphasises the sensitivity of these calculations to the level of accuracy of the computational method and the choice of charge analysis.

The calculated spin density and HOMO distribution of the indole radical cation gives rise to speculation on the effect of radical electron distribution on the polymerisation process and trimer formation. It has already been previously suggested that the formation of the asymmetric trimer could be achieved by the oxidative coupling of two monomer radical cations to form a 3,3'-dimer, which upon further oxidation couples with a monomer radical cation which would lead to the asymmetric trimer rather than a symmetric trimer (Figure 4.12).
The calculated location of greatest spin density supports this hypothesis, as they confirm that those indoles with electron withdrawing substituents would be expected to couple at the 3-position (the position of maximum radical electron concentration). In contrast, when electrooxidised at a bare platinum electrode, indoles with electron donating substituents do not readily form asymmetric trimers. However if these were oxidised on a predeposited film of indole trimers with electron withdrawing substituents (for example 5-cyanoindole) trimer films with electron donating substituents can be obtained. This result can now be explained by coupling in solution due to an alternative mechanism of coupling in this case, due to the observed difference in spin density distribution, which would lead to a different product. However asymmetric trimer formation can occur as adsorption of the radical cations onto a predefined and preoriented template overcomes this problem. A theoretical study of the polymerisation mechanism of the 5-position and other substituted indoles is discussed in Chapter 6.

4.8 References


16. The ADF energy differences were calculated relative to the constituent atoms in their ground states, rather than the atomic "fragments" used by default in ADF.
Chapter 5
The Electronic Effect of Substituent Position and Nature

5.1 Introduction

The electrochemical synthesis of electronically conducting polymers is an important technique in developing novel polymeric materials. These materials have been proposed as potential candidates for a variety of applications such as electrochemical sensors\(^1\) or as the active species in light emitting devices.\(^2,3\) For many of these applications it is desirable to produce a wide range of functionalised electroactive films in order to explore the substituent effect on the overall properties. It has been shown in numerous reported cases that variation of the substituent placed strategically on the thiophene\(^4\) or pyrrole\(^5\) monomer has allowed modification of the polymer film properties. By doing this the electronic and optical properties can be finely tuned in order to optimise the polymer function.

In particular it has been observed that the electrochemical properties of the 5-substituted indoles and their oxidation products (electroactive asymmetric trimers) are dependent on the nature of the substituent.\(^6,7\) Also of interest are the variations observed in the spectroscopic properties.\(^8,9\) Electrochemical studies of other benzene ring substituted indoles are few. In a preliminary study by Waltman, a comparison of the 1-, 2-, 3-, 4-, 5-, 6- and 7-methylindoles was reported.\(^10\) These authors observed the growth of electroactive films for the 4-, 6- and 7-isomers, though these were never characterised. Another study focused on 4-nitroindole and the authors reported that the monomer forms an electroactive cyclic trimer in a similar manner to its 5-isomer.\(^11\) This suggests that investigation of other 4-substituted indoles may be rewarding and indeed a detailed exploration of the effect of a substituent in other positions would also be invaluable. This would help to probe the electronic structure of the monomer and trimer and elucidate the substituent effect on the polymerisation mechanism and polymer properties. In this chapter electrochemical, spectroscopic and computational investigations focus on some 4-, 6-, 7-monosubstituted indoles and a disubstituted indole. Some 1-, 2- and 3-substituted indoles are also included for discussion.
5.2 Electropolymerisation of 4-, 6-, or 7-substituted indoles at the RDE

5.2.1 Monomer peak oxidation potentials

The monomer oxidation peak potentials of various substituted indoles (substituent positions are shown in Figure 5.1) were measured using linear sweep voltammetry of 1mM solutions and these potentials are presented in Table 5.1. The polymerisation potentials where chosen to ensure that the electrode kinetics of monomer oxidation are not rate limiting and the polymerisation process would consequently be under mass transport control.

The peak oxidation potentials of the 5-substituted indoles have been observed to show a good correlation with the Hammett substituent parameter, (σ'), for para substituents, with the notable exception of the methoxy and hydroxy (and amino) indoles. The same parameters have been used to explore a similar correlation of the peak oxidation potentials for 4-substituted indoles and this shown in Figure 5.2. It appears that the transmission of electronic effects through the aromatic system to the reactive site in the heterocycle are similar for substituents in the 4- and 5-positions.

A linear correlation is obtained which suggests that there is good conjugation of the substituent into the indole moiety and that steric effects in the oxidation are not important. The formation of a delocalised indole radical cation is the result of the removal of a π electron from the delocalised system. It is expected that electron withdrawing groups will destabilise the radical cation causing higher oxidation potentials than unsubstituted indole, whilst electron donating groups will stabilise the radical cation producing lower oxidation potentials. The positive slope (Figure 5.2) confirms that as the substituents have a greater electron withdrawing effect, the monomers become more difficult to oxidise. The gradient of the slope is very close to that of the similar plot for the 5-substituted indoles. A similar departure of the hydroxy and methoxyindoles from the regression as discussed in Section 4.3 is also observed. There is however a slight difference in that the 4-methoxy and 4-hydroxyindole have a lower oxidation potential than their 5-substituted isomers suggesting that they have a greater stabilising effect on the monomer radical cation.
Table 5.1 The monomer peak oxidation potentials, \( E_{pa} \), for a variety of substituted indoles where substituent nature and position are shown and 5,6-(OCH\(_3\)) denotes 5,6-dimethoxyindole. \( E_{pol} \) is the polymerisation potential.

*indicates the formation of a film, (-) indicates no film formation.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>( E_{pa} \pm 0.02 ) / V</th>
<th>( E_{pol} ) / V</th>
<th>Film Formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>4NO(_2)</td>
<td>1.27</td>
<td>1.71</td>
<td>+</td>
</tr>
<tr>
<td>4CN</td>
<td>0.89</td>
<td>1.29</td>
<td>-</td>
</tr>
<tr>
<td>4Cl</td>
<td>1.02</td>
<td>1.42</td>
<td>+</td>
</tr>
<tr>
<td>H(^a)</td>
<td>0.91</td>
<td>1.31</td>
<td>+</td>
</tr>
<tr>
<td>4OCH(_3)</td>
<td>0.67</td>
<td>1.07</td>
<td>+</td>
</tr>
<tr>
<td>4OH</td>
<td>0.64</td>
<td>1.04</td>
<td>+</td>
</tr>
<tr>
<td>1CAI</td>
<td>1.28</td>
<td>1.02</td>
<td>-</td>
</tr>
<tr>
<td>2CAI</td>
<td>1.20(^c)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3CAI</td>
<td>1.20(^c)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4CAI</td>
<td>1.06</td>
<td>1.47</td>
<td>-</td>
</tr>
<tr>
<td>5CAI(^a,b)</td>
<td>1.05(^a)</td>
<td>1.46</td>
<td>+</td>
</tr>
<tr>
<td>6CAI</td>
<td>1.05(^a)</td>
<td>1.46</td>
<td>+</td>
</tr>
<tr>
<td>1CH(_3)(^a)</td>
<td>0.89(^a)</td>
<td>1.29</td>
<td>-</td>
</tr>
<tr>
<td>2CH(_3)(^a)</td>
<td>0.73(^c)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3CH(_3)(^a)</td>
<td>0.76(^c)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4CH(_3)(^a)</td>
<td>0.80(^a)</td>
<td>1.20</td>
<td>+</td>
</tr>
<tr>
<td>5CH(_3)(^a)</td>
<td>0.86(^a)</td>
<td>1.26</td>
<td>-</td>
</tr>
<tr>
<td>6CH(_3)(^a)</td>
<td>0.80(^a)</td>
<td>1.20</td>
<td>+</td>
</tr>
<tr>
<td>7CH(_3)(^a)</td>
<td>0.84(^a)</td>
<td>1.24</td>
<td>+</td>
</tr>
<tr>
<td>5,6-(OCH(_3))</td>
<td>0.56(^a)</td>
<td>0.96</td>
<td>+</td>
</tr>
</tbody>
</table>

\(^{a}\)this work and ref. 10
\(^{b}\)see reference 6.
\(^{c}\)have not attempted polymerisation for these indoles.
\(^{d}\)(+) indicates the formation of a film, (-) indicates no film formation.
Variation of the substituent position does have some surprising effects. With the carboxylic acid group at various positions on the benzene ring there is little variation in oxidation potential. However ICAI was found to have a much higher oxidation potential close to the values obtained for 2CAI and 3CAI. It appears that with the carboxylic acid substituent in any of the 1-, 2- or 3- positions the group has a greater destabilising effect than on the benzene ring making it more difficult to oxidise the monomer. Variation of methyl group position yields a different influence over the oxidation potential. There is a small variation in oxidation potentials with the substituent in the 4-, 5-, 6-, and 7-positions. The range over which this occurs is outwith experimental error and so appears to be a real effect. However 2- and 3-methyllindole have much lower oxidation potentials than benzene substitution whilst n-methyl indole has the highest oxidation potential.

5,6-dimethoxyindole has a much lower oxidation potential with respect to 5-methoxyindole. This is not surprising as two electron donating groups will have a greater stabilising effect than one.
5.2.2 Polymer film formation

Presented in Table 5.1 is the ability of the indole to form an electroactive film upon electrooxidation. Attempted electropolymerisation of the 4-substituted indoles was carried out using a bare platinum electrode and in some cases a thin film of oxidation product was deposited onto the electrode surface. These films, are significantly thinner in comparison to those substantial films formed from 5-substituted indoles such as 5CAI and 5N1 under the same conditions. The resultant discoloration of the monomer solution during these experiments suggests that a sizeable proportion of the oxidation product is soluble, which does not form a deposit on the electrode but instead diffuses into the bulk solution. The striking difference between 4- and 5-indoles however lies with the electron donating groups. Electropolymerised films of 4OH and 4OCH$_3$ can be obtained on a bare platinum electrode with steady state currents observed. This is in complete contrast to the 5-substituted isomers, especially 5-hydroxyindole, which forms a passivating film upon electropolymerisation and have been observed to form trimers only with the aid of a preformed template film$^6$. The 5,6-dimethoxyindole also forms a thin film which is accompanied by a large amount of red soluble product. It was observed to polymerise more readily with the introduction of a template film.

The variation of substituent position gives rise to differing polymerisation abilities. The 2- and 3-substituted indoles were not expected to form trimer species upon electrooxidation and therefore polymerisation was not attempted. The polymerisation of 2- and 3-methylindole to produce linear polymers has been reported previously$^{12}$ and so these have not been considered here. 5$^{13}$ and 6-indole carboxylic acids form thick green polymeric films upon electropolymerisation and steady state currents are observed. However a thick polymeric film is not formed upon electrooxidation of 1CAI or 4CAI on a bare platinum electrode. The current, during a chronoamperometric experiment, drops sharply with time with no rotation dependence. The solution becomes discoloured as a soluble oxidation product is formed at the electrode which then diffuses back into the bulk solution. Using templates of 5-cyanoindole (5CI) the polymerisation transient shows high steady state currents for 4CAI which are comparable in magnitude to those for 5CAI and 6CAI under similar conditions on a bare platinum electrode. The effect of the template is illustrated in Figure 5.3. As with other 4-substituted indoles the template acts as to promote the formation of a solid electropolymerised film which may consist of trimer species. 1-methylindole has previously been reported to form trimers species$^{14}$ and 6- and 7-methylindoles form thick reproducible films as previously reported by Waltman et al.$^{10}$
5.2.2 Koutecky-Levich analysis of the electropolymerisation of indole carboxylic acids

A comparative Koutecky-Levich study was carried out for the indole carboxylic acids in order to investigate the electropolymerisation process. 5CAI and 6CAI, which readily form films, show a rotation rate dependence of the current at concentrations from 10mM to 100mM at a bare platinum electrode. However this comparative study was carried out on templates due to the high solubility of the 4CAI oxidation product and employed a similar procedure as in Chapter 7. In Table 5.2 the results of typical Koutecky-Levich (K-L) analysis for the electropolymerisation of 4-, 5-, 6-indole carboxylic acids on a template film are presented. The inverse limiting current data, \( i_{\text{L}}^{-1} \), were plotted against the inverse square root of the rotation speed, \( W^{-1/2} \), according to the Koutecky-Levich equation\(^\text{15}\) (Section 2.2) and the plots are shown in Figures 5.3 and 5.4.
### Table 5.2 Koutecky-Levich analysis for the electropolymerisation of 4-, 5-, and 6-indole carboxylic acid on templates of 5-cyanoindole.

<table>
<thead>
<tr>
<th>Substituent position</th>
<th>Concentration / mM</th>
<th>Gradient</th>
<th>Number of electrons, n</th>
<th>(i_c \pm 0.7)/mA</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>5</td>
<td>0.698</td>
<td>3.36</td>
<td>(\frac{1}{10.5})</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.410</td>
<td>2.87</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.185</td>
<td>3.18</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.140</td>
<td>2.70</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.047</td>
<td>4.50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.026</td>
<td>4.44</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>0.506</td>
<td>2.33</td>
<td>(\frac{1}{10.0})</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.253</td>
<td>2.33</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.089</td>
<td>2.64</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.040</td>
<td>2.94</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>10</td>
<td>0.453</td>
<td>2.59</td>
<td>(\frac{1}{13.0})</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.253</td>
<td>2.33</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.102</td>
<td>2.31</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.050</td>
<td>2.36</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5.4 Koutecky-Levich analysis of the electropolymerisation of 4CAI on a SCI template.
The current at infinite rotation speed, \( i_{\infty} \), was determined from the intercepts of the three Koutecky-Levich graphs, and these are included in Table 5.2. The values of \( i_{\infty} \) for 4CAI and 5CAI are the same within the experimental error and so we can draw the conclusion that the 4- and 5-substituted carboxyindoles share a similar reactivity during the oxidative polymerisation. However it is strange that 6CAI appears to be slightly more reactive although experimental error may contribute to this value.

Theoretically one would expect between 2 and 3 electrons per indole unit passed in order to form a trimer. However the calculated value of \( n \) may be expected to vary from the theoretical value due to the assignment of a value for the diffusion coefficient as discussed in Chapter 7. It may also be noted that \( n \) increases as concentration increases. This may be a result of the layer composition changing as the amount of linked trimers in relation to free trimers may increase causing an increase of \( n \). The values of \( n \) calculated from the gradients of the 5CAI and 6CAI K-L plots are in general close to the theoretical value with some higher than the expected 2.33 electrons. A direct comparison of the 5CAI and 6CAI K-L data would lead us to believe that the 6CAI undergoes the same electropolymerisation reaction as the 5CAI with a similar number of electrons passed for each. However 4CAI has a constant high value of \( n \).
with a large increase in the number of electrons observed as the concentration increases. The number of electrons involved in the polymerisation reaction may change due to the formation of oligomers other than cyclic trimer also being formed. It is possible that species such as linear dimers, trimers, tetraters and pentaters may also be formed as a result of radical cation coupling in solution.

5.3 Electrochemical characterisation of the electrooxidation product

5.3.1 Rotating ring disc studies

Experiments involving a rotating ring disc electrode (RRDE) downstream of the RDE were used to characterise the oxidation product generated at the disc electrode. Let us make the assumption that asymmetric trimer species are electropolymerised from 4-substituted indoles. During the experiments steady state currents were obtained using either a bare platinum electrode or a preformed template of polymerised SCl. The current at the disc was monitored (remained approximately constant) and the potential of the ring was swept to negative potentials. An electroactive product was observed as a wave at potentials lower than the onset of monomer oxidation for all 4-substituted indoles. This wave can be attributed to an oxidised species generated at the disc electrode arriving at the ring electrode where it becomes reduced as the ring is swept to more negative potentials. In the experiments involving a template for polymerisation very little of the oxidation product is in its reduced form. A typical RRDE wave for a 4-substituted indole, in this case 4-carboxylic acid indole, is shown in Figure 5.6. This polarogram is evidence for the oxidation product generated at the disc being oxidised before dissolution. If the product were a trimer as with 5-substituted indoles the ring current is due to the reduction of this oxidised species in solution, (Scheme 5.1 where (In₃)⁺ is the oxidised trimer and (In₃) is the neutral form).

\[(In₃)⁺ + e⁻ \rightarrow (In₃)\]  

Scheme 5.1

A typical modified Tafel plot for the reducible species, (In₃)⁺, is shown in Figure 5.7. Theory predicts that for a one electron reversible process the gradient (F/RT) would be 39mV⁻¹ at 298K. In this case (Figure 5.7) Tafel analysis has been carried out for 4-methoxyindole polarogram and a gradient of 37±0.5mV⁻¹ obtained, however for 4-chloroindole a gradient of 38±0.5mV⁻¹ was calculated. For other 4-substituted indoles the gradients are also close to the theoretical value. The gradients are given by equation 5.1
Where $i_L$ is the mass transport limited current for reduction and $i$ is the current at electrode potential $E$. $E_{1/2}$ is the halfwave potential which is related to the standard potential $E^\circ$ for the reaction by equation 5.2. The gradient values indicate that the redox reaction is electrochemically reversible and is indeed a one electron transfer.

$$E_{1/2} = E^\circ + \frac{RT}{F \ln \frac{D_R^{1/2}}{D_O^{1/2}}}$$

$D_O$ and $D_R$ are the diffusion coefficients of $(\ln 3)^+$ and $(\ln 3)$ respectively. As these are large molecules one can approximate $D_R \approx D_O$ and so $E_{1/2} \approx E^\circ$. $E_{1/2}$ was measured for various substituted indole electrooxidation products and these potentials are shown in Table 5.3.

These $E_{1/2}$ values for the 4-substituted indoles were plotted against their Hammett substituent parameter and this plot is shown in Figure 5.5. To aid comparison, the $E_{1/2}$ values for the 5-substituted indoles are also included. With the exception of hydroxy and methoxy substituents the $E_{1/2}$ and hence the $E^\circ$ of the reduction reaction shows a close correlation with the Hammett parameter. This indicates that in all cases there is good $\pi$-electron delocalisation in the oxidation product. This trend is in good agreement with the trend in monomer oxidation potentials and also with identical plots involving 5-substitued indoles. A similar departure of the oxy substituents (OH, OCH$_3$) from the regression drawn through the electron withdrawing substituted indoles can also be observed. The gradient of the regression (0.431) is extremely close to that constructed for the 5-substituted indoles (0.427) suggesting a very similar electronic effect of substituent in both positions as observed for the monomers.

The $E_{1/2}$ previously determined for 5CAI was 600mV. There is little variation from this value observed between the $E_{1/2}$ for the carboxylic acid group in different positions. $E_{1/2}$ for the 4-, 5- and 6-carboxylic acid indole trimers are similar within experimental error. $E_{1/2}$ for the methylindoles however follow a trend similar to that observed for the methylindole monomer oxidation potentials with the exception of 6-methylindole. The electrooxidation product of 6CH$_3$ has a $E_{1/2}$ observed at much higher potentials than the trend in $E_{pa}$ would suggest. 5,6-dimethoxyindole has a $E_{1/2}$ consistent with the general trend in monomer oxidation potentials indicating that the two electron donating groups also have a greater electronic influence than one methoxy substituent on the trimer species.
Figure 5.6 A ring polarogram of 4CAI electopolymerised products at the disc electrode. 
(a) A polarogram with the disc off and (b) with the disc on ($i_{\text{disc}} = 5.4\text{mA}$).

Figure 5.7 A Tafel plot for a 4-methoxyindole ring electrode reduction wave for the redox reaction in Scheme 5.1. Disc potential was held at $E_{\text{pol}}$ for this monomer.
Table 5.3 Half wave potentials, \( E_{1/2} \), of substituted trimers.

<table>
<thead>
<tr>
<th>Trimer</th>
<th>( E_{1/2} / \text{V} ) ± 0.05V</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-nitroindole</td>
<td>0.75</td>
</tr>
<tr>
<td>4-chloroindole</td>
<td>0.53</td>
</tr>
<tr>
<td>indole(^a)</td>
<td>0.41</td>
</tr>
<tr>
<td>4-methylindole</td>
<td>0.34</td>
</tr>
<tr>
<td>4-methoxyindole</td>
<td>0.25</td>
</tr>
<tr>
<td>4-hydroxyindole</td>
<td>0.24</td>
</tr>
<tr>
<td>4-carboxylic acid indole</td>
<td>0.58</td>
</tr>
<tr>
<td>5-carboxylic acid indole(^a)</td>
<td>0.60</td>
</tr>
<tr>
<td>6-carboxylic acid indole</td>
<td>0.61</td>
</tr>
<tr>
<td>1-methylindole(^b)</td>
<td>0.20</td>
</tr>
<tr>
<td>5-methylindole(^a)</td>
<td>0.32</td>
</tr>
<tr>
<td>6-methylindole</td>
<td>0.40</td>
</tr>
<tr>
<td>7-methylindole</td>
<td>0.38</td>
</tr>
<tr>
<td>5,6-dimethoxyindole</td>
<td>0.18</td>
</tr>
</tbody>
</table>

\(^a\) ref 6

\(^b\) ref 14

Figure 5.8 A plot of \( E_{1/2} \) for the trimer reduction reaction of 4-substituted indoles against the Hammett substituent parameter (\( \sigma^+ \)). The data for 5-substituted indoles is included for comparison\(^6\).
The soluble fraction, \( (x) \), of the oxidised product that reaches the ring electrode can be calculated (Section 7.2.2). In Table 5.4 the calculated values of \( x \) at the polymerisation potentials on a bare electrode and on a template are presented. If significant amounts of trimer are formed by radical cation coupling in the diffusion layer, away from the electrode, then the trimer would be produced in the neutral form. This is observed during polymerisation on the bare electrode with an appreciably large soluble fraction. This neutral trimer is detected at the ring electrode as an oxidisable species.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>( x ) on a bare electrode</th>
<th>( x ) on a template</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-nitroindole</td>
<td>0.15</td>
<td>0.11</td>
</tr>
<tr>
<td>4-indole carboxylic acid</td>
<td>0.45</td>
<td>0.10</td>
</tr>
<tr>
<td>4-chloroindole</td>
<td>0.16</td>
<td>0.09</td>
</tr>
<tr>
<td>indole</td>
<td>0.25</td>
<td>- ( ^a )</td>
</tr>
<tr>
<td>4-methylindole</td>
<td>0.23</td>
<td>0.16</td>
</tr>
<tr>
<td>4-methoxyindole</td>
<td>0.14</td>
<td>0.14</td>
</tr>
<tr>
<td>4-hydroxyindole</td>
<td>0.15</td>
<td>0.13</td>
</tr>
</tbody>
</table>

\( ^a \) \( x \) has not been measured

Table 5.4 The values of the soluble fraction, \( x \), for the electrooxidation of 4-substituted indoles from a 50mmol dm\(^{-3}\) solution with the electrode rotated at 2Hz.

In general, with the exception of 4-hydroxy and 4-methoxyindole, the soluble fractions are larger than for the identical 5-substituted indoles. These have a lower soluble fraction of oxidation product detected at the ring than their 5-isomers. In all cases the soluble fraction is decreased by using a template for polymerisation. However \( x \) remains higher than that for a 5-substituent on bare platinum. This illustrates the difference in the abilities to form thick films on platinum RDE between the 4 and 5-substituted indoles. Steric effects may well cause this high soluble fraction of product. The presence of a substituent in the 4-position may lead to steric clashing of these groups causing geometrical distortion of the trimer structure.

The structures of 4-, 5- and 6-indole carboxylic acid trimers are presented in Figure 5.9. These have been optimised using force field methods and therefore are not absolutely accurate representations of the trimer structures however they do illustrate the probable loss of planarity due to steric hindrance that may be expected to occur in 4-indole carboxylic acid trimer.
Figure 5.9 The force field optimised structures of (a) 4CAI, (b) 5CAI and (d) 6CAI trimers. The 4CAI trimer (c) has been rotated to show the loss of planarity.

This steric clashing would not be expected to occur in 5- or 6-substituted indole trimers as these groups point away from the trimer system. The expected result of 4-position steric problems would be that the trimers produced are not flat and therefore will not lie favourably in stacks in order to generate good polymer film growth.
5.3.2 Cyclic voltammetry

The 4-substituted indole films grown on bare platinum electrodes and on a template were investigated using cyclic voltammetry (CV). Figure 5.10 shows a CV for 4-nitroindole polymerised under both these conditions. On bare platinum the CVs all appeared to show a broad one electron redox couple and this is attributed to oxidation / reduction of the 4-substituted trimer. A second irreversible oxidation peak is observed at higher potentials which reduces in size with each sweep. This is illustrated in Figure 5.11 and it supports previous observations involving electropolymerised 5-substituted indoles of a irreversible second oxidation which has been attributed to the gradual irreversible linking of trimers within the film. A cyclic voltammetric study on bare platinum was carried out at a range of scan speeds and the oxidation peak current plotted against scan speed. The linear relationship, shown in Figure 5.12, implies that the whole film is involved in the reversible redox reaction and the reaction is not diffusion limited.

![Graph showing cyclic voltammetry results](image)

**Figure 5.10** CV of 4NI electropolymerised (30mM, 4Hz ,1.71V ) (a) on bare platinum and (b) on a 5CI template.

1CH₃, 4CH₃ and 5CH₃ have been found to electropolymerise to form chiefly soluble oxidation products consisting mainly of trimer species, however 6 CH₃ and 7CH₃ form thick green polymeric films. With successive CV sweeps (Figure 5.12), films of 6CH₃ gradually dissolve from the electrode upon reduction as a soluble blue species and the current under the CV peak decreases accordingly. It appears that the neutral form of the 6CH₃ oxidation product is more soluble than the oxidised form in which it is produced. A linear response between scan speed and CV oxidation peak current shows that, for 6CAI and 7CH₃ (Figure 5.13), the whole layer is involved in the redox cycle and consequently the process occurring is a reversible redox
reaction due to the electrode immobilised species.

![Cyclic Voltammogram](image1)

**Figure 5.11** A cyclic voltammogram of electropolymerised 4-chloroindole cycled (50mM, 4Hz, 50mVs\(^{-1}\)).

![Oxidation Peak Heights](image2)

**Figure 5.12** CV oxidation peak heights (\(i_p\)) against the scan speed (V) for electropolymerised films of 4-nitroindole, 4-hydroxyindole and 4-methylindole.
Figure 5.13 Cyclic voltammogram of a electropolymerised 6-methyindole film (50mVs⁻¹), with successive sweeps the oxidation (1, 2, 3) and the reduction (1', 2', 3') peaks are labelled.

Figure 5.14 A typical CV of an electropolymerised film of 7-methylindole (30mmol monomer solution with the electrode rotated at 4Hz) 50mVs⁻¹.
5.4 Characterisation by mass spectrometry

The electrochemical investigation above implies that 4-, 6- and 7-substituted indoles form indole trimer species in a similar manner to the 5-isomers. However complementary characterisation techniques are required to confirm this. The major electrooxidation product of 6CAI is an indole trimer which has been characterised by L^2TOFMS mass spectrometry, (Figure 5.14). The molecular ion peak at 477D is equivalent to three indole monomers with the loss of 6 protons and the fragmentation pattern shows successive loss of three CO₂ units from the carboxy groups on the trimer. The mass spectrum of 5CAI is very similar and was reported previously by Mount and co-workers.¹³

The oxidation products of the 4-substituted indoles were characterised by electrospray mass spectrometry. In all cases only positively charged species were observed. In Figure 5.15 the electrospray mass spectrum of electropolymerised 4-chloroindole is shown. The peaks (at 449.8 and 450.9D) correspond to the oxidised trimer of 4-chloroindole. A fragmentation peak is observed at 414.2D and the separation between this and the trimer peak is 35.6 mass units which corresponds to the loss of a chlorine atom. The peak observed at 898.4D corresponds to two linked oxidised trimers. This may be evidence of the irreversible linking of trimers that occurs during electropolymerisation and also during voltammetry at suitable potentials. A peak at 299D is also observed and can be assigned as a dimer species. However, it is well known that electrospray ionisation methods favour the formation of clusters of charged species therefore the dimer, linked trimer and the occurrence of a pentamer species (751D) may be due to cluster formation and / or further reaction in the electrospray nozzle and not actually be a real oxidation product. Similar mass spectra were obtained for 4CH₃, 6CH₃, and 7CH₃. Each showed the presence of an oxidised dimer, trimer and linked trimer. Although electrospray mass spectroscopy is quick and easy technique for characterisation the results must be interpreted with caution and used only as an indication of species that may be produced during electropolymerisation.

A more sensitive and accurate method is therefore required to identify the oxidation products. As the indole monomer and electropolymerised products have been observed to be highly fluorescent a fluorescence spectroscopy investigation was carried out and this is discussed in Section 5.6.
Figure 5.15 The L2MS mass spectrum of electropolymerised 6- indole carboxylic acid.

Figure 5.16 An electrospray mass spectrum of the oxidation product of 4CII (30mmol monomer solution with the electrode rotated at 2Hz) in an ethanol solution.
5.5 Fluorescence spectroscopy

The fluorescence properties of the indole monomers and electropolymerised films were studied in solution at room temperature and low temperature (77K). The 5-substituted monomers and electropolymerised films have been studied previously and some are included here for comparison.

5.5.1 Room temperature steady state fluorescence spectroscopy

The excitation and emission spectra of the substituted indole monomers were collected at room temperature in solutions of isopentane. The spectra for some 4-substituted indoles and indole carboxylic acids are presented in Figures 5.17 and 5.18 respectively and the data for all the indoles is displayed in Table 5.5. As discussed in Section 1.4.5 the emission of indole monomers is sensitive to the solvent environment. In non polar solvents the emission is expected to originate from the \( ^1L_b \) state and the interaction of solvent with the excited state is small. In Figure 5.17 the emission spectra display a small amount of vibrational structure which allows the \( ^1L_b,0-0 \) transition to be identified together with the onset of the \( ^1L_a \) transition in the excitation spectra. In Table 5.5 the effect of the substituent can be observed by the variations in the tabulated Stokes shift values, \( \Delta \nu_{\text{max}} \) and \( \Delta \nu_{0-0} \). The Stokes shift value, \( \Delta \nu_{\text{max}} \), is calculated from the difference between \( \lambda_{\text{max}} \) of maximum peaks in the excitation and emission spectra and the second, \( \Delta \nu_{0-0} \), represents the difference between the values for the 0-0 transition of the \( ^1L_b \) state. For all substituted indoles the emission wavelength is bathochromically shifted with respect to that of indole suggesting that substitution causes a lowering in energy of the \( S_1 \) \( ^1L_b \) state whilst the \( ^1L_a \) is relatively unaffected. This is reflected in the corresponding increase in Stokes shift, \( \Delta \nu_{\text{max}} \) between the excitation maximum \( ^1L_a \) and the emission maximum \( ^1L_b \). All substituted indoles have a greater Stokes shift value compared with unsubstituted indole. This is consistent with previous work by Jones et al and Aaron et al for unsubstituted indole and 5-substituted indoles who observed a correlation between the magnitude of this shift and the electron donating / withdrawing nature of the substituents.
Chapter 5 The Electronic Effect of Substituent Position and Nature

Figure 5.17 Room temperature fluorescence properties for the 4-substituted indoles in isopentane. Excitation spectra ($\lambda_{\text{em}} = 320\text{nm}$) for (A) 4-chloroindole, (C) 4-methylindole and (E) 4-methoxyindole. Emission spectra ($\lambda_{\text{ex}} = 250\text{nm}$) for (B) 4-chloroindole, (D) methylindole and (F) 4-methoxyindole.

Figure 5.18 Room temperature fluorescence properties for the indole carboxylic acids in isopentane. Excitation spectra for (A) 4CAI $\lambda_{\text{em}} = 340\text{nm}$, (C) 5CAI $\lambda_{\text{em}} = 330\text{nm}$ and (E) 6CAI $\lambda_{\text{em}} = 335\text{nm}$. Emission spectra $\lambda_{\text{ex}} = 280\text{nm}$ for (B) 4CAI, (D) 5CAI and (F) 6CAI. (*) refers to Raman scattering by the solvent.
Chapter 5 The Electronic Effect of Substituent Position and Nature

Substituent Position | Excitation / nm | Emission / nm | Stokes shift $\Delta v_{0,0}$/cm$^{-1}$ | Stokes shift $\Delta v_{\text{max}}$/cm$^{-1}$
---|---|---|---|---
Indole$^a$ | 278 / 286 | 289 / 298 | 400 | 2400
4-Chloroindole | 265 / 276 / 285 | 290 / 300 | 600 | 3200
4-Methoxyindole | 260 / 277 / 285 | 292 / 303 | 840 | 4200
4-Hydroxyindole | 260 / 275 / 286 | 293 / 306 | 840 | 4600
1CAI | 276 / 286 | 291 / 303 | 400 | 3800
4CAI | 279 | 325 / 337 / 353 | 580 | 6200
5CAI$^a$ | 274 | 311 / 329 | 6100
6CAI | 279 | 321 / 336 / 350 | 6100
4-Methylinole | 264 / 275 / 287 | 292 / 302 | 600 | 4700
5-Methylinole | 270 / 285 | 296 / 308 | 1000 | 4200
6-Methylinole | 266 / 276 / 288 | 294 / 303 | 700 | 4600
7-Methylinole | 269 / 276 / 286 | 293 / 303 | 700 | 4200
5,6-Dimethoxyindole | 293 / 305 | 316 / 327 | 1100 | 3600

$^a$Reference 8,9

Table 5.5 Excitation and emission data for substituted indole monomers in isopentane solution at room temperature. The Stokes shift values, $\Delta v_{\text{max}}$ and $\Delta v_{0,0}$, are explained in the text. The values underlined are the 0-0 transitions of the $^1L_b$ state.

The electron donating / withdrawing nature of the substituent and its influence on the $^1L_b$ excited state can be described by plotting the emission wavelength against Hammett substituent parameter, $\sigma^+$. In the study of the 5-substituted indoles the electron donating groups were found to stabilise the excited state to a greater extent than electron withdrawing groups. This is not apparent with the 4OH and 4OCH$_3$ substituents which appear to have less influence on the excited state than the electron withdrawing groups as compared to the 5-isomers. A larger range of 4-substituted indoles may clarify this.

The effect of substitution in different positions depends on the nature of the substituent. In general it can be seen that methyl substitution does not affect excitation and emission properties to any great extent. In contrast the carboxylic acid indoles have a much larger Stokes shift which is consistent with the relative electron withdrawing ability of this group.
The spectroscopic properties of these indoles are very sensitive to concentration. The 5CAI monomer has been observed to cluster, probably as dimers, via hydrogen bonding\textsuperscript{17}. With less dilute solutions 4CAI was shown to have a red shifted emission and an excitation spectrum which extends to longer wavelengths indicative of aggregation occurring possibly due to dimerisation.

Disubstitution with two methoxy groups causes a large bathochromic shift of the emission of 5,6-dimethoxyindole and a large Stokes shift ($\Delta\nu_{0,0}$). This effect is larger than monosubstituted 4-methoxyindole. This observation is consistent with the two electron donating groups at the 5,6-position lowering the energy of the $S_1$ state and it is perhaps predictable that two electron donating groups will stabilise the excited state to a larger extent than one.

The excitation and emission spectra of all the monomers were collected using ethanol as a solvent. These are displayed in Figure 5.19 and 5.20 for some 4-substituted indoles and the 4-, 5-, 6-indole carboxylic acids respectively. The emission maxima, excitation maxima and the Stokes shift are summarised in Table 5.6. Due to the high polarity of the solvent it is thought that the energy of the $^1L_a$ state is lowered as a result of solvent-solute relaxation causing inversion of the $^1L_a / ^1L_b$ states to occur and so emission is expected to occur from the $^1L_a$ state. This accounts for the bathochromic shift of the emission in polar solvents relative to isopentane for 4-, 5-, 6-, and 7-methylindole, 4-, 5-, and 6-indole carboxylic acid and 4-chloroindole. This is consistent with work carried out by Lami\textsuperscript{18} and the study on the 5-substituted indoles.\textsuperscript{8,9} It is not apparent however, that inversion of the $^1L_a / ^1L_b$ states occurs for 4-methoxyindole, 4-hydroxyindole and 5,6-dimethoxyindole. For these indoles the emission maximum ($^1L_b$) remains unchanged in EtOH whilst the excitation $^1L_a$ is bathochromically shifted with respect to that in isopentane. This has been observed previously for 5-methoxyindole by Lami \textit{et al}\textsuperscript{18} and is reflected by the smaller Stokes shift values between the excitation and emission maxima in EtOH. The degree of $^1L_a / ^1L_b$ inversion depends on the separation between these states in the unsolvated molecule, which is substituent dependent.

A further interaction is expected to occur for indoles such as 4- and 6-carboxylic acid indole monomers which are able to interact with the protic solvent via hydrogen bonding. This causes a further lowering in energy of the emitting state and results in a broad structureless emission
spectra at longer wavelengths with a larger Stokes shift than observed with solutions of isopentane. A similar case was found for 5-carboxyindole\(^9\) and 5-carboxaldehyde indole (Section 8.4). Those indoles without groups able to interact with the solvent in this way show sharper excitation and emission spectra. Indole 4-carboxylic acid appears to be affected by the solvent environment in a similar manner as the 5-isomer, however it appears that 6-indole carboxylic acid does not. The 6-isomer emission is less bathochromically shifted and this is accompanied with a corresponding hypsochromic shift of the S\(_1\) excitation compared to the other isomers.

4-Nitroindole has an extremely low intensity emission. This is not unusual for aromatic compounds with nitro substituents which show n to \(\pi^*\) transitions from a non-bonding, (n) orbital to an antibonding \(\pi^*\) orbital. The presence of a n,\(\pi^*\) state promotes spin orbit coupling allowing intersystem crossing to the triplet state. This provides an efficient non-radiative de-excitation pathway which is expected to result in a low intensity emission. This is also observed for 5-nitroindole.\(^9\)

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Excitation Maximum / nm</th>
<th>Emission Maximum / nm</th>
<th>Stokes Shift (\Delta u_{\text{max}}) / cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-chloroindole</td>
<td>273</td>
<td>328</td>
<td>6100</td>
</tr>
<tr>
<td>4-methoxyindole</td>
<td>271</td>
<td>305</td>
<td>4100</td>
</tr>
<tr>
<td>4-hydroxyindole</td>
<td>272</td>
<td>308</td>
<td>4300</td>
</tr>
<tr>
<td>4 CAI</td>
<td>297</td>
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<td>7700</td>
</tr>
<tr>
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<td>5,6-dimethoxyindole</td>
<td>295</td>
<td>329</td>
<td>3500</td>
</tr>
</tbody>
</table>

\(^a\)reference 8, 9

Table 5.6 Excitation and emission data for substituted indole monomers in ethanol solution at room temperature. The stokes shift (\(\Delta u_{\text{max}}\)) is calculated from the difference in wavenumbers between the maximum peaks in the emission and excitation spectra.
Figure 5.19 Room temperature fluorescence properties for the 4-substituted indoles in ethanol. Excitation spectra for (A) 4-chloroindole $\lambda_{eq}=350\text{nm}$, (C) 4-methoxyindole $\lambda_{eq}=340\text{nm}$ and (E) 4-hydroxyindole $\lambda_{eq}=320\text{nm}$. Emission spectra for (B) 4-chloroindole $\lambda_{ex}=260\text{nm}$, (D) 4-methoxyindole $\lambda_{ex}=260\text{nm}$ and (F) 4-hydroxyindole $\lambda_{ex}=240\text{nm}$.

Figure 5.20 Room temperature fluorescence properties for the indoles carboxylic acids in ethanol. Excitation spectra for (A) 4CAI $\lambda_{eq}=350\text{nm}$, (C) 5CAI $\lambda_{eq}=340\text{nm}$ and (E) 6CAI $\lambda_{eq}=320\text{nm}$. Emission spectra ($\lambda_{ex}=280\text{nm}$) for (B) 4CAI, (D) 5CAI and (F) 6CAI.(*)) indicate peaks due to Raman scattering by the solvent.
The substituted indoles were electropolymerised under conditions that favour trimer formation (50mmol, 9Hz). The fluorescence properties of the resultant films were studied at room temperature in ethanol. The excitation and emission spectra for some 4-substituted indoles and methylindoles are shown in Figures 5.21 and 5.22 respectively and these data are summarised in Table 5.7. From the previous study by Jones et al it was observed that fluorescence properties of the 5-substituted indole films in solution differ from the monomers in several ways. Firstly, there is greater vibrational structure which is accompanied by a bathochromic shift of emission wavelength, consistent with a system with greater delocalisation than the monomer. Also, the Stokes shift value, which can be calculated as the difference in wavenumber between the $S_1$ origin bands in the excitation and emission spectra, is considerably reduced for the trimers with respect to the corresponding monomers.

The fluorescence properties of the majority of electropolymerised 5-substituted indole revealed that the chief fluorophore formed from each monomer was a distinctive species with fluorescence properties similar in energy and peak shape. Consequently to some degree fluorescence spectroscopy of any electropolymerised indole can help to identify the species formed upon electrooxidation. The same distinctive fluorophore was observed for electropolymerised 4-, 5-, 6- and 7-methylindole, 4-chloroindole, 4-methoxyindole and also 4-hydroxyindole and was inferred to be the asymmetric indole trimer. The $S_1$ excitation spectra of the trimers show vibrational structure that mirrors the emission spectra. Transitions to higher excited singlet states ($S_2$, $S_3$) can also be clearly identified. These are, with the exception of electropolymerised 4-hydroxyindole, very similar in peak shape and energy to the spectra obtained from the 5-substituted indoles. The 4-hydroxyindole trimer sample was polymerised on a bare platinum electrode. However, to obtain the familiar trimer fluorophore for the 5-isomer polymerisation with the aid of a preformed template film of 5-nitroindole is required. Electropolymerised films of 4-nitroindole were observed to have a low intensity emission in solutions of ethanol. The low intensity emission can again be attributed to the presence of a low lying $n,\pi^*$ state due to the presence of nitro substituents. This low intensity emission makes the films of both electropolymerised 4- and 5-nitroindole extremely useful as they can be employed as templates to promote film growth during polymerisation for indoles that would otherwise form soluble oxidation products at a bare platinum electrode.
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Figure 5.21 Room temperature fluorescence properties for the electopolymerised 4-substituted indoles in ethanol. Excitation spectra for (A) 4-methylindole $\lambda_{ex}=450\text{nm}$ (C) 4-methoxyindole $\lambda_{em}=480\text{nm}$ and (E) 4-hydroxyindole $\lambda_{em}=440\text{nm}$. Emission spectra for (B) 4-methylindole $\lambda_{ex}=340\text{nm}$, (D) 4-methoxyindole $\lambda_{ex}=320\text{nm}$ and (F) 4-hydroxyindole $\lambda_{ex}=340\text{nm}$. Raman peaks due to scattering by the solvent are labelled (*).

<table>
<thead>
<tr>
<th>Electropolymerised Monomer</th>
<th>Excitation Maximum / nm</th>
<th>Emission Maximum / nm</th>
<th>Stokes Shift / cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-chloroindole</td>
<td>312 / 344 / 362 / 390 / 411</td>
<td>436 / 459</td>
<td>1300</td>
</tr>
<tr>
<td>4-nitroindole</td>
<td>307 / 319 / 363 / 393</td>
<td>416 / 436</td>
<td>1400</td>
</tr>
<tr>
<td>4-methoxyindole</td>
<td>294 / 312 / 330 / 389 / 419</td>
<td>434 / 455</td>
<td>820</td>
</tr>
<tr>
<td>4-hydroxyindole</td>
<td>310 / 339 / 344 / 395</td>
<td>417 / 439</td>
<td>1330</td>
</tr>
<tr>
<td>4-methylindole</td>
<td>305 / 337 / 354 / 383 / 402</td>
<td>421 / 439</td>
<td>1100</td>
</tr>
<tr>
<td>5-methylindole$^a$</td>
<td>305 / 337 / 353 / 377 / 396</td>
<td>413 / 433</td>
<td>1100</td>
</tr>
<tr>
<td>6-methylindole</td>
<td>309 / 337 / 351 / 372 / 389</td>
<td>406 / 425</td>
<td>1100</td>
</tr>
<tr>
<td>7-methylindole</td>
<td>301 / 329 / 345 / 369 / 387</td>
<td>402 / 421</td>
<td>1000</td>
</tr>
<tr>
<td>5,6-dimethoxyindole</td>
<td>EtOH 323 / 354 / 367 / 389</td>
<td>420</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ether 323 / 353 / 366 / 386</td>
<td>404 / 424</td>
<td>1150</td>
</tr>
</tbody>
</table>

$^a$ reference 17

Table 5.7 Excitation and emission data for the electopolymerised indoles at room temperature in ethanol. The Stokes shift is calculated from the difference in wavenumbers of the $S_1$ origin bands in the excitation and emission. The transition to the $S_1$, $S_2$ and $S_3$ in the excitation spectra are underlined. The emission from the $S_1$ is in bold type.
Figure 5.22 Room temperature fluorescence properties for the electropolymerised methylindoles in ethanol. Excitation spectra for (A) 5-methylindole $\lambda_{em}=450\text{nm}$, (C) 6-methylindole $\lambda_{em}=480\text{nm}$ and (E) 7-methylindole $\lambda_{em}=460\text{nm}$. Emission spectra for (B) 5-methylindole $\lambda_{ex}=320\text{nm}$, (D) 6-methylindole $\lambda_{ex}=320\text{nm}$ and (F) 7-methylindole $\lambda_{ex}=300\text{nm}$. Peaks due to Raman scattering by the solvent are indicated(*)..

Figure 5.23 4-Chloroindole films electropolymerised under different conditions. 50mmol, 9Hz (A) Excitation spectra $\lambda_{em}=450\text{nm}$ and (B) emission spectra $\lambda_{ex}=340\text{nm}$. 20mmol, 2Hz (C) Excitation spectra $\lambda_{em}=550\text{nm}$ and (D) emission spectra $\lambda_{ex}=340\text{nm}$.
At high rotation speeds and high concentrations (50mmol, 9Hz) a 4-chloroindole trimer is observed with typical excitation and emission spectra as shown in Figure 5.23(A) and (B). However at lower rotation speeds (20mmol, 0Hz,) a broad emission at longer wavelengths (540nm) becomes apparent as illustrated in Figure 5.23(C) and (D). This has been observed for electropolymerised 5-bromoindole and is consistent with the variation of the polymerisation conditions which provide some control over the proportion of linked trimers formed in the film. It is thought that the lower energy emission is due to a polymeric system such as linked trimer units where the excitation energy would be delocalised over several trimer units. The broadness suggests that there are various conjugation lengths present in the film.

The similarities in peak shape of the electropolymerised 4-, 5-, 6- and 7-methylindole is clearly illustrated in Figure 5.22. A gradual hypsochromic shift in the emission and excitation of the methylindole trimers is observed as the position of the substituent is placed in the 4 to 7 positions on the indole monomer. However the Stokes shift remains almost constant suggesting that overall, methyl groups in different position have similar effects on the trimer excited state. This is directly due to the small influence the methyl substituent has on the excited state as it is only weakly electron donating.

The electropolymerised indole carboxylic acids do not share the same fluorescence properties. The excitation and emission spectra of the 5CAI and 6CAI trimers produced under the same conditions, are shown in Figure 5.24. The emission spectra both have a large tail at lower energies (longer wavelengths) possibly be due to aggregation or a greater proportion of polymer species within the film. However the emission and excitation for 6CAI trimer species both occur at a lower energy to that of the 5CAI trimer. One possible explanation is that the flatter structure of the 6-substituted trimer gives rise to better π-orbital overlap and therefore slightly better conjugation (Figure 5.9).
Figure 5.24 Fluorescence properties of the electropolymerised indole carboxylic acids. Excitation spectra for the trimers (A) 5-carboxylic acid $\lambda_{em}=460\text{nm}$ and (B) 6-carboxylic acid $\lambda_{em}=500\text{nm}$. Emission spectra for the trimers of (C) 5-carboxylic acid $\lambda_{ex}=320\text{nm}$ and (D) 6-carboxylic acid $\lambda_{ex}=320\text{nm}$ (* indicates a peak due to Raman scattering by the solvent).

Figure 5.25 The 4CAI monomer (A) excitation $\lambda_{em}=450\text{nm}$ and (B) emission spectra $\lambda_{ex}=280\text{nm}$ and the excitation spectra for an electropolymerised film on a 5NI template (C) $\lambda_{em}=500\text{nm}$ and (E) $\lambda_{em}=550\text{nm}$. The emission spectrum exciting at (D) $\lambda_{ex}=350\text{nm}$ and (F) $\lambda_{ex}=420\text{nm}$.
The fluorescence properties of electropolymerised 4-indole carboxylic acid are very different from the other carboxylic acid indoles. A species with an emission at 420nm is in the correct position for a trimer species although no vibronic structure is observed. When the sample is excited at a longer wavelength (greater than 380nm) a second species can be selectively excited. This second emission is broad and of low intensity and the excitation spectrum associated with this species extends much further to lower energy. A similar observation has been made for the N-methylindole oxidation product generated in solution where at high excitation wavelengths a trimer species is observed but at longer excitation wavelengths a broad polymer species is observed.\textsuperscript{14} The structureless emission of the N-methylindole trimer has been attributed to the underlying emission of the large fraction of linear polymers also produced during electrooxidation as characterised by MALDI mass spectra.\textsuperscript{14} A similar case can be assumed for 4-indole carboxylic acid and this is consistent with the Koutecky-Levich study of electropolymerisation (Section 5.2.2) which suggests that at these high concentrations (50mmol) a greater number of electrons are passed perhaps in the formation of linear trimers tetrarners or even pentamers.

<table>
<thead>
<tr>
<th>Electropolymerised Monomer</th>
<th>Excitation Maximum / nm</th>
<th>Emission Maximum / nm</th>
<th>Stokes Shift / cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-Carboxylic acid indole</td>
<td>($\lambda_{em}$=500nm)</td>
<td>($\lambda_{ex}$=350nm)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>332 / 369 / 397 / 442</td>
<td>420 / 432</td>
<td></td>
</tr>
<tr>
<td></td>
<td>($\lambda_{em}$=550nm)</td>
<td>($\lambda_{ex}$=420nm)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>335 / 371 / 397 / 441</td>
<td>540</td>
<td></td>
</tr>
<tr>
<td>5-Carboxylic acid indole$^a$</td>
<td>320 / 335 / 358 / 378 / 397</td>
<td>415/435</td>
<td>1100</td>
</tr>
<tr>
<td>6-Carboxylic acid indole</td>
<td>323 / 358 / 371 / 398 / 419</td>
<td>445/469/500</td>
<td>1400</td>
</tr>
</tbody>
</table>

\textsuperscript{a}reference 8, 9

Table 5.8 The fluorescence properties of the electropolymerised indole carboxylic acids.

The Stokes shift for the 5CAI and 6CAI trimers are calculated from the $S_1$ origin bands.
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Figure 5.26 The solvent effect on 5,6-dimethoxyindole trimer. (A) Excitation spectrum $\lambda_{ex}=450\text{nm}$ and (B) the emission spectrum $\lambda_{em}=350\text{nm}$ in ether. (C) Excitation spectrum $\lambda_{em}=480\text{nm}$ and (D) the emission spectrum $\lambda_{ex}=330\text{nm}$ in ethanol. Peaks due to Raman scattering by the solvent are indicated (*).

In general, the solvent environment has a smaller effect on the fluorescence properties of the trimers than on monomers. This is indicated by the smaller Stokes shift in solutions of ethanol. There is also increased vibronic structure of emission in ethanol than with the monomers which implies that there is a weaker interaction with the solvent indicating a smaller excited state dipole. However, electropolymerised 5,6-dimethoxyindole appears to be sensitive to polar solvents such as ethanol with which a broad, rounded emission peak is obtained at 420nm. In solutions of ether, a less polar solvent, the familiar peak shape of an indole trimer is observed with emission peaks at 404 and 421nm. The excitation spectra in both solvents remain unaffected and clearly show the $S_2$ and $S_3$ excitation transitions typical of an indole trimer although the $S_1$ excitation is less well resolved due to some overlapping of the $S_1$ and $S_2$ excited states. The $S_1$-$S_2$ separation of the 5,6-dimethoxyindole trimer is much smaller ($1500\text{cm}^{-1}$) than for other trimers studied here ($3000\text{cm}^{-1}$) which is indicative of a quite different electron distribution in the excited state to that of other trimers. This is most likely due to the effect of the six electron donating methoxy groups attached to the trimer inducing a larger excited state dipole giving rise to the sensitivity of the emission properties to polar solvents and loss of vibrational structure.
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The room temperature fluorescence studies of the electropolymerised films help to identify the major fluorophore produced from each monomer. With the exception of 4CAI we can conclude that for these different substituted indoles a trimer is the major fluorescent species present in the film.

5.5.2 The fluorescence properties of the indole monomers and trimers at 77K

The monomers were studied in solutions of ethanol at 77K. At this temperature the solvent freezes to form a clear glass causing some remarkable differences in the excitation and emission properties to be observed. At low temperature there is a well resolved vibronic structure apparent, in both the excitation and emission and this is illustrated in Figure 5.27 for 5,6-dimethoxyindole. It is thought that at low temperature $^1L_a / ^1L_b$ inversion does not occur as the rigid matrix of the glass reduces the solvent-solute relaxation, consequently the emitting level is expected to be $^1L_b$ even in the polar solvent ethanol as opposed to $^1L_a$ when at room temperature. The mirror image association between the excitation and emission spectra becomes immediately apparent and there is a distinct 0-0 transition of the $^1L_b$ state. At higher energy in the excitation spectra the onset of transitions to the $^1L_a$ are also obvious.

The fluorescence data are presented in Table 5.9. The $S_1$ origin bands in the excitation and emission are underlined. The Stokes shifts $\Delta \tilde{\nu}_{0,0}$ are observed to be smaller than at room temperate, which is consistent with the previous work on 5-substituted isomers. The $^1L_a / ^1L_b$ separation value can be approximated by calculation of the difference in wavenumbers of the excitation maxima and the emission 0-0 transition. These values are very similar to the Stokes shift observed in isopentane at room temperature. Both the $^1L_a / ^1L_b$ separation value and the Stokes shift $\Delta \tilde{\nu}_{0,0}$ imply that the emission at 77K is from the $^1L_b$ state.
Figure 5.27 The excitation $\lambda_{\text{ex}}=350\text{nm}$ and emission $\lambda_{\text{em}}=270\text{nm}$ spectra of 5,6-dimethoxyindole at 77K.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Excitation Maximum / nm</th>
<th>Emission Maximum / nm</th>
<th>Stokes shift $\Delta\nu_{0,0}$ / cm$^{-1}$</th>
<th>$^{1}L_{\alpha}-^{1}L_{\beta}$ separation / cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>indole$^a$</td>
<td>272 / 279 / 288</td>
<td>295 / 307 / 320 / 326</td>
<td>800</td>
<td>2900</td>
</tr>
<tr>
<td>4Cl</td>
<td>265 / 270 / 275 / 280 / 285</td>
<td>290 / 295 / 307 / 314 / 329</td>
<td>600</td>
<td>2550</td>
</tr>
<tr>
<td>4CH$_3$</td>
<td>268 / 273 / 276 / 282 / 286</td>
<td>290 / 297 / 303 / 313</td>
<td>480</td>
<td>2830</td>
</tr>
<tr>
<td>4CH$_3$O</td>
<td>263 / 271 / 275 / 284</td>
<td>289 / 296 / 302 / 307 / 314</td>
<td>600</td>
<td>2300</td>
</tr>
<tr>
<td>4OH</td>
<td>269 / 277 / 281 / 288</td>
<td>292 / 305 / 317 / 330</td>
<td>480</td>
<td>3100</td>
</tr>
<tr>
<td>6CH$_3$</td>
<td>267 / 271 / 277 / 286</td>
<td>291 / 303 / 312</td>
<td>600</td>
<td>3100</td>
</tr>
<tr>
<td>7CH$_3$</td>
<td>266 / 270 / 276 / 286</td>
<td>290 / 302 / 311</td>
<td>480</td>
<td>3110</td>
</tr>
<tr>
<td>4CAI</td>
<td>272 / 278 / 281 / 288 / 311</td>
<td>320 / 325 / 335 / 340 / 351</td>
<td>900</td>
<td>5510</td>
</tr>
<tr>
<td>5CAI$^a$</td>
<td>275 / 282 / 291 / 300 / 312</td>
<td>321 / 330 / 336 / 346</td>
<td>900</td>
<td>5200</td>
</tr>
<tr>
<td>6CAI</td>
<td>271 / 280 / 285 / 292 / 311</td>
<td>320 / 326 / 340 / 351</td>
<td>900</td>
<td>5650</td>
</tr>
<tr>
<td>5.6(CH$_3$O)$_2$</td>
<td>286 / 292 / 297 / 303</td>
<td>306 / 313 / 320 / 327</td>
<td>320</td>
<td>1570</td>
</tr>
</tbody>
</table>

$^a$reference 9

Table 5.9 Excitation and emission properties for indoles at 77K in ethanol. The transitions $^{1}L_{\alpha}$ are underlined.
All monomers have emission spectra at longer wavelengths which can be attributed to phosphorescence. This is not observed at room temperature as collisional quenching of the triplet state takes place. In order to confirm that phosphorescence originates from the same species, identical excitation spectra were obtained observing in both the fluorescence and phosphorescence regions of the spectra. The phosphorescence emission for all the monomers, with the exception of 4-nitroindole have considerable vibrational structure and these data are summarised in Table 5.10. The wavelength of phosphorescence emission is insensitive to the nature of the substituent. This is consistent with the triplet $3L_\alpha$ state having a smaller dipole moment than the singlet $1L_\alpha$ as proposed by Callis who has studied the triplet state of indole using semi-empirical calculations. This is also observed for the 5-substituted indoles. However, the intensity of the phosphorescence emission depends on the functional group, as shown in Figure 5.28. For 4-chloroindole the phosphorescence is of greater intensity relative to the fluorescence and perhaps the internal heavy atom effect provides an efficient pathway for intersystem crossing resulting in an increased quantum yield of the radiative transition from the $T_1$ to $S_0$. The separation of the $S_1$ and $T_1$ states can be determined from these data and this is also included in Table 5.10. Interestingly the phosphorescence emission for 4-methoxyindole is more intense than that for either 5-methoxyindole or 5,6-dimethoxyindole.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Phosphorescence Maxima / nm</th>
<th>$S_1$-$T_1$ separation/ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>indole$^a$</td>
<td>405 / 417 / 432 / 439 / 447 / 454</td>
<td>9210</td>
</tr>
<tr>
<td>4-chloroindole</td>
<td>414 / 421 / 440 / 463</td>
<td>8400</td>
</tr>
<tr>
<td>4-methylindole</td>
<td>409 / 418 / 435 / 451 / 468</td>
<td>10030</td>
</tr>
<tr>
<td>4-methoxyindole</td>
<td>406 / 415 / 434 / 445 / 457</td>
<td>9970</td>
</tr>
<tr>
<td>4-hydroxyindole</td>
<td>407 / 418 / 435 / 446 / 459</td>
<td>9680</td>
</tr>
<tr>
<td>6-methylindole</td>
<td>409 / 434 / 455</td>
<td>9910</td>
</tr>
<tr>
<td>7-methylindole</td>
<td>408 / 430 / 457</td>
<td>9970</td>
</tr>
<tr>
<td>4-CAI</td>
<td>407 / 436 / 465</td>
<td>6680</td>
</tr>
<tr>
<td>5-CAI$^a$</td>
<td>410 / 436 / 464</td>
<td>6700</td>
</tr>
<tr>
<td>6-CAI</td>
<td>405 / 420 / 455</td>
<td>6600</td>
</tr>
<tr>
<td>5,6-dimethoxyindole</td>
<td>393 / 416 / 430 / 461</td>
<td>7230</td>
</tr>
</tbody>
</table>

$^a$ reference 9, 17

Table 5.10 Phosphorescence data for indole monomers in EtOH at 77K. The $S_1$-$T_1$ separation has been calculated in wavenumbers. The emission from $T_1$ is underlined.
Figure 5.28 The fluorescence and phosphorescence emission spectra of (A) 4-chloroindole $\lambda_{ex}=270$nm and (B) 4-hydroxyindole at 77K $\lambda_{ex}=270$nm.

Figure 5.29 (A) The low temperature emission $\lambda_{ex}=280$nm spectra of 4-indole carboxylic acid showing both fluorescence and phosphorescence and (B) the fluorescence gated out.
Low temperature studies were carried out on a selection of the electropolymerised indoles. In all cases the emission was observed to be shifted to shorter wavelengths in comparison to the room temperatures studies, although this occurred to a smaller extent than with the corresponding monomers. The low temperature excitation and emission spectra are shown in Figure 5.29 for the electropolymerised 6-methylindole and 5,6-dimethoxyindole. The vibronic structure was well resolved and new peaks could be observed in the emission at longer wavelengths. Phosphorescence emission was difficult to observe as it was masked by the fluorescence emission at longer wavelengths; however its proximity to the fluorescence emission suggest that in the trimer species the $S_1$ and the $T_1$ are close in energy. Shutters were used to try to distinguish phosphorescence for the 6-carboxylic acid indole trimer and the resulting spectra is shown in Figure 5.30. Two well resolved peaks are shown in the phosphorescence spectra at 508nm and 544nm. These are due to transitions from $T_1$ to $S_0$. The $S_1$-$T_1$ separation for 6CAI was found to be 3197cm$^{-1}$. This is comparable to that for 5CAI (3188cm$^{-1}$), however the triplet state of the 6CAI trimer is lower in energy than that for 5CAI trimer. This has implications for electrochemiluminescence studies (ECL) as discussed in Chapter 9. The mechanism of triplet triplet annihilation allows the production of ECL in systems with insufficient energy for direct excitation to the singlet state. This pathway is attractive for application in light emitting devices as it requires less energy input than that required for the production of the singlet state. The low temperature emission spectra help to locate the singlet and triplet states.

<table>
<thead>
<tr>
<th>Electropolymerised Monomer</th>
<th>Excitation Maximum / nm</th>
<th>Emission Maximum / nm</th>
<th>Stokes shift $\Delta\nu_{00}$/ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-methoxyindole</td>
<td>332 / 353 / 371 / 393</td>
<td>402 / 427 / 455 / 499 / 544</td>
<td>569</td>
</tr>
<tr>
<td>6-methylindole</td>
<td>295 / 308 / 337 / 354 / 373 / 392</td>
<td>403 / 425 / 451 / 473 / 506</td>
<td>696</td>
</tr>
<tr>
<td>7-methylindole</td>
<td>307 / 335 / 355 / 374 / 391</td>
<td>402 / 426 / 452 / 473 / 507</td>
<td>699</td>
</tr>
<tr>
<td>6-indole carboxylic acid</td>
<td>359 / 375 / 403 / 429</td>
<td>437 / 464 / 493 / 506 / 427</td>
<td>427</td>
</tr>
<tr>
<td>5,6-dimethoxyindole</td>
<td>260 / 312 / 324 / 354 / 372 / 386</td>
<td>394 / 416 / 440 / 469 / 525</td>
<td>525</td>
</tr>
</tbody>
</table>

Table 5.11 Excitation and emission properties for electropolymerised indoles at 77K in ethanol. The transitions to the $S_1$, $S_2$ and $S_3$ levels in the excitation spectra are underlined. The $S_1$ emission are in bold. The Stokes shift ($\Delta\nu_{00}$) is calculated from the 0-0 transitions in the excitation and emission spectra.
Figure 5.29 The fluorescence properties at 77K of electropolymerised 6-methylindole. The (A) excitation ($\lambda_{em}=450\text{nm}$) and (B) emission ($\lambda_{ex}=300\text{nm}$) spectra. Also the (C) excitation ($\lambda_{em}=430\text{nm}$) and emission ($\lambda_{ex}=300\text{nm}$) of electropolymerised 5,6-dimethoxyindole. The phosphorescence underlies the fluorescence emission.

Figure 5.30 (A) The excitation spectrum ($\lambda_{em}=470\text{nm}$), (B) fluorescence and phosphorescence emission spectra ($\lambda_{ex}=360\text{nm}$) and (C) the phosphorescence spectrum ($\lambda_{ex}=360\text{nm}$) of 6-carboxylic acid indole trimer at 77K.
5.5.3 Time resolved emission experiments

Electropolymerised films of substituted indoles have been observed to consist of various different units. These include trapped monomer, trimer, linked trimers units of varying lengths and in some cases linear polymers. The complex nature of the 4CAI fluorescent properties were studied in greater detail using time resolved emission spectroscopy, a technique which provides a useful indication of the species present in an electropolymerised film. The time resolved properties of 4CAI and 6CAI films were examined and are compared to 5CAI.

The time resolved emission spectra for electropolymerised 6CAI (20mmol, 4Hz) are presented in Figure 5.32. A short lived species is observed in the first 250ps has the typical trimer energy and peak shape. Longer lived species are also observed indicated by the increase in intensity of the emission tail at longer wavelengths. The time resolved spectra of 4CAI film formed (4Hz, 50mmol) on a 5NI template is shown in Figure 5.33. A short lived species which has a narrower emission can be seen at short wavelength. If the first 10ns is gated out a longer lived species is apparent at longer wavelengths. This long lived species is broad and of much lower intensity. This is consistent with the model proposed previously that longer polymer chain segments act as energy traps into which excitation energy is transferred before returning to the ground state.

<table>
<thead>
<tr>
<th>Electropolymerised Indole</th>
<th>Section of emission decay</th>
<th>Fluorescence emission maxima / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>4CAI</td>
<td>0-250ps</td>
<td>503</td>
</tr>
<tr>
<td></td>
<td>10ns onwards</td>
<td>620</td>
</tr>
<tr>
<td>5CAI</td>
<td>0-250ps</td>
<td>408 / 427</td>
</tr>
<tr>
<td></td>
<td>0-500ps</td>
<td>408 / 428</td>
</tr>
<tr>
<td></td>
<td>10ns onwards</td>
<td>409 / 429 (broad shoulder 436)</td>
</tr>
<tr>
<td>6CAI</td>
<td>0-250ps</td>
<td>437 / 459</td>
</tr>
<tr>
<td></td>
<td>0-500ps</td>
<td>443 / 462</td>
</tr>
<tr>
<td></td>
<td>10ns onwards</td>
<td>475</td>
</tr>
</tbody>
</table>

Table 5.12 The emission maxima from time resolved emission spectroscopy.
Chapter 5 The Electronic Effect of Substituent Position and Nature

Figure 5.32 Sections of time resolved emission spectrum of electropolymerised 6-indole carboxylic acid. (20mmol, 4Hz) A) the first 250ps, B) the first 500ps and C) the first 10ns gated out.

Figure 5.33 The time resolved emission spectrum of electropolymerised 4-indole carboxylic acid. A) the full spectrum, B) the first 250pS and C) the last 10ns λω=320nm.
Chapter 5 The Electronic Effect of Substituent Position and Nature

5.6 Quantum chemical studies

Computational studies were carried out with both semiempirical and DFT methods to simulate the effect of placing the substituent in various positions on the indole moiety. The electronic effect of the substituent on the energy of the system is explored leading to the calculation of oxidation potentials. This is followed by a discussion of the electronic distribution in various substituted indole radical cations.

5.6.1 The electronic effect of the substituent on energy

5.6.1.1 Gas phase calculations

The energies of the gas phase 4-substituted neutral indole molecules and their radical cations were calculated. In Table 5.13 the gas phase energy differences, \( \Delta E \), between neutral and radical cations for both PM3 and the more rigorous DFT results are presented. These are plotted against the Hammett substituent parameter (\( \sigma^+ \)) in Figure 5.34. The semiempirical \( \Delta E \) are higher than the DFT results. The DFT energy differences for the 4- and 5-substituted indoles are compared in Figure 5.35. It can be seen that the gradients are very similar and this is consistent with the experimentally observed peak oxidation potentials, discussed in Section 5.2. Furthermore the experimentally observed differences between 4- and 5-indoles are mirrored in these quantum chemical studies. The most striking examples of this are the 4-hydroxy and 4-methoxy indoles which are lower in energy than the calculated energy difference for the 5-isomers.

<table>
<thead>
<tr>
<th>Substituent</th>
<th>PM3</th>
<th>( \Delta E / \text{eV} )</th>
<th>DFT</th>
</tr>
</thead>
<tbody>
<tr>
<td>4NO(_2)</td>
<td>8.64</td>
<td>8.13</td>
<td></td>
</tr>
<tr>
<td>4CN</td>
<td>8.35</td>
<td>8.04</td>
<td>7.87</td>
</tr>
<tr>
<td>4CHO</td>
<td>8.29</td>
<td>7.64</td>
<td>7.65</td>
</tr>
<tr>
<td>4COOH</td>
<td>8.23</td>
<td>7.64</td>
<td>7.65</td>
</tr>
<tr>
<td>4Br</td>
<td>8.14</td>
<td>7.54</td>
<td></td>
</tr>
<tr>
<td>4Cl</td>
<td>7.97</td>
<td>7.44</td>
<td>7.01</td>
</tr>
<tr>
<td>H</td>
<td>8.01</td>
<td>7.44</td>
<td>7.01</td>
</tr>
<tr>
<td>4CH(_3)</td>
<td>7.88</td>
<td>7.22</td>
<td></td>
</tr>
<tr>
<td>4OCH(_3)</td>
<td>7.67</td>
<td>7.22</td>
<td></td>
</tr>
<tr>
<td>4OH</td>
<td>7.73</td>
<td>6.71</td>
<td></td>
</tr>
<tr>
<td>4NH(_2)</td>
<td>7.34</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.13 The energy differences, \( \Delta E \), between neutral and radical cations for the semiempirical and DFT gas phase 4-substituted indoles.
Chapter 5 The Electronic Effect of Substituent Position and Nature

8.5

8.0

w7.5

wJ

7.0

6.5

Figure 5.34 The gas phase energy differences, ΔE, calculated using (●) PM3 and (□) DFT (PW91) against the Hammett substituent parameter (σ+) for the 4-substituted indoles.

-1.5 -1.0 -0.5 0.0 0.5 1.0

Figure 5.35 The DFT gas phase energy differences ΔE, plotted against Hammett substituent parameter, (σ+). The gradient of the regressions through the electron withdrawing groups for (▲) 5-substituted indoles is 0.86eV⁻¹ and (□) 4-substituted indole is 0.87eV⁻¹.
In addition to investigating the effect of changing the nature of the substituent, the effect on the energy difference of changing the position of a given substituent was investigated by studying a variety of indole carboxylic acids and methyl indoles. In Table 5.14 results of DFT and PM3 gas phase calculations to investigate the variation of the neutral-radical cation energy difference for 4-, 5-, 6-, 7-methyl and carboxylic acid substituted indoles are presented.

The calculated $\Delta E$ data for the 1-, 2- and 3-substituted isomers are also included for comparison. The effect of substituent position on the benzene ring was found to be relatively small, and could be comparable in magnitude to the error associated with the calculation method ($\pm 0.1 \text{eV}$) discussed in Section 4.3. This is consistent with the experimental data, however, it is also encouraging that the order of $\Delta E$ and $E_{1/2}$ data correlate well. This is especially true for the methylindoles. Consistency with experimental data is also found with substitution in the 1-, 2- and 3-positions. In general the heterocyclic substituted carboxylic acid indoles have higher oxidation potentials than the benzene ring derivatives and the heterocyclic methylindoles have slightly lower oxidation potentials than their 4-, 5-, 6-, 7-isomers. This is mirrored in both the PM3 and DFT calculations. The DFT $\Delta E$ value for 5,6-dimethoxyindole is also consistent with the low experimentally measured oxidation potential.

<table>
<thead>
<tr>
<th>Substituent</th>
<th>PM3 $\Delta E / \text{eV}$</th>
<th>DFT $\Delta E / \text{eV}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1CAI</td>
<td>8.37</td>
<td>7.97</td>
</tr>
<tr>
<td>2CAI</td>
<td>8.31</td>
<td>-</td>
</tr>
<tr>
<td>3CAI</td>
<td>8.32</td>
<td>7.97</td>
</tr>
<tr>
<td>4CAI</td>
<td>8.23</td>
<td>7.87</td>
</tr>
<tr>
<td>5CAI</td>
<td>8.27</td>
<td>7.92</td>
</tr>
<tr>
<td>6CAI</td>
<td>8.27</td>
<td>7.93</td>
</tr>
<tr>
<td>7CAI</td>
<td>8.23</td>
<td>7.89</td>
</tr>
<tr>
<td>1CH$_3$</td>
<td>7.88</td>
<td>7.43</td>
</tr>
<tr>
<td>2CH$_3$</td>
<td>7.89</td>
<td>-</td>
</tr>
<tr>
<td>3CH$_3$</td>
<td>7.81</td>
<td>7.35</td>
</tr>
<tr>
<td>4CH$_3$</td>
<td>7.88</td>
<td>7.42</td>
</tr>
<tr>
<td>5CH$_3$</td>
<td>7.94</td>
<td>7.51</td>
</tr>
<tr>
<td>6CH$_3$</td>
<td>7.91</td>
<td>7.41</td>
</tr>
<tr>
<td>7CH$_3$</td>
<td>7.92</td>
<td>7.47</td>
</tr>
<tr>
<td>5,6(OCH$_3$)$_2$</td>
<td>-</td>
<td>6.78</td>
</tr>
</tbody>
</table>

Table 5.14 Gas phase energy differences, $\Delta E$, between neutral and radical cation species, for 1-, 2-, 3-, 4-, 5-, 6- and 7-substituted indole carboxylic acids and methyl indoles. The DFT $\Delta E$ value for 5,6-dimethoxyindole is also included.
5.6.1.2 The effect of solvation

Acetonitrile solvated energy differences were calculated with PM3 and DFT methods. As with the 5-substituted indoles solvation lowered the energy of the radical cation with respect to the gas phase energy giving rise to the subsequent decrease in the energy difference with respect to the gas phase. In Figure 5.36 the solvated 4-substituted indole energy differences are plotted against their Hammett substituent parameter. It can be seen that the magnitude of $\Delta E$ and the gradients are reduced by the effect of solvation. A similar effect is observed in the DFT results for the 4-substituted indoles. Interestingly, the same deviation of hydroxy and methoxy indoles from the regression through the electron withdrawing groups is observed as in the gas phase. However 4-aminoindole now lies below the regression contrary to the gas phase results although this change is within the error introduced by the solvation model ($\pm 0.1 \text{eV}, 2 \text{ kcal mol}^{-1}$). This again emphasises the differences in solvation energy for different substituents.

![Figure 5.36](image)

**Figure 5.36** The effect of acetonitrile solvation on the PM3 4-substituted indole energy differences, $\Delta E$ (•) plotted against the Hammett substituent parameter, $\sigma^+$. The gas phase $\Delta E$ (■) are also included for comparison.
5.6.1.3 Prediction of oxidation potentials

Oxidation potentials were calculated in a similar manner to that discussed in Section 4.6. Again a combination of semi-empirical frequency calculation and DFT energy differences were used to predict oxidation potentials with respect to the ferrocene / ferrocinium couple. The PM3 frequency calculation data are presented in Table 5.15 showing the oxidation potentials of the solvated monomers at 0K ($E_{0,c}$), the heats of formation of neutral and radical cation at 300K, the difference in entropy at 300K ($\Delta S_{300}$) and the oxidation potential at 300K ($E_{300,c}$). From these data the correction for temperature, ($E_{corr}=E_{300,c}-E_{0,c}$) is obtained which can be used to allow for the effect of temperature in the DFT results. The obvious test for accuracy of these theoretical oxidation potentials is by comparison with experimentally measured values, $E_{298}$ with respect to Fc/Fc$^+$. 

<table>
<thead>
<tr>
<th>Substituent</th>
<th>$E_{0,c}$/eV</th>
<th>Heat Of Formation$^a$ / kcal mol$^{-1}$</th>
<th>$\Delta S$(rc-n)/cal K$^{-1}$mol$^{-1}$</th>
<th>$E_{300,c}$/eV</th>
<th>$E_{corr}$/meV</th>
</tr>
</thead>
<tbody>
<tr>
<td>4NO$_2$</td>
<td>1.25</td>
<td>8.59</td>
<td>151.70</td>
<td>1.75</td>
<td>1.23</td>
</tr>
<tr>
<td>4CN</td>
<td>1.12</td>
<td>64.46</td>
<td>204.46</td>
<td>-0.19</td>
<td>1.11</td>
</tr>
<tr>
<td>4CAI</td>
<td>1.09</td>
<td>-61.79</td>
<td>77.46</td>
<td>0.85</td>
<td>1.08</td>
</tr>
<tr>
<td>4Br</td>
<td>1.05</td>
<td>42.47</td>
<td>181.61</td>
<td>-0.32</td>
<td>1.04</td>
</tr>
<tr>
<td>4Cl</td>
<td>1.04</td>
<td>28.44</td>
<td>166.34</td>
<td>-0.30</td>
<td>1.03</td>
</tr>
<tr>
<td>4CH$_3$</td>
<td>0.94</td>
<td>26.25</td>
<td>161.96</td>
<td>-0.88</td>
<td>0.94</td>
</tr>
<tr>
<td>4OCH$_3$</td>
<td>0.85</td>
<td>-3.65</td>
<td>130.02</td>
<td>-2.00</td>
<td>0.87</td>
</tr>
<tr>
<td>4OH</td>
<td>0.84</td>
<td>-13.08</td>
<td>120.38</td>
<td>-0.97</td>
<td>0.85</td>
</tr>
<tr>
<td>4NH$_2$</td>
<td>0.42</td>
<td>29.59</td>
<td>153.40</td>
<td>-1.16</td>
<td>0.43</td>
</tr>
</tbody>
</table>

$^a$ note this is not a standard free energy of formation as the entropy is not the standard entropy of formation

Table 5.15 The data from the PM3 frequency calculations for the acetonitrile solvated 4-substituted indoles.

In Figure 5.37 the predicted oxidation potentials for the 4-substituted indoles are plotted against the Hammett substituent parameter. This illustrates how the PM3 values are higher than the experimental $E_{298}^0$ and that the DFT values are much closer to the experimental values, with the exception of 4-methoxyindole. Also included in the plot is the $E_{300,c}$ for 4CN (PM3 and DFT), 4Br (PM3) and 4NH$_2$ (PM3). The experimental oxidation potential has not been measured for these however the predicted values for 4CN and 4Br lie very close to the regression drawn through the electron withdrawing group data and so the true value will be expected to be very similar. The electron donating groups 4OCH$_3$ and 4OH deviate from this regression line in a similar manner to that of the experimental values.
In Figure 5.38 the predicted oxidation potentials for the 4-substituted indoles are plotted against the experimentally measured values of $E_{298}^0$. A good agreement was obtained for DFT $E_{300,c}^0$ values however the PM3 data predicted oxidation potentials are higher than the observed values. This is also true for the methyl and carboxylic acid indoles (Table 5.16) the $E_{300,c}^0$ for these follow the trends in the experimentally measured.

Overall it can be noted that prediction of oxidation potentials in this way is sensitive to the accuracy of method used. The most important implication of these calculations is that prediction of oxidation potentials of any substituted indole, as yet not investigated experimentally is now made possible using this method.

<table>
<thead>
<tr>
<th>Substituent</th>
<th>PM3 $E_{300,c}^0$/eV</th>
<th>DFT$^a$ $E_{300,c}^0$/eV</th>
<th>$E_{1/2}$ vs Fe/Fe$^{b}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4NO$_2$</td>
<td>1.25</td>
<td>-</td>
<td>1.18</td>
</tr>
<tr>
<td>4CN</td>
<td>1.12</td>
<td>1.11</td>
<td>-</td>
</tr>
<tr>
<td>4CAI</td>
<td>1.09</td>
<td>-</td>
<td>0.95</td>
</tr>
<tr>
<td>4Br</td>
<td>1.05</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4Cl</td>
<td>1.04</td>
<td>0.79</td>
<td>0.91</td>
</tr>
<tr>
<td>4CH$_3$</td>
<td>0.94</td>
<td>0.59</td>
<td>0.69</td>
</tr>
<tr>
<td>4OCH$_3$</td>
<td>0.85</td>
<td>0.37</td>
<td>0.56</td>
</tr>
<tr>
<td>4OH</td>
<td>0.84</td>
<td>0.42</td>
<td>0.53</td>
</tr>
<tr>
<td>4NH$_2$</td>
<td>0.42</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1CAI</td>
<td>1.45</td>
<td>-</td>
<td>0.51</td>
</tr>
<tr>
<td>2CAI</td>
<td>1.21</td>
<td>-</td>
<td>1.09</td>
</tr>
<tr>
<td>3CAI</td>
<td>1.28</td>
<td>-</td>
<td>1.09</td>
</tr>
<tr>
<td>5CAI</td>
<td>1.01</td>
<td>0.94</td>
<td>0.94</td>
</tr>
<tr>
<td>6CAI</td>
<td>1.06</td>
<td>0.96</td>
<td>0.93</td>
</tr>
<tr>
<td>7CAI</td>
<td>1.08</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1CH$_3$</td>
<td>1.07</td>
<td>-</td>
<td>0.78</td>
</tr>
<tr>
<td>2CH$_3$</td>
<td>0.98</td>
<td>-</td>
<td>0.62</td>
</tr>
<tr>
<td>3CH$_3$</td>
<td>0.82</td>
<td>-</td>
<td>0.65</td>
</tr>
<tr>
<td>5CH$_3$</td>
<td>1.00</td>
<td>0.68</td>
<td>0.74</td>
</tr>
<tr>
<td>6CH$_3$</td>
<td>0.92</td>
<td>0.61</td>
<td>0.69</td>
</tr>
<tr>
<td>7CH$_3$</td>
<td>0.99</td>
<td>0.64</td>
<td>0.72</td>
</tr>
</tbody>
</table>

$^a$ (-) indicates DFT $E_{300,c}^0$ not calculated  
$^b$ Section 5.2 (-) indicates not measured  

Table 5.16 $E_{300,c}^0$ and observed oxidation potential, $E_{298}^0$ ($E_{1/2}$), relative to Fe / Fe$^+$, for 4-, 5-, 6-, 7-substituted indoles. Some 1-, 2-, 3-, substituted indoles are included for comparison.
Figure 5.37 Predicted oxidation potentials, $E_{300,\text{c}}^0$, for 4-substituted indoles. PM3 (■) results and DFT(▲) values and measured $E_{298}^0$ (■) plotted against the Hammett substituent constant ($\sigma^+$).

Figure 5.38 Predicted oxidation potentials, $E_{300,\text{c}}^0$, for 4-substituted indoles. PM3 (■) results and DFT(●) values plotted against the measured $E_{298}^0$. 
5.6.2 The substituent effect on the electronic distribution

The highest occupied molecular orbitals (HOMO) of the radical cations were calculated for various substituted indoles via the DFT method in order to determine the most probable location of the radical electron. The HOMO isosurfaces were all plotted at a constant value of 60% with the blue and yellow colouring referring to the + / -lobes of the HOMO orbitals. In Figure 5.39 the HOMOs of the 4-substituted indole radical cations are presented. The 4-cyanoindole and 4-chloroindole radical cation HOMOs shown are representative of the other indole radical cations with an electron withdrawing substituent in the 4-position. This group of indole radical cations all share a similar HOMO distribution as each other and also with the 5-substituted isomers which were discussed in Chapter 4 (Section 4.7.2).

However if one compares the electron donating substituted 4- and 5-indole radical cations a quite different case is found. In Figure 5.38 the HOMO of 4-hydroxy and methoxy are presented and these can be compared to their 5-isomers (Section 4.7.2). It can be seen that the HOMO distribution varies with substituent position. The 4-isomers have a HOMO pattern very similar to that of the electron withdrawing substituted radical cations of both 4 and 5-indoles. Whilst both the 4 and 5-hydroxy and methoxy radical cation have the HOMO orbital on and near the substituent, with the 4-isomers the HOMO orbital also extends over the 2- and 3-positions. This may explain the observed differences (experimentally and theoretically) in the oxidation potentials, more importantly, this may be the reason why different oxidation products are obtained upon a platinum RDE. 4-aminoindoles also share a similar HOMO distribution and although not studied experimentally the radical electron may possibly be located in a favourable position for trimerisation.

The variation of substituent position is investigated by comparison of the 1-, 2-, 3-, 4-, 5-, 6-, 7-methylindole radical cations and the HOMOs of these are presented in Figure 5.40. For all methylindoles, the calculated HOMO distribution is consistent. This supports the similar electrochemical properties observed and the formation of asymmetric trimer upon electropolymerisation of 1-, 4-, 5-, 6- or 7-substituted monomers. The calculated HOMO for the 3-methyl radical cation has been reported previously using a hybrid HF-DFT(B3LYP) method. The HOMO pattern calculated is identical to that presented in this work. The HOMOs were also calculated for all the substituted indole carboxylic acids and a similar pattern was also obtained for all 1-, 2-, 3-, 4-, 5-, 6-, 7-isomers. It appears that those benzene substituted indoles which do form indole trimers share a similar HOMO distribution suggesting that those not yet studied but share this HOMO pattern may also form a trimer.
Figure 5.39 Comparison of the HOMO orbitals of the radical cations of (a) 4-cyanoindole, (b) 4-bromoindole, (c) 4-chloroindole, (d) 4-methoxyindole, (e) 4-hydroxyindole, and (f) 4-aminomindole.
Figure 5.40 Comparison of the HOMO orbitals for the methylindole radical cations of (a) 1-methylindole, (b) 3-methylindole, (c) 4-methylindole, (d) 5-methylindole, (e) 6-methylindole, and (f) 7-methylindole.
A more sensitive measure of the radical electron location can however be obtained from a spin density calculation which is discussed next. The distribution of the unpaired electron on the radical cation was simulated by calculating the spin density (\(\alpha-\beta\) electrons) using DFT methods. This was then mapped onto a 99% total electron density isosurface to give a pictorial representation of the radical electron distribution over the whole molecule. Representative plots for a selection of 4-substituted indoles together with the molecular orientation used in these plots are shown in Figure 5.41. The spin density is chiefly at the 3 and 4 positions and is dominated by the unpaired electron in the HOMO. This distribution, with the notable exception of the hydroxy and methoxyindole radical cations are very similar to those of the 5-substituted isomers. This is consistent with the observation that experimentally the 4 and 5-substituted indoles behave in a similar fashion. This also suggests that for the electron withdrawing group substituted indoles the linkage of radical cations during electropolymerisation occurs at a similar position (C3) as the 5-substituted indoles producing similar oxidation products. Interestingly the four position is blocked on the 4-substituted indole and whilst the spin density concentration appears to be comparable but slightly inferior to that in the C3 position, linkage at this site cannot occur due to the presence of the substituent.

However there are also some major differences. The spin density plots for 4OH and 4OCH\(_3\) are very different to the 5-isomers, consistent with the HOMO distributions. The 5-isomers have a large spin density on the substituent and close to it at the C5 and C4 position with little at the 3-position. In contrast the 4-isomer has spin density in the C3, C7 and C4 positions. This may account for the observed film formation and steady state currents during electropolymerisation on bare platinum for the 4OH and 4OCH\(_3\) whereas with the 5-isomers insulating thin films are obtained. The spin density plots for these 4-substituted indoles are in fact very similar to those of the electron withdrawing group of both 4- and 5-substituted indoles, this spin density distribution appears to favour the formation of a timer species as the major oxidation species. This difference, which is summarised in Table 5.17, may also account for the lower oxidation potentials for these indoles.

<table>
<thead>
<tr>
<th>substituent</th>
<th>4-substituted indoles</th>
<th>5-substituted indoles</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCH(_3)</td>
<td>3&gt;7&gt;4&gt;2&gt;6&gt;5</td>
<td>5&gt;4&gt;3&gt;7&gt;6&gt;2</td>
</tr>
<tr>
<td>OH</td>
<td>3&gt;7&gt;4&gt;2&gt;6&gt;5</td>
<td>4&gt;5&gt;3&gt;7&gt;6&gt;2</td>
</tr>
</tbody>
</table>

Table 5.17 Summary of the spin density distributions between 4- and 5OH and 5OCH\(_3\).
Figure 5.41 Comparison of the spin density distribution in the 4-substituted indole radical cations. (a) 4-Cyanoindole, (b) 4-carboxaldehydeindole, (c) 4-chloroindole, (d) 4-methoxyindole (e) 4-hydroxyindole and (f) 4-aminoindole.
Furthermore one may be able to predict from these spin density calculations that those 4-substituted indoles, not yet investigated experimentally, would most probably share similar electroactive properties as those studied. Specifically, 4-cyanoindole and 4-carboxaldehyde indole may well be expected to form an asymmetric electroactive trimer upon electropolymerisation. The greatest curiosity is whether or not an asymmetric indole trimer could be electrosynthesised from 4-aminooindole without the aid of a preformed template. Its spin density is located chiefly near the 7-position as opposed to the 5-position as found with the 5-isomer, but also has increased spin density in the 3-positions which may be sufficient to favour trimer formation.

The spin density distribution was also calculated for the radical cation of the indole carboxylic acids and methylindoles. These are compared in Figure 5.42 and Figure 5.43 respectively. For the carboxyindoles a similar distribution of the radical electron is observed for all the benzene substituted indoles which may account for their similar electrochemical properties. The 2- and 3-carboxyindole radical cations have a very similar distribution to the benzene substituted isomers and so it is interesting that their measured oxidation potentials are higher. The methylindole radical cations also show the same spin density pattern with the radical electron distributed over the 3- and 4-position with each isomer. This includes the 2CH₃ or 3CH₃, so it is unexpected that their measured oxidation potentials are lower than the benzene substituted isomers. Amongst these benzene substituted methylindoles the 6-isomer has considerable spin density at the C6 atom and its oxidation potential is slightly lower than the 4-, 5- and 7-isomers. From these observations a correlation can be drawn between the variations in the oxidation potentials and spin density with substituent position. Where the substituent is directly attached to a position of largest spin density the substituent is able to probe the radical electron distribution to a greater extent than when attached to a position of little or no spin density. The radical cations of 2CAI and 3CAI have the substituent placed near the positions of largest spin density. The electron withdrawing nature of the substituent at these position may destabilise the radical cation to a greater extent than an electron withdrawing substituent in any other position, making it harder to oxidise and so increasing the oxidation potential (this is observed experimentally). Conversely an electron donating substituent attached at a position of large spin density may have a greater stabilising effect on the radical cation than the same group attached at a position of little or no spin density resulting in lower observed oxidation potentials. This is particularly the case for the 2-, 3- and 6CH₃ radical cations where the substituent attached at a position of large spin density concentration.
Figure 5.42 Spin density plots of the indole carboxylic acid radical cations (a) indole 1-carboxylic acid, (b) 3-carboxylic acid, (c) indole 4-carboxylic acid (d) indole 5-carboxylic acid (d) indole 6-carboxylic acid and (f) indole 7-carboxylic acid.
Figure 5.43 Spin density plots of the methylindole radical cations (a) 1-methylindole, (b) 3-methylindole, (c) 4-methylindole, (d) 5-methylindole, (d) 6-methylindole, (f) 7-methylindole.
If one substituent can cause a subtle variation in electronic distribution and energy it would be interesting to investigate the influence of disubstitution. The electrochemical properties of 5,6-dimethoxyindole have been studied in Section 5.2 and it was observed that two electron donating groups have a greater stabilising effect on the radical cation than a single methoxy group. This perhaps is predictable and accounts for the low oxidation potential. However the dimethoxy groups have a dramatic effect on the electronic distribution in the system and this is illustrated by the HOMO and spin density of the radical cation (Figure 5.44). A completely different spin density is observed, with the radical electron density concentrated primarily near the C2 position. Furthermore the radical electron distribution is slightly asymmetrical which is most probably due to the influence of the nitrogen in the heterocyclic ring. This different spin density distribution may be expected to induce a different polymerisation mechanism possibly involving the formation of a 2,2'-dimer to obtain the asymmetric trimer. This is discussed more fully in the next section.

Figure 5.44 5,6-dimethoxyindole radical cation (a) the HOMO (b) the spin density mapped onto a 99% electron density isosurface.
The discussion above raises two interesting points. Firstly, where one substituent is placed in different positions the variations in the spin density distribution follows the variation in the observed oxidation potential, at least this is true for the methylindoles and indole carboxylic acids. Secondly, the electron donating substituents appear to have a larger influence on the spin density distribution than electron withdrawing groups. A brief DFT study of the methoxyindole radical cations seems to illustrate this point clearly. The spin density plots for 4-, 5-, 6- and 7-methoxyindole radical cations are presented in Figure 5.45. It is immediately obvious that no two are alike. It is clear that for strongly electron donating substituents, such as methoxy, the transmission of electronic effects through the indole moiety are different than for methyl and carboxy indoles.

![Figure 5.45](image)

Figure 5.45 The spin density of (a) 4-methoxyindole, (b) 5-methoxyindole, (c) 6-methoxyindole and (d) 7-methoxyindole radical cations.
This is supported by several studies by Prota et al on the acid induced polymerisation of 4-, 6- and 7-hydroxyindoles and 5,6-dihydroxyindole. These researchers observed that upon chemical acid induced (persulfate) oxidative polymerisation of these indoles, oligomeric species have been obtained and the coupling reactions to produce them are dictated by the substituent position. The oligomers obtained for 4OH had 3,7'- and 7,7'-linkages, for 6OH 2,7'- and 7,7'-linkages and for 7OH 4,4'- and 3,4'-linkages. All of these linkages coincide with the most reactive positions of the methoxyindole radical cations as indicated by the spin density distribution. Although acid induced polymerisation and radical cation coupling during electropolymerisation occur via a different mechanism, the most reactive positions are dictated by the substituent position for both reactions. It is interesting to speculate whether the 6- or 7-methoxyindole would be able to form a trimer upon electrooxidation. The 7-isomer may be able to do this as it has some spin density concentration at the C3 position, although radical cation coupling via 4,4'-linkage may also be possible. The 6-isomer may possibly form a trimer via a 2,2'-dimer. A prediction of the polymerisation process of 6-methoxyindole is discussed further in the next chapter. Prota et al observed that acid induced coupling reaction of 5,6-dihydroxyindole was observed to proceed via 2,2'-linkages (and also 2,4'- and 2,7'-). They also reported that some of the reaction products were cyclic indole trimers. These observations are consistent with the spin density distributions of both the 5,6-dimethoxyindole (Figure 5.44) and 5,6-dihydroxyindole radical cation as shown in Figure 5.46.

Note that disubstitution with an electron withdrawing substituent, such as cyano, in the 5- and 6- positions does not alter the position of greatest spin density (C3 position), compared to the monosubstituted form. Disubstitution at these positions does however have a dramatic effect on the energy difference between neutral and radical cation when compared to the monosubstituted form. The gas phase $\Delta E$ for 5,6-dicyanoindole (8.60eV) is larger than that for 5-cyanoindole (8.22eV see Chapter 4) and also for 5-nitroindole (8.30eV). This implies it should be possible to produce an asymmetric trimer with a much higher oxidation potential than those already studied. Furthermore, if disubstitution with a range of substituents is possible then a much wider range of functionalisation and oxidation potentials can be achieved.
5.7 Conclusions

The most important conclusion of this chapter is that trimers can be produced from any of the benzene ring substituted indoles. These indoles can be electropolymerrised to form redox active films of trimers and we can tune the electrochemical properties i.e. the monomer and trimer oxidation potential by varying the substituent nature and position. Electrochemically the 4-substituted indoles behave in a very similar fashion to the 5-substituted indoles. This suggests that electronic effect of placing the substituent in the 4-position is small. However there are some subtle differences with the electron donating group substituted indoles (4OH, 4OCH$_3$). The solubility of the electropolymerised product may be related to the substituent position possibly due to the geometric structure of trimer. It is interesting that indole trimers can also be produced from a disubstituted indole. This suggests that the scope for functionalisation of the trimer moiety is much larger than previously explored. This has implications for tuning the electrochemical properties of the trimer over a wide range of values.

The fluorescence properties of the monomer are dependent on the nature of the substituent and solvent. In polar solvents a large Stokes shift was observed consistent with previous studies on indoles. The trimer excitation and emission occur at longer wavelength than the monomer consistent with greater π-delocalisation around the trimer conjugated system. Fluorescence spectroscopy of the electropolymerised films aided the characterisation of oxidation products.
The substituent nature has little effect on trimer with the exception of 4Cl, 4CAI, 6CAI and 5,6-dimethoxyindole. A common fluorophore was observed for most electropolymerised indoles with the exception of 4CAI. This indole most probably forms a range of linear oligomers upon electropolymerisation possibly due to some interaction (steric clashing) of the carboxy substituents in the 4-position which favour linear oligomers over trimerisation. This observation is consistent with the K-L study. The 5,6-dimethoxyindole trimer does appear to have a slightly different electron distribution in the excited state which results in a bigger excited state dipole than the other indole trimers. This effect is most likely due to the 6 electron donating methoxy groups attached to the indole trimer. The 6-carboxylic acid indole trimer emission is bathochromically shifted as compared to that 5CAI trimer. Low temperature emission spectroscopy was employed to determine the energy of the triplet which was also lower than that of 5CAI.

Computational studies of the electronic structure revealed that the energies follow the same trend as the experimentally measured oxidation potentials, specifically the differences between the 4- and 5-indole oxidation potentials are mirrored in these values. The predicted oxidation potentials are in good agreement with the measured values suggesting that this method of calculation can be used to predict the oxidation potential of any substituted indole and perhaps of any molecule of the similar size and behaviour.

A correlation can be drawn between the electrochemical properties of the substituted indole monomers and the spin density distribution in the radical cation. The spin density varies with substituent position because all positions are different due to the asymmetrical nature of the indole molecule introduced by the N-atom. A large difference was noted between the heterocyclic substituted position and the benzene ring substituted indoles. This suggests that when the electron withdrawing groups, such as COOH, are attached to position of largest spin density, the substituent will have a more pronounced influence on the distribution of the unpaired radical electron.

The substituents have different influences due to the two mechanisms by which substituents can donate or withdraw electrons to or from an aromatic system. These are inductive effects and resonance effects. Inductive effects are due to the intrinsic electronegativity of the atoms and the polarity of the bonds in the functional groups. These act through sigma bonds whilst
resonance effects act through \( \pi \)-bonds. The \( \text{NO}_2 \), \( \text{COOH} \), \( \text{CN} \) and \( \text{CHO} \) substituents all withdraw electrons from the aromatic system \textit{via} strong resonance effects. The effects are greatest at the \( o \) or \( p \)-positions. Methyl groups are inductively electron donating whilst \( \text{OH} \), \( \text{OCH}_3 \), and \( \text{NH}_2 \) substituents can donate a lone pair of electrons \textit{via} the much stronger effect of resonance. This must account for the similar spin density distributions and electrochemical behaviour of the methyl indoles to the indoles with electron withdrawing groups. However with \( \text{OH}, \text{OCH}_3 \) and \( \text{NH}_2 \) substituents the resonance donation of electrons is greatest at the \( o \) and \( p \)-positions and this is reflected in the spin density of the \( 4-, 5-, 6-, \) and \( 7\)-methoxyindole. This means that we can probe the electronic structure of radical cation by variation of substituent position and nature.

The subtle differences observed in the electrochemical experiments are mirrored in the theoretical studies with the prediction of the oxidation potentials of \( 4\text{OH} \) and \( 4\text{OCH}_3 \) to be lower than the corresponding \( 5 \)-isomers. These differences can be correlated to the variation in spin density distribution which also account for the formation of \( 4\text{OH} \) and \( 4\text{OCH}_3 \) trimers on bare platinum. The polymerisation mechanism most likely follows the same path as the \( 5\)-substituted indoles most probably by linking \textit{via} the \( 3,3' \)-positions. However the \( 5,6\)-dimethoxyindole is an exception. This indole has been shown to form an trimer as a result of electropolymerisation, yet has the largest concentration of the spin density at the 2-position which has a similar spin density distribution as the \( 5,6\)-dihydroxyindole radical cation. In contrast the spin density for the \( 5,6\)-disubstituted cyanoindole is similar to the monosubstituted form. Is it possible that for \( 5,6\)-dimethoxyindole and possibly the dihydroxy analogue trimerisation occurs \textit{via} a \( 2,2' \)-linkage rather than a \( 3,3' \)-linkage as proposed for the other indoles. The polymerisation mechanism is investigated in Chapter 6 \textit{via} computational methods.

5.8 References

Chapter 6
A Computational Study of the Indole Polymerisation Process

6.1 Introduction

The mechanism widely accepted for the electropolymerisation of heterocycles such as pyrrole\(^1\) or thiophene\(^2\) by anodic coupling proceeds via the coupling of radical cations. A schematic of this general mechanism is shown in Chapter 1 (Figure 1.3). The first step of the process is a one electron electrooxidation of the monomer at the electrode which forms a reactive radical cation. The second step involves the coupling of two radical cations to produce a dihydrodimer dication which leads to a dimer after loss of two protons and rearomatisation. Due to the applied potential, the dimer (which is more easily oxidised than the monomer) is immediately oxidised to its cationic form by the electrode and undergoes further coupling with a monomeric radical cation. The polymer is generated by a succession of these coupling reactions which occur at the most reactive sites on the radical cation species.

However electrooxidation does not always result in the formation of electroactive materials. Some reactions instead produce insulating films or soluble oligomers. Much study has been devoted to experimentally determine the properties of these materials and the factors which effect electropolymerisation. However few attempts have been made to elucidate the mechanism of electropolymerisation using theoretical methods. Computational studies are useful methods for calculating the electronic structure and energy of molecules. This information can be used to help understand the oxidative polymerisation mechanism and make it possible to predict the most probable structure of the product. They could perhaps also be used as a predictive technique in the design of conducting polymers from novel monomers.

There are various approaches to a computational study of the polymerisation reaction that one can adopt and these were introduced in Chapter 1 (Section 1.4.3). Two such approaches are the calculation of the reaction to form the protonated dicationic species or consideration of the coupling positions at the most reactive sites on the radical cation.
species. The former approach can be achieved via transition state calculations however these are computationally demanding and so have not been considered here.

The electrochemical polymerisation process of indole has attracted much controversy in the past. This polymerisation mechanism and the structure of the final oxidation product has been debated in several electrochemical\textsuperscript{3,4,5} and spectroscopic\textsuperscript{6,7} studies with various structures proposed as discussed in Chapter 1 (Section 1.3.1). A theoretical study would complement the existing experimental data and would aid further understanding of the factors which affect the electropolymerisation mechanism of substituted indoles. Few quantum chemical studies have focused on these aspects and those that have been published are of a solely semi-empirical nature.

The two most recent theoretical studies (Chapter 1, Section 1.4.4) of indole polymerisation have used a semi-empirical (AM1) method.\textsuperscript{8,9} These have considered propagation of the polymer by reaction between radical cation and neutral monomers driven by the electrical charges carried by the atoms. Apart from the shortcomings of Mulliken charge analysis, employed to assign these charges, these studies completely neglect radical cation - radical cation coupling. They concluded that both dimer and linear trimer formation involves C2-C3 bond linkage between monomer units.

Evidence for radical cation coupling of indole has been reported by Mount \textit{et al.}\textsuperscript{10} This lies in the rotation dependence of the initial step of the electropolymerisation experiment at a RDE. If the rotation speed is very high then little or no polymerisation is observed with only a slight discoloration of the monomer solution and no film is formed even with indoles that would otherwise form good films. This is consistent with the radical cations formed at the electrode being immediately swept away from the electrode out into the bulk monomer solution where they are unable to react with other radical cations. Changing the bulk concentration would be expected to influence both the coupling reaction and the nature of the product if the reaction mechanism followed a neutral - radical cation coupling. The rate of a neutral monomer (M) - radical cation (M\textsuperscript{+}) coupling reaction would be proportional to [M\textsuperscript{+}][M] and the rate would change as the rotation speed and monomer concentration changes. However the rate of a radical cation coupling reaction would be proportional to [M\textsuperscript{+}]\textsuperscript{2} and galvanostatic experiments\textsuperscript{11} have shown that same reaction occurs over a range...
of bulk concentrations and rotation speeds. The rate of the radical cation coupling reaction depends solely on the concentration of radical cations and a constant current indicates that a constant concentration of radical cations are being generated at the electrode. The coupling reaction rate and the product (the asymmetric trimer) does not alter over a large range of monomer concentration and this suggests that the same reaction is occurring, most likely by radical cation coupling. In Chapter 8 the correlation between the reactivity of the radical cations and the rate of coupling of the active species, which are most likely to be radical cations, on a preformed polymer film is discussed. The obvious relationship between these properties seems to suggest that radical cation coupling is the major mechanism for indole electropolymerisation. Also the structural and electronic similarity of indole and pyrrole makes it reasonable to expect a similar mechanism for polymerisation.

It cannot be excluded that it is possible that radical cation, once formed during electrooxidation, undergoes proton elimination assisted by the solvent to give rise to a neutral monomer radical. Subsequent coupling reactions between two neutral radicals will then afford a neutral dimer. This mechanism has been proposed for an I2 oxidative polymerisation of furan derivatives based on ab initio calculations (HF / MP2) and EPR measurements.\(^{12}\) However the spin density distribution of the neutral and cationic form of the 3-methylindole radical have been calculated with little difference observed between them.\(^{13}\) Hence calculations based on an indole radical cation would to a large extent apply to a radical - radical coupling process. The calculations in the previous chapter for 3-methylindole supports this observation.

The chief product, isolated and fully characterised by Mount et al, from the electropolymerisation reaction of most 5-substituted indoles is the asymmetric trimer. It has already been proposed by Mount et al that the formation of the asymmetric trimer could be achieved by the initial coupling at the 3-position to form a 3,3'-dimer and that further oxidation and coupling of this dimer with a monomer radical cation would lead to an asymmetric trimer.\(^{10}\) In this chapter the polymerisation mechanisms of indole and its substituted derivatives are investigated using computational methods to help elucidate the structure of the final product. Both semi-empirical and DFT (Dmol\(^3\)) methodologies are employed. Theoretical oxidation potentials are calculated with temperature corrections provided by PM3 frequency calculations for various 5-substituted dimers. The electronic
distribution in a range of 4-, 5-, 6- and 7-substituted indole dimer radical cations are investigated with respect to their potential to form asymmetric trimers upon electrooxidation.

6.2 The formation of indole dimers

6.2.1 Comparison of $\Delta E$ for dimer linkages and conformations

In the previous two chapters the energies and electronic structure of the indole neutral and radical cations were discussed, whereas this chapter concentrates on the linking of two monomers to form a dimer. There are two theoretical approaches one can adopt to study the formation of dimer. One of these concerns the reaction under thermodynamic control involving the most stable species obtained. The other approach concerns kinetic control which is related to the reaction between species (radical cation and radical cation) proceeding via the lowest energy transition state.

Under thermodynamic control the species formed during polymerisation will be the most stable. The most stable having the smallest energy and the least stable having the largest energy. In the previous study by Talbi et al.89 thermodynamic control was discounted on the basis of the similarities (±0.1 eV) of geometry optimised energies (AM1) of the neutral 2,2', 2,3' and 3,3'-dimers. This has been repeated using a more rigorous DFT method and the energies of these acetonitrile solvated dimers were found to lie within 0.01 eV (Table 6.1).

<table>
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<tr>
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<th>Energy /eV</th>
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</thead>
<tbody>
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</tr>
<tr>
<td>2,3'</td>
<td>-726.465</td>
</tr>
<tr>
<td>3,3'</td>
<td>-726.464</td>
</tr>
</tbody>
</table>

Table 6.1 The acetonitrile solvated energies (DFT) of the neutral indole dimers.

Thermodynamic control is unlikely as the radical cations produced at the electrode are extremely reactive. Coupling between these reactive radical cations is an irreversible and exothermic process and it is therefore more likely that the reactivities of different sites on the monomer will control the coupling.
The dimers of 5-nitroindole, 5-cyanoindole, 5-carboxylic acid indole, indole and 5-aminoindole have been studied in order to determine if the electronic influence of the substituent on the energy difference ($\Delta E$) between neutral and radical cation is important with the dimer as it is in the monomer (Chapter 4). Different dimer connectivities and conformations have been considered to determine if one can distinguish between these dimers energetically. The connectivities of 2,2'-, 2,3'- and 3,3'- have been included and each of these in both their cis and trans conformations. In Figure 6.1 these different linkages are illustrated. The optimised geometry of these acetonitrile solvated dimers were calculated using PM3 parameterisation using the COSMO solvation model. Spot checks (5-cyanoindole and indole) were carried out using a DFT method. The energy differences ($\Delta E$) between neutral molecules and their radical cations were calculated and these are presented in Table 6.2.

Figure 6.1 The different connectivities and conformations of indole dimers. (a) trans 2,2'-dimer, (b) trans 2,3'-dimer, (c) trans 3,3'-dimer, and (d) cis 3,3'-dimer.
### Table 6.2 The solvated (acetonitrile) energy differences (ΔE) calculated using PM3 and DFT.

<table>
<thead>
<tr>
<th>Linkage</th>
<th>Substituent</th>
<th>Geometry</th>
<th>PM3 ΔE / eV</th>
<th>DFT ΔE / eV</th>
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Figure 6.2 The electronic effect of the substituent on the energy differences (PM3) between the solvated neutral and radical cation, (ΔE) is plotted against the Hammett parameter ($\sigma^+$).  

![Graph showing the electronic effect of the substituent on the energy differences (PM3)](image-url)
In general the PM3 energy differences follow the trend NO$_2$ > CN > H > NH$_2$ indicating that the electronic effect of the substituent is present in the dimers as observed for the monomers, discussed in Chapter 4. This substituent effect can be described by the Hammett substituent parameter ($\sigma^+$). In Figure 6.2 the energy differences are plotted against $\sigma^+$ and it can be seen that, in general, a correlation is found for any particular dimer type similar to that observed for the monomers. Dimer $\Delta E$ are all lower than $\Delta E$ for the corresponding monomers. This is consistent with the larger conjugated system for the dimers compared to the monomers, described in Chapters 4 and 5 (Sections 4.3 and 5.3) which is easier to oxidise. This is important as it confirms that the calculated dimer is not behaving like two attached individual monomers, and that further oxidation at the electrode to form a trimer is likely.

The data in Table 6.1 suggest that firstly one cannot differentiate between cis and trans conformations as $\Delta E$ (<10kJmol$^{-1}$) are less than the accuracy of these semi-empirical calculations. The difference in $\Delta E$ for the trans 2,2'-indole dimer and the cis (or trans) 3,3'-indole dimer is 0.7eV whilst all 5-nitroindole dimer conformers are much closer in energy. This suggests that energetically one could distinguish between these linkages. However when optimising using the PM3 method, there is a dependency on the initial dihedral angle between monomer units of the dimer. The unconstrained nature of the dimer (the indole units can rotate around the dihedral angle) combined with the increase in size of the system as compared to the monomer causes difficulties in the geometry optimisation. The large differences between linkages may reflect the poor optimisation achieved using semi-empirical results. The $\Delta E$ data follows a trend from least to most stable of 2,2'-> 2,3'-> 3,3'- however it is unwise to attach great importance to these semi-empirical results. The DFT calculations presented in Table 6.2 for indole dimers are much more consistent than the PM3 results. These follow the trend 2,2'- > 3,3'- >2,3'- however the difference between $\Delta E$ is never greater than 0.17eV and this is marginally larger than the error involved in the calculation (±0.1eV). This suggests that the 2,2'-, 2,3'- and 3,3'- linkages may be energetically distinguishable whilst the cis / trans conformational differences are not.
6.2.2 Calculation of theoretical dimer oxidation potentials

The oxidation potentials, with respect to the Fc/Fc⁺ couple, were calculated in a similar manner to the description in Chapter 4. Notwithstanding the suspected poor convergence of the geometry optimisation calculations, semi-empirical methods were used to carry out frequency calculations to provide the temperature correction from 0K to 300K for DFT ΔE data. These are presented in Table 6.3. The theoretical oxidation potentials for dimers with electron withdrawing potentials are lower than those predicted for the indole monomers and therefore consistent with the value expected for a dimer. The calculated PM3 oxidation potential for the 5-aminoindole dimer is much higher than expected, based on the other dimer calculations, however the monomer E₃₀₀,ₑ (PM3) value was much higher than the experimental value. The DFT calculated oxidation potentials are more consistent. They suggest that it may be possible under suitable conditions to electrochemically distinguish the oxidation potential of dimers with different linkages on a ring electrode downstream of a disc electrode where monomer coupling is occurring. This is also consistent with the premise that if a dimer is formed it will immediately undergo further oxidation to form a dimer radical cation at the electrode. However it has not proved possible so far to isolate dimer species or to determine if different linkages exist by RRDE experiments and so these can only give an indication of the dimer oxidation potentials.

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<th>PM3 E₃₀₀,ₑ /eV</th>
<th>PM3 E₃₀₀,ₑ /meV</th>
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</table>

Table 6.3 Theoretical oxidation potentials semi-empirical (PM3) at 0K, E₀,ₑ, and at 300K, E₃₀₀,ₑ and DFT E₃₀₀,ₑ. (Ecorr = E₃₀₀,ₑ - E₀,ₑ).
Under kinetic control the reactivities of the monomers and oligomers involved in the reaction must be considered. In the previous study by Talbi et al.\textsuperscript{8,9} propagation of polymer growth was studied by coupling driven by the electrical charges carried by the atoms at the most negative position of the neutral (C3) and most positive position of the radical cation (C2) and hence this gives rise to a 2,3'-dimer. However, as the polymerisation reaction is more likely to proceed via radical cation - radical cation coupling the location of maximum spin density will govern the coupling reaction and the spin density distribution will help elucidate the most likely mechanism. The monomer spin density plots for the 5-substituted indoles with an electron withdrawing group have their maximum spin density at the C3 position which indicates that the location of the unpaired electron is most probable in this position and therefore this is the most likely position of coupling to produce a 3,3'-dimer.

From a previous study Mount et al.\textsuperscript{14} have characterised the asymmetric trimer as the major product from electropolymerisation at a platinum electrode of a 5-substituted indole with an electron withdrawing group. There was no presence of the symmetric form of the trimer detected. Pure asymmetric trimer can only be formed via a 2,2'- or a 3,3'-dimer whereas if a 2,3'-linkage was involved a mixture of asymmetric and symmetric trimer would be expected. This evidence indicates that the 3,3'-dimer is the most likely product and so the subsequent theoretical study of indole polymerisation will focus on this dimer. As the \textit{cis} and \textit{trans} conformations are energetically indistinguishable the \textit{cis} orientation has been chosen as this will be the most favourable conformation for trimer formation.

Figure 6.3 The indole asymmetric trimer with a) the 3,3'-linkage highlighted and b) the 2,2'-linkage highlighted.
6.2.3 The electronic distribution of the dimer radical cation

During electrooxidation, due to the applied electrode potential, the following step in the polymerisation mechanism will involve the dimer in its radical cation form. The dimer radical cation will then undergo further coupling with a monomer radical cation and the calculated HOMO of the radical cation (the $\pi$-spin density distribution) will help predict the most reactive sites for coupling on the oxidised dimer. The HOMOs for \textit{cis} 3,3'-radical cation dimers of indole, 5-cyanoindole and 5-carboxylic acid indole were calculated and these are shown in Figure 6.4. All three display a HOMO distributed over the whole conjugated system with large lobes located over the C2-C3 bonds. This is the most probable location of greatest unpaired radical electron concentration.

DFT calculations have been shown to yield $\pi$-spin densities in good agreement with the experimental results obtained using EPR and have been employed in studies of the polymerisation process of monomers such as pyrrole.\textsuperscript{15} The DFT spin density plots for the radical cations of the \textit{cis} indole 3,3'-dimer, the \textit{cis} 5CNI 3,3'-dimer and the \textit{cis} 3,3'-5CAI dimer were calculated by mapping the spin density on to a 99\% electron density isosurface. These are shown in Figure 6.4.

It can be seen that for each substituted dimer the unpaired electron density is largest around the C2-C3 positions in both monomer units of the dimer with the concentration greatest near the C2 atom. This indicates that a redistribution of the spin density occurs in the dimer in comparison with the monomer. This is the most likely position for the reaction of the dimer radical cation and a third monomer radical cation since the largest radical electron density is at the C3 position in the monomer. This predicts the coupling to occur between the C2 position of the dimer and the C3 position of the monomer giving the Scheme illustrated in Figure 6.5. Further oxidation leads to the formation of the central aromatic ring by ring closure at the highlighted positions (*). This is consistent with the formation of an asymmetric trimer. The three spin density plots are very similar which suggests that the same product is formed from each indole. These geometry optimised \textit{cis} conformation dimers are not flat, they are in fact twisted by 30-60\degree most probably due to steric hindrance due to the close proximity of the 4H on the neighbouring indoles.
Figure 6.4 The HOMO for the radical cations of the (a) 5-cyanoindole, (b) 5-carboxylic indole and (c) indole cis 3,3'-dimers. The spin density of the cis 3,3'-dimer radical cation of (d) 5-cyanoindole, (e) 5-carboxylic acid and (f) indole mapped onto a 99% electron density isosurface.

A DFT theoretical investigation was made into the possible polymerisation mechanism of 4-, 6- or 7-substituted indoles. With a few exceptions the most reactive site on the monomer radical cation, inferred from the DFT spin density plots, for the indoles studied in Chapter 5 is at the C3 position and so 3,3'-dimers have been considered.
The gas phase energy differences for a variety of substituted indole cis 3,3'-dimers were calculated and these are displayed in Table 6.4. The $\Delta E$ data are consistent with a conjugated system of intermediate size to monomers and trimers [Section 6.3] and the magnitudes follow the trends in the $\Delta E$ for the monomers illustrating that the substituent has influence over the electronic properties of the dimer. The similarities in $\Delta E$ can be noted between the methyl dimers where the same substituent is placed in different positions. The deviation of the $\Delta E$ for 6CAI and 5CAI illustrates the sensitivity of the calculation to the convergence criteria.

In Figure 6.6 the spin density and HOMO distributions are presented for the cis 3,3'-dimers of 4-hydroxyindole, 6-indole carboxylic acid and 7-methylindole. It can be seen that for these 4-, 6- or 7-substituted dimer radical cations the HOMO and the spin density is distributed over the whole system with the largest lobes of the HOMO located over the C2 - C3 bond. All of these dimers have increased spin density near the C2 position of each indole unit indicating that the following step in the polymerisation process is most likely to occur at these positions on the dimer radical cation. This suggests that for these very different substituents at different positions on the indole the same mechanism is involved in the polymerisation reaction and this is illustrated by Figure 6.7.
Figure 6.6 HOMO distributions of cis 3,3'-dimer radical cations of (a) 4-hydroxyindole, (c) 6-indole carboxylic acid and (e) 7-methylindole and the spin density distribution of the cis 3,3'-dimer radical cations of (b) 4-hydroxyindole, (d) 6-indole carboxylic acid and (f) 7-methylindole.
Table 6.4 The gas phase DFT $\Delta E$ values for cis 3,3'-dimers of various substituted indoles. (*) indicates the calculations run with coarse convergence criteria (max. grad < 0.01H/Å) the others run with finer convergence criteria (max. grad < 0.001H/Å).

<table>
<thead>
<tr>
<th>cis 3,3'-dimer</th>
<th>$\Delta E$ / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>5Cl</td>
<td>7.28</td>
</tr>
<tr>
<td>5CAI</td>
<td>6.90</td>
</tr>
<tr>
<td>6CAI*</td>
<td>7.19</td>
</tr>
<tr>
<td>Indole</td>
<td>6.52</td>
</tr>
<tr>
<td>5CH$_3$*</td>
<td>6.37</td>
</tr>
<tr>
<td>7CH$_3$*</td>
<td>6.58</td>
</tr>
</tbody>
</table>

Figure 6.7 The most probable polymerisation mechanism for the formation of asymmetric trimers via the 3,3'-dimer linkage.

The radical cation of the 5,6-dimethoxyindole is an exception as its spin density is chiefly located in the C2 position (Section 5.6.2) which suggests that radical cation - radical coupling will most likely occur at these positions on the monomer. The spin density of the 2,2'-dimer radical cation was calculated and this is presented with the HOMO distribution in Figure 6.9. The HOMO pattern (Figure 6.8 (a)) is different to the 3,3'-dimers discussed above, even so, a lobe of this orbital is located over the C2-C3 bond which appears to be the requisite distribution for trimerisation to occur. There is increased spin density at the C3 position in both units of the dimer and so it is believable that the 2,2'-dimer radical cation may be involved in the polymerisation mechanism which in this case occurs by the coupling of the C2 position of the monomer to the C3 positions of the dimer. However, the 5,6-dimethoxyindole trimer was inferred from electrochemical and fluorescence studies.
(Chapter 5) and this must be clarified with an $^1$H NMR study to unambiguously determine the structure of the electrooxidation product. The 5,6-dimethoxyindole trimer is therefore not only the first reported electropolymerised disubstituted trimer, but it is quite possible that the mechanism to form this species proceeds via a different pathway compared to other indoles previously reported. This polymerisation mechanism is shown in Figure 6.9 and shows clearly that only an asymmetric trimer can be obtained from a 2,2'-dimer linkage. It is likely that 5,6-dihydroxyindole mentioned in Chapter 5 will also polymerise via 2,2'-dimer.

**Figure 6.8** The (a) HOMO and (b) the spin density distribution of a cis 2,2'-dimer radical cation of 5,6-dimethoxyindole.

**Figure 6.9** An alternative polymerisation mechanism for asymmetric trimer formation involving a 2,2'-dimer.
6.2.4 Computational studies as a predictive tool for the polymerisation mechanism

Computational methods of predicting the most probable product formed from a radical cation - radical cation polymerisation reaction can be used as a screening technique in the design of conducting polymers from novel monomers. Amongst the various substituted monomers discussed in Chapter 5 an experimental investigation has not been carried out on 4-cyanoindole. The radical cation of this monomer has a spin density distribution similar to that of the unsubstituted indole with the largest concentration of π-spin density at the C3 position. As coupling is most likely to occur at the C3 position the dimer neutral and radical cation species were calculated with a 3,3'-linkage and the spin density plotted over an electron density isosurface (90%). These is shown in Figure 6.10(a). The spin density is chiefly located along the C2-C3 bond with greatest concentration at the C2 position which is a suitable position for the approach of a third monomer radical cation to link and form the asymmetric trimer. Consequently the formation of an asymmetric trimer upon the electrooxidation of 4-cyanoindole can be predicted.

The 6-methoxyindole monomer has not been investigated experimentally and like the 5,6-dimethoxyindole it has the greatest concentration of spin density at the C2 position. The calculated spin density for the 2,2'-dimer radical cation reveals that the greatest concentration lies along the C2-C3 bond with the largest concentration at the C3 position of each indole unit. Again trimerisation seems likely upon the coupling of a third monomer radical cation at the C3 positions of the 2,2'-dimer radical cation. This is shown in Figure 6.10(b).

Using a computational study in this way we can therefore predict which monomers are likely to form cyclic trimers and we may also be able to predict the polymerisation mechanism. It is interesting that we may obtain the same product (the asymmetric cyclic trimer) via two different routes and by simply varying the substituent and / or its position and therefore influence the polymerisation pathway.
The next step of polymerisation involves reaction of the dimer radical cation with a third radical cation species as illustrated in Figure 6.5. The driving force for this linking reaction is the rearomatisation of the trimer species to create a large delocalised system with a benzene ring at the centre. Therefore even though the linkage of the monomer radical cation may initiate at the position of greatest spin density of the dimer radical cation (C2 or C3) this will be immediately followed by linkage at the second position of the dimer (C3 or C2) as a comparable concentration of spin density is predicted. The product of this step is the asymmetric indole trimer.

Figure 6.10 The spin density mapped onto a total electron density isosurface (90%) of the radical cations of the (a) cis 3,3'-dimer of 4-cyanoindole and (b) cis 2,2'-dimer of 6-methoxyindole.
6.3 The asymmetric indole trimer

The trimer species are generated in their oxidised state at the electrode during electropolymerisation. The neutral and radical cations of the indole and 5-cyanoindole asymmetric trimers were calculated using DFT methods. The structures of the neutral and radical cation indole trimer (Figure 6.12) were examined for changes in structure upon oxidation. It was observed that oxidation has little effect on the bond lengths of the peripheral benzene rings however increases in some bond lengths are observed around the central benzene ring, which are highlighted in Figure 6.12(b). The removal of a bonding electron to form a radical cation will have an overall antibonding effect and this is mirrored in the structural changes by the increase in bond lengths of the radical cation.

These trimer structures are relatively flat with only a slight deviation of the N3 indole and N2 units from the plane occupied by the N1 indole unit. The torsional angles between units are presented in Table 6.5. This structure is favourable to the stacking of trimer units which is expected to occur during the growth of a film in an electropolymerisation reaction.

![Figure 6.11 The torsional angles between the indole units of an asymmetric indole trimer](image)

<table>
<thead>
<tr>
<th>Indole trimer</th>
<th>Torsional N1/N2 / degrees</th>
<th>Torsional N3/N1 / degrees</th>
<th>Torsional N3/N2 / degrees</th>
</tr>
</thead>
<tbody>
<tr>
<td>neutral</td>
<td>0.0</td>
<td>13.1</td>
<td>-2.1</td>
</tr>
<tr>
<td>radical cation</td>
<td>-2.0</td>
<td>12.1</td>
<td>-1.8</td>
</tr>
</tbody>
</table>

Table 6.5 The torsional angles between the indole units of an asymmetric indole trimer
The gas phase energy difference ($\Delta E$) between the neutral and radical cation trimers are presented in Table 6.6. $\Delta E$ for the 5-cyanoindole trimer is larger than for the parent indole trimer indicating that the substituent effect is present for the trimeric systems, consistent with experimental measurements of the half wave reduction potentials for trimers. The magnitude of $\Delta E$ is also consistent with a larger conjugated system than either the monomer or dimer species. $\Delta E$ follows the expected trend, monomer $>$ dimer $>$ trimer, (Table 6.6). This trend is expected, as the amount of energy needed to oxidise a system decreases as the size of the conjugated system increases.

<table>
<thead>
<tr>
<th>Indole</th>
<th>Monomer $\Delta E$ /eV</th>
<th>3,3'-Dimer $\Delta E$ /eV</th>
<th>Asymmetric trimmer $\Delta E$ /eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>indole</td>
<td>7.65</td>
<td>6.52</td>
<td>6.36</td>
</tr>
<tr>
<td>5-cyanoindole</td>
<td>8.22</td>
<td>7.28</td>
<td>7.25</td>
</tr>
</tbody>
</table>

Table 6.6 The gas phase energy differences, $\Delta E$, (DFT) for asymmetric indole trimers.

The location of the unpaired radical electron was investigated by calculating the HOMO orbital and the spin density ($\alpha - \beta$ electrons) for the radical cation. The HOMOs for the indole and 5-cyanoindole trimer radical cation are shown in Figure 6.13. It can be seen that the HOMO orbital for both trimers extend over the whole aromatic system with large lobes located over the central benzene ring. These coincide with the positions of calculated structural change which occurs upon oxidation and gives an indication of the most likely distribution of the unpaired radical electron in the oxidised trimer.

The spin density plots of the trimer radical cation are shown in Figure 6.14. These reveal that the unpaired electron is chiefly located around the central benzene ring with sizeable spin density distributed over the entire conjugated system. This is consistent with the observed stability of the electropolymerised indole, 5-nitroindole, 5-cyanoindole, 5-carboxaldehydeindole, 5-carboxylic acid indole and 5-bromoindole trimers which are produced in their oxidised form and can exist in this state for some considerable time. The locations of maximum spin density coincide with the changes in structure that occur upon oxidation.
Figure 6.12 The calculated (DFT) structures of (a) neutral and (b) the radical cation indole asymmetric trimer. The red boxes in (b) highlight the changes in bond lengths upon oxidation.
Figure 6.13 The HOMO for the radical cation of the (a) indole and (b) 5-cyanoindole trimers (isosurface value=0.025).
Figure 6.14 Spin density distribution mapped on to the total electron density isosurface (0.05) for (a) the indole asymmetric trimer and (b) the 5-cyanonindole trimer.
6.4 Conclusions

Thermodynamic control over the polymerisation process involving the most stable product has been shown to be unlikely as more than one product would be likely to be formed as their energies are extremely similar. This is not what is found experimentally. This has been discounted on the basis of DFT calculations. The calculation of $\Delta E$ for the indole dimers illustrate how sensitive the accuracy of the results are to the level of theory used. The various semi-empirical and DFT calculations suggest that cis / trans conformers are energetically indistinguishable. However, notwithstanding the unreliable optimisation achieved with semi-empirical methods, the calculations suggest that it may be possible to differentiate (energetically) between dimers of different linkages experimentally. Although the PM3 methods were less rigorous they were used to provide temperature corrections for the DFT calculated $\Delta E$ from 0K to 300K. These frequency calculations must be treated with caution as meaningful results are only obtained when started from a fully optimised geometry ($\delta E/\delta x=0$). Fortunately $E_{corr}$ is a small correction term and therefore errors in these calculations will also be small. Approximate theoretical oxidation potentials were calculated. These are an indication of the potential at which the dimer would be oxidised if it was possible to isolate them. They suggest that if the dimer species at the ring electrode during a ring disc experiment that perhaps the 2,2'- and the 3,3'- (and 2,3'-) dimers may be distinguishable however the cis and trans conformations would be indistinguishable.

As the reaction would most likely proceed via a radical cation coupling under kinetic control the coupling steps in the anodic electropolymerisation reaction would be most likely governed by the locations of maximum spin density. Spin density calculations have enabled the initial coupling sites of the monomer to be identified and by examining the changes in spin density distribution in the dimer radical cation species the most likely coupling sites on the dimer can be ascertained. Two potential polymerisation mechanisms can be identified. The first pathway is via the 3,3'-dimer. The changes in the spin density from monomer to dimer are consistent with this mechanism which was previously proposed in initial studies involving 5-subsituted indoles. This mechanism can also be considered for the majority of other indoles studied in this thesis where the spin density of the monomer is located at the 3-position. A second mechanism may account for the formation of asymmetric trimers from monomers which have their spin density at the 2-position. The spin density changes from the monomer to dimer are again consistent with this pathway. This type of calculation
can help elucidate the polymerisation mechanism of indole monomers already studied and is also is a useful predictive tool to screen novel monomers before experimental investigation. Computational investigations such as these could therefore be used in the design of novel conducting polymers.

The stability of the oxidised trimer can be explained by the location of the spin density which is chiefly located around the central benzene ring with substantial spin density spread over the whole system. The asymmetric distribution of the spin density is directly due to the asymmetric nature of the trimer species. Finally, it is important to note that the findings in this chapter are consistent with previous experimental studies by Mount et al and those contained in Chapter 5.

6.5 References

Chapter 7
The Coupling Reaction of 5-substituted Indole Radical Cations

7.1 Introduction

In previous electrochemical studies on 5-carboxylic acid indole (5CAI) and 5-cyanoindole (5CI) the potential independent electrooxidation of these indoles at a RDE gave rise to the growth of a polymer film. During this process steady state currents were observed after an initial period of growth which corresponds to the time required to cover the electrode surface with a film of oxidised trimer. These steady state currents represent a steady state electropolymerisation reaction occurring on an oxidised trimer film. The electropolymerisation data (limiting steady state currents and rotation speeds) can be plotted according to the Koutecky-Levich (K-L) equation.

\[
1/i = 0.643\nu^6 / \left( n F A D^2 C_\infty W^2 \right) + 1/i_w
\]  

[7.1]

Where \(i\) is the current obtained upon oxidation, \(W\) is the electrode rotation speed in Hz, \(n\) is the number of electrons transferred during the reaction, \(F\) is Faradays constant, \(D\) is the diffusion coefficient, \(C_\infty\) is the bulk concentration of monomer in the solution and \(\nu\) is the kinematic viscosity of acetonitrile. The current, as the rotation speed tends to infinity when \(i\) is independent of mass transport, is represented as \(i_w\).

Plots of \(1/i\) against \(W^{-1/2}\) reveals that a straight line can be fitted to the current data for 5CAI. This suggests that the oxidation reaction is first order with respect to the monomer which is the assumption of the K-L equation. Similar behaviour has been observed for 5CI and copolymers of 5CI / 5CAI and 5NI. These indoles are 'well behaved' in the sense that reproducible conducting films are formed with a low fraction of soluble product accompanied by reproducible steady state currents.
After the initial layer formation each monomer reaching the electrode surface is oxidised to form a radical cation which couples to form a cyclic trimer according to the surface reactions (Scheme 7.1).

\[
3\text{In}^{\text{bulk}}(\text{aq}) \xrightarrow{k_d} 3\text{In}^{(0)}(\text{aq}) \xrightarrow{k_{\text{ox}}} 3\text{In}^+\text{(ads)} \xrightarrow{k_c} \text{In}_3^+(s)
\]

This involves the monomer, \( \text{In}^{\text{bulk}}(\text{aq}) \), in solution at bulk concentration, \( C_{\text{In}} \), moving towards the electrode surface \( \text{In}^{(0)}(\text{aq}) \) under convective diffusion controlled by the rate of mass transport, \( k_d \). At the electrode these monomers adsorb to the surface and oxidise to \( \text{In}^{+\text{(ads)}} \), with an adsorption / oxidation rate constant \( k_{\text{ox}} \), forming radical cations. These adsorbed radical cations then link on the surface to form trimers, \( \text{In}_3^+(s) \), with a coupling rate constant \( k_c \).

The creation of these trimers form the most recent layer of the film and creates further sites for adsorption and coupling to occur. As three monomers are involved, this reaction might be expected to be third order with respect to the monomer if it occurred in solution. However the reaction occurs on the template surface and the process has been observed to be first order with respect to the monomer (see Section 7.3).

The electropolymerisation of a range of 5-substituted indoles yield not only reproducible well behaved films but some give rise to soluble oxidation products and those indoles with electron donating substituents give rise to passivating layers. During the production of soluble oxidation products the trimers are formed by oxidative linking at the electrode which then diffuse away into the bulk solution and are not deposited as a polymer film. The observed currents change with time as other non-conducting products such as linear polymers are also formed by radical cation coupling in solution. 5-substituted indoles with electron donating substituents (OCH\(_3\), OH, NH\(_2\)) form passivating layers upon electropolymerisation\(^4\). The currents during electrooxidation are observed to drop sharply with time indicating a fast irreversible oxidation and adsorption of species which quickly cover the electrode surface with an insulating layer. It is thought that this layer may be produced by the radical cations preferentially adsorbing via their electron rich substituent and are therefore not favourably orientated to form trimer products (this is borne out with the theoretical studies of the spin density distribution as discussed in Chapter 4). It is thought that the initial deposition of trimer film is crucial in the film growth process and
when an initial film layer is absent subsequent layers do not grow on top. However it has been shown that indoles such as NH$_2$ or OCH$_3$ can form cyclic trimers via the adsorption of monomer radical cation and coupling on a preformed electrodeposited 5-cyanoindole or 5-nitroindole films$^4$ which act as a template for adsorption and trimerisation. The template alters the indole adsorption orientation increasing the probability that three radical cations adsorb favourably for trimer formation.

In contrast to an attempted polymerisation on a bare platinum, after an initial burst of current due to redox reaction of 5Cl trimers in the template near the electrode surface, steady state currents are observed and Koutecky-Levich analysis of the electropolymerisation data can be carried out. The linearity of the slopes of the K-L plots indicate that as for 5Cl or 5CAI the coupling of 5NH$_2$ on a template is first order with respect to the monomer and therefore it is likely that the electrooxidation reaction follows a similar process. The value of $i_0$ for 5-aminoindole and 5-hydroxyindole on a preformed template$^4$ were observed to be lower than observed for 5Cl$^2$ and 5CAI$^1$. This is consistent with a slower surface coupling rate for the radical cation because of the stabilisation effect of the substituent which would reduce the reactivity of the radical cation.

In this chapter a comparative investigation into the coupling rate of a range of 5-substituted indoles as a function of the radical cation reactivity is carried out. This is made possible by using a preformed film which provides an initially formed trimer layer so that the reaction in Scheme 7.1 can occur. This preformed film can act as a template to promote favourable radical cation adsorption and oxidation which will result in trimer formation. In this case it must be reproducible in order to provide an identical surface for a range of 5-substituted indoles to adsorb on and 5-cyanoindole films were chosen as they fulfil these requirements.

7.2 Measurement of monomer oxidation potentials on template films

The polymerisation potential chosen must be sufficiently above the monomer oxidation potential to ensure a mass transport limited reaction. Measurement of the peak monomer oxidation for a selection of indoles were carried out by performing LSV on a template film modified electrode to test whether the preformed layer influenced the monomer oxidation
potential. These results are presented in Table 7.1 with those monomer oxidation potentials measured using a bare platinum electrode. This experiment is difficult to carry out as at a high potentials the underlying template films oxidise and undergo irreversible linkage to form linked trimers. This effectively masks the oxidation of the monomer and is most important at low monomer concentrations. At high monomer solution concentrations, the linking reaction of the monomer complicates the voltammogram. However due to the electron withdrawing nature of the cyano substituent the trimer has a high redox $E_{1/2}$ potential and so it is possible to measure the peak potentials of the monomers that oxidise under 800mV where the template film does not undergo any further irreversible oxidation at low monomer concentrations (2mM).

<table>
<thead>
<tr>
<th>Substituent</th>
<th>Monomer oxidation potential on bare platinum / V ±0.02V</th>
<th>Monomer peak oxidation potential on 5Cl Template / V ±0.04V</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_2$</td>
<td>1.31</td>
<td>-</td>
</tr>
<tr>
<td>CN</td>
<td>1.25</td>
<td>-</td>
</tr>
<tr>
<td>CHO</td>
<td>1.20</td>
<td>-</td>
</tr>
<tr>
<td>COOH</td>
<td>1.07</td>
<td>-</td>
</tr>
<tr>
<td>Cl</td>
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</tr>
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<td>Me</td>
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</tr>
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<td>CH$_3$O</td>
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</tr>
<tr>
<td>HO</td>
<td>0.73</td>
<td>0.74</td>
</tr>
<tr>
<td>NH$_2$</td>
<td>0.19</td>
<td>0.21</td>
</tr>
</tbody>
</table>

Table 7.1 The monomer oxidation potentials as measured by LSV, polymerisation potential chosen on bare platinum electrode and a 5Cl template.

This study revealed that a template film does not cause a large difference in monomer oxidation potential when compared to those measured at a platinum electrode. Complication is added by the small increase in the broadness of the monomer oxidation peak attributable to a small range of different polymerisation sites on the template film in comparison to a Pt surface.
7.3 Koutecky-Levich analysis of electropolymerisation on a preformed 5-cyanoindole film

In previous K-L investigations such as the steady state copolymerisation of 5CI and 5CAI\(^3\) a mean coupling rate, \(k\), was determined compromising of both \(k_{\text{ox}}\) and \(k_c\) components. The following derivation\(^5\) explains how it is possible to isolate the \(k_d\), \(k_{\text{ox}}\) and \(k_c\) terms so that we can directly determine \(k_c\).

Under steady state conditions the fluxes in each separate reaction step (Scheme 7.1) are all equal and by considering the mass transport and oxidation adsorption reactions equation 7.2 holds. This assumes that adsorption is governed by the Langmuir isotherm, for a fixed number of sites for adsorption and oxidation which has been assumed previously.\(^3\)

\[
k_d(c_\infty - c_0) = k_{\text{ox}}(1 - \theta)c_0 \quad [7.2]
\]

\(k_{\text{ox}}\) depends on the number of sites available for adsorption and oxidation (or the area of electrode not covered by In\(^{\text{in+}}\), \((1-\theta)\), where \(\theta\) is the fraction of sites covered by In\(^{\text{in+}}\). This is equal to the flux of the radical cations coupling to form trimers, described by \(k_c\) (equation 7.3).

\[
k_{\text{ox}}(1 - \theta)c_0 = k_c\theta \quad [7.3]
\]

The variation of \(\theta\) is equivalent to the desorption rate constant for the Langmuir isotherm, equations 7.4 and 7.5.

\[
\theta = \frac{Kc_0}{(1 + Kc_0)} \quad [7.4]
\]

\[
and \quad (1 - \theta) = \frac{1}{1 + Kc_0} \quad [7.5]
\]

where \(K = \frac{k_{\text{ox}}}{k_c}\) \quad [7.6]

Here we note that \((1-\theta) \approx 1\) and a constant value. Under these conditions first order kinetics are expected (assumption of the K-L analysis) consistent with experimentaly observations. This means that \(Kc_0 << 1\) and \(k_{\text{ox}}c_0 << k_c\). The rate of coupling \(j_c\) can now be rewritten by substituting equation 7.4 into 7.7.

\[
j_c = k_c\theta \quad [7.7]
\]
\[ j_c = k_c \frac{Kc_0}{1 + Kc_0} \]  

However we wish to express this in terms of \( c_\infty \) rather than \( c_0 \) and we can do this by rearranging equation 7.2 (to give equation 7.9)

\[ c_0 = \frac{k_d c_\infty}{k_{ox} + k_d} \]  

This term can be substituted into equation 7.8 and therefore the rate \( j_c \) can now be written as 7.10.

\[ j_c = \frac{k_c K c_\infty}{1 + K k_d + k_{ox} + k_d c_\infty} \]  

Substitution of this term into \( i = nF A j_e \) (where \( F \) is the Faraday constant and \( A \) is the electrode area) with some rearrangement allows the following equation to be obtained.

\[ \frac{1}{i} = \frac{1}{nFA} \left[ \frac{1}{k_d c_\infty} + \frac{1}{k_{ox} c_\infty} + \frac{1}{k_c} \right] \]  

or (as \( k_d = D/x_D \))

\[ \frac{1}{i} = \frac{1}{nFA} \left[ \frac{0.643 \nu^{1/6}}{W^{1/2}D^{2/3} c_\infty} + \frac{1}{k_{ox} c_\infty} + \frac{1}{k_c} \right] \]

This suggests that in the case of an electropolymerisation reaction the intercept of a K-L analysis, \( 1/i_{ll} \), has two components which we can separate by their dependence on the bulk concentration (equation 7.12). The first term, \( 1/k_{ox} c_\infty \), is concentration dependent and the second, \( 1/k_c \), is concentration independent. This implies that the intercept of a K-L plot will vary with concentration. When \( c_\infty \) is small \( 1/k_{ox} c_\infty \) is therefore a large term which dominates the intercept. However as \( c_\infty \) increases this term has less influence and the intercept value will tend towards \( 1/k_c \). As this term is independent of concentration the intercept should reach a constant value when \( c_\infty \) is sufficiently large.
This derivation explains the spread of intercept values with low monomer concentration observed previously\(^4\) and furthermore it allows one to assume that \(i_\infty = nF A_k c\) when a constant value of intercept has been reached and so directly determine \(k_c\) for the coupling reaction of the radical cations. It must be noted that when \(c_c\) is very small (<10 mmol dm\(^{-3}\)) then \(1/k_\infty c_c\) term has greater influence over the intercept, however at higher concentrations, (>10 mmol dm\(^{-3}\)) \(1/k_\infty c_c\) is much smaller and \(i_\infty\) tends to a constant value.

Rotating disc studies of electropolymerisation were carried out, using two concentrations (30 mmol dm\(^{-3}\), 50 mmol dm\(^{-3}\)) and a variety of electrode rotation speeds. A 5-cyanoindole template was used in each case. In Figures 7.3 and 7.4 the data from the K-L analysis are plotted for the polymerisation of 5-substituted indoles at 30 mmol dm\(^{-3}\) and 50 mmol dm\(^{-3}\) concentrations respectively. In table 7.2 \(i_\infty\) values for polymerisation at a bare electrode and a template are presented for comparison. The value \(i_\infty\) is calculated from equation 7.1 and the intercept. The number of electrons involved in the polymerisation process have been calculated from the gradients of the plots and equation 7.1, these are presented in Table 7.3. K-L studies on bare platinum were only carried out for those indoles (5NI, 5CI and 5CAI) which form well behaved films on these surfaces.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Substituent</th>
<th>SCI Template</th>
<th>Bare platinum</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Intercept (i_\infty) mA (^{-1})</td>
<td>sd mA (^{-1})</td>
<td>(i_\infty) mA ±0.5</td>
</tr>
<tr>
<td>30 mmol</td>
<td>NO (_2)</td>
<td>0.058</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td>CN</td>
<td>0.074</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td>CHO</td>
<td>0.089</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td>CAI</td>
<td>0.091</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td>Cl</td>
<td>0.010</td>
<td>0.007</td>
</tr>
<tr>
<td></td>
<td>Br</td>
<td>0.010</td>
<td>0.007</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>0.108</td>
<td>0.075</td>
</tr>
<tr>
<td></td>
<td>OCH (_3)</td>
<td>0.113</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td>HO</td>
<td>0.137</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td>NH (_2)</td>
<td>0.166</td>
<td>0.005</td>
</tr>
<tr>
<td>50 mmol</td>
<td>CHO</td>
<td>0.085</td>
<td>0.003</td>
</tr>
<tr>
<td></td>
<td>COOH</td>
<td>0.099</td>
<td>0.005</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>0.102</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td>OH</td>
<td>0.120</td>
<td>0.002</td>
</tr>
</tbody>
</table>

\(^a\) this work and reference 1

\(^b\) Chapter 8 [Section 8.2]

Table 7.2 K-L plot intercepts for polymerisation at 30 mmol dm\(^{-3}\) and 50 mmol dm\(^{-3}\) on a 5CI template and a selection on bare platinum electrode.
Figure 7.3 Koutecky-Levich plot for the polymerisation of 5-substituted indoles with a monomer concentration of 30mmol.

Figure 7.4 Koutecky-Levich plot for the polymerisation of 5-substituted indoles with a monomer concentration of 50mmol.
Chapter 7 The Coupling Reaction of 5-Substituted Indole Radical Cations

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Substituent</th>
<th>Gradient /mA\cdot \text{s}^{1/2}</th>
<th>n, No. of electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 mmol</td>
<td>NO$_2$</td>
<td>0.164</td>
<td>2.39</td>
</tr>
<tr>
<td></td>
<td>CN</td>
<td>0.157</td>
<td>2.48</td>
</tr>
<tr>
<td></td>
<td>CHO</td>
<td>0.154</td>
<td>2.55</td>
</tr>
<tr>
<td></td>
<td>COOH</td>
<td>0.139</td>
<td>2.83</td>
</tr>
<tr>
<td></td>
<td>Cl</td>
<td>0.150</td>
<td>2.62</td>
</tr>
<tr>
<td></td>
<td>Br</td>
<td>0.150</td>
<td>2.62</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>0.154</td>
<td>2.55</td>
</tr>
<tr>
<td></td>
<td>CH$_3$O</td>
<td>0.136</td>
<td>2.89</td>
</tr>
<tr>
<td></td>
<td>HO</td>
<td>0.105</td>
<td>3.74</td>
</tr>
<tr>
<td></td>
<td>NH$_2$</td>
<td>0.178</td>
<td>2.20</td>
</tr>
<tr>
<td>50 mmol</td>
<td>CHO</td>
<td>0.103</td>
<td>2.30</td>
</tr>
<tr>
<td></td>
<td>COOH</td>
<td>0.076</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>0.091</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>HO</td>
<td>0.065</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Table 7.3 K-L analysis of 5-substituted indoles on 5CI template gradients, and the number of electrons involved in the polymerisation process.

After an initial burst of current due to redox reaction of the underlying template a constant polymerisation current is observed. The assumption is made here that the current and therefore the rate of the coupling reaction is not altered by the template. This would be extremely difficult to determine experimentally as the initial burst of current due to the template would mask any change in the current due to the polymerisation in the initial stages of the reaction. The currents subsequent to the initial current spike for all the K-L studies on 5CI templates were observed to be constant with time. This is quite remarkable and indicates that a range of indoles can polymerise on a surface of 5CI trimers. This is illustrated in Figure 7.5 The initial layer of indole (In) will adsorb and polymerise on the surface of the 5-cyanoindole film. Subsequent layers of In however will adsorb and polymerise at a surface of polymerised In.

![Figure 7.5](image-url) The polymerisation of an indole (In) on a template of 5-cyanoindole trimers.
In general, similar gradients are observed with polymerisation on a template in comparison to that on a bare platinum electrode. This indicates that the number of electrons in the coupling process are similar. If trimer formation did occur then a value of $n$ in the range $3.0 > n > 2.3$ is expected. In general, 2.3 to 2.7 electrons are involved in the polymerisation process for Cl, Br, OH, CH$_3$, NO$_2$, CHO 5-substituted indoles. This observation, coupled with the observation of steady state currents, indicate that oxidation is occurring by the same reaction in Scheme 7.1.

It can be observed for 5-hydroxyindole that the number of electrons are higher than expected for the formation of a trimer. Interestingly this is observed at both 30mmol and 50mmol concentrations. This anomalously high Koutecky-Levich gradient has been observed previously$^4$ and was attributed to an anomalously high diffusion coefficient for 5-hydroxyindole in comparison with the other indoles. The values for 5CAI and 5CH$_3$O are also quite high and as all these indoles may have the facility to be involved in hydrogen bonding via the substituent this may increase the diffusion coefficient as a result of aggregation occurring.

The magnitude of the monomer oxidation potential has been found to be related to the electronic effect of the substituent. This relationship can be described by plotting the monomer oxidation potential against the Hammett substituent parameter, $\sigma^+$. The monomer oxidation potential is a direct measure of the reactivity of the monomer radical cation. If a correlation exists between the coupling reaction of the radical cations and their reactivity then plotting $\ln(i_o)$ against $\sigma^+$ would be expected to give a similar relationship. This plot in presented in Figure 7.6.
There does appear to be a correlation of $i_\infty$ with the Hammett parameter for the indoles with electron withdrawing substituents and therefore also with the electronic nature of the substituent. The values of $\ln(i_\infty)$ for electron donating substituents all appear above the regression drawn through the indoles with an electron withdrawing substituent. We can see that for the electron withdrawing substituents the reactivity of the radical cation in the polymerisation reaction is dictated by the electron withdrawing effect of the group. However as discussed in Chapter 4, the Hammett parameter has limitations when it comes to predicting the electronic properties of 5-substituted indoles with electron donating groups and is therefore not an ideal method of describing the correlation of the radical cation reactivity with the coupling rate.

A plot of $\ln(i_\infty)$ against the monomer oxidation potential is presented in Figure 7.9. Based on the work in Chapter 4 it may be expected that the monomer oxidation potential should give a more accurate test of the correlation between $i_\infty$ and radical cation reactivity than the Hammett parameter. The plot of $\ln(i_\infty)$ against the monomer oxidation potential ($E_{pa}$) suggests there is a correlation between the reactivity of the indole radical cation and the
rate of the coupling reaction. This correlation can be explained by a free energy diagram based on Transition State theory. Central to this theory is that the reaction proceeds via a well defined activated complex or transition state, denoted by ($^\dagger$). Figure 7.7 shows the free energy reaction profile for such a reaction. The free energy of activation ($\Delta G^+$) is the difference in free energy between the reactants and the activated complex (if the reactants and products are in their standard states then $\Delta G^+$ is the standard free energy of activation). The rate of reaction is related to the height of the free energy barrier for the reaction by equation 7.13.

$$k = Ae^{-\Delta G^+/RT}$$  \[7.13\]

![Figure 7.7 The free energy reaction profile for a reaction described by transition state theory.](image)

Consider now a case where the free energy of the initial reactants is changed systematically. This is the case for comparison of the coupling reaction of various substituted indole radical cations. This is illustrated in Figure 7.8. The radical cation of indole $\text{In}_B$ has a greater redox potential than $\text{In}_A$ and so is more reactive. If the energy difference between the neutral $\text{In}$ monomer and the linked monomers is fixed this gives rise to a smaller energy barrier to the linking reaction and therefore a faster rate. The difference in the free energy of activation for $\text{In}_A$ and $\text{In}_B$ is given by equation 7.14. The free energy for the activation and the rate of the linking reaction are now given by equations 7.15 and 7.16.

$$\Delta G_A^+ = \Delta G_B^+ + \alpha nFE$$  \[7.14\]

$$k = Ae^{\alpha nFE/RT}$$  \[7.15\]

$$\ln k = \ln \alpha + \alpha nFE / RT$$  \[7.16\]
Figure 7.8 The reaction profile for the linking of different monomer radical cations.

Figure 7.9 The correlation of \( \ln(\text{i}_o) \) against the monomer oxidation potential, \( E_{pa} \). The regression is drawn through the electron withdrawing substituted indoles (■). The data not included in the regression are 5OH, 5OCH\(_3\), 5NH\(_2\) and 5NO\(_2\) (○). The data point indicated by (▲) is \( \text{i}_o \) for 5NI polymerised on bare platinum.
The natural logarithm of this rate equation (equation 7.16) gives the relationship plotted in Figure 7.9. This confirms that a correlation between the monomer oxidation potential and the logarithm of the coupling reaction rate ($\ln(i_c)$) is expected. The straight line relationship in Figure 7.9 is evidence for this. The regression line can be fitted to the data for the electron withdrawing substituted indoles, and also through 5-hydroxyindole and 5-methoxyindole. This suggests that for the latter two indole radical cations couple on a template film in a manner similar to that of the electron withdrawing substituted indole radical cations.

The notable exceptions are 5NH$_2$ and 5NI both of which lie above the regression. The following section discusses possible reasons why the coupling rate for 5NH$_2$ and 5NO$_2$ radical cations appear higher than expected. There is a possibility that for 5NH$_2$ protonation may occur of the substituent by protons released as the polymerisation process proceeds. This would alter the electron donating / withdrawing nature of the substituent, perhaps forming NH$_3^+$ which has a Hammett parameter of similar value to that for carboxylic acid. (\(\sigma^+\) for NH$_3^+$Cl\(=+0.57\))\(^6\) indicating the greater electron withdrawing nature of this substituent. However from the plot in Figure 7.9 this would lead one to expect an even higher $i_c$ value than is actually observed. It is possible that partial protonation of the 5-aminoindole film occurs giving rise to an $i_c$ value intermediate to both 5-aminoindole and 5NH$_3^+$. This is not observed when polymerising on bare platinum as a different reaction occurs with adsorption of the indole most probably via the electron rich amino substituent.

In the case of 5NI the polymerisation potential used is higher than that used to create the 5Cl template and $i_c$ is approximately 1mA higher on a template than on bare platinum (this data point is included in Figure 7.9). Due to the high polymerisation potential the underlying template undergoes some further oxidation via the irreversible linking of trimers. The $i_c$ for polymerisation of 5NI on bare platinum is much closer to the regression. This probably gives a more accurate indication of the reactivity of the radical cation.
7.4 Conclusions

Koutecky-Levich analysis for the polymerisation surface reaction at a template reveals that the rate determining step is most likely the coupling reaction of the indole radical cations on the polymer film surface. The coupling reaction rate of the electron withdrawing group substituted indole radical cations are correlated to the monomer radical cation reactivity and so the work in this Chapter validates previous assumptions. A straight line relationship for the plot of ln(\(i_0\)) against the monomer oxidation potential is evidence for this. Because of this relationship we can obtain a measure of the relative coupling rates of a range of 5-substituted indoles. The coupling rate of 5OH and 5OCH\(_3\) also appear to be related to the monomer reactivity.

A major implication of this work is that if we can probe the coupling rate of a range of substituted indoles by using a template then we can produce a whole range of copolymers for which we can predict and quantify the products of the copolymerisation. During the copolymerisation of 5Cl and 5CAI there was only a small difference in the reactivity of indole radical cations and they formed well behaved trimer films. However providing there is a high enough electrode potential applied we can expect to produce a statistical distribution of copolymers from known mixtures of indoles with different monomer radical cation reactivities.

7.5 References

Chapter 8
Electrooxidation and Fluorescence Spectroscopy of 5-Carboxaldehydeindole

8.1 Introduction

Indole and its 5-substituted derivatives have been the subject of extensive electrochemical and spectroscopic investigations by Mount and co-workers. Electropolymerisation of 5-substituted indoles involves the formation of a cyclic trimer as a deposit on the electrode surface which becomes linked to form a redox active polymer of linked trimers. These films have been found to be highly photoluminescent. The photophysical properties of these films and of their monomers have been characterised with respect to substituent and solvent effects.

This chapter explores the electrochemical and photophysical properties of 5-carboxaldehyde indole (5CHOI) and its electrooxidation product. This indole was selected to produce indole polymers with a high oxidation potential and interesting fluorescence properties. The electron withdrawing carbonyl group was expected to destabilise the monomer radical cation causing a higher oxidation potential than unsubstituted indole. The electrochemical properties of both monomer and the polymerisation product were investigated to determine if this holds true. Interesting photophysical properties were expected due to the presence of the carbonyl group. In many aromatic carbonyl compounds the main absorption is a \( n \rightarrow \pi^* \) transition associated with the carbonyl chromophore. A detailed fluorescence spectroscopy study was carried out both the monomer and the polymerisation product to determine if the carbonyl chromophore influenced the fluorescent properties.

![Figure 8.1 5-Carboxaldehydeindole.](image-url)
8.2 Electrooxidation of 5-carboxaldehyde indole at the RDE

Preliminary studies were carried out to determine the oxidation potential of 5CHOI. The monomer peak oxidation potential was measured using linear sweep voltammetry and was determined to be +1.20V. The electronic effect of the 5-substituent has been previously described by plotting the oxidation potential against the Hammett substituent parameter ($\sigma^+$). This is shown in Figure 8.2 and it can be seen that the 5CHOI monomer oxidation potential lies close to the regression line of the existing plot for the 5-substituted indoles (drawn through the electron withdrawing groups) suggesting that as for the other monomers such as 5-cyanoindole (5CI), or 5-carboxylic acid indole (5CAI), it is the electronic withdrawing or attracting nature of this substituent and conjugation of the substituent into the aromatic system which is the important influence on the monomer oxidation potential and not steric factors.

It would be reasonable to expect the 5-carboxaldehyde monomer to undergo a similar polymerisation reaction as 5CI and 5CAI. Both indoles undergo mass transport controlled polymerisation when the working electrode is held at a potential approximately 400mV higher than the monomer oxidation potential. This ensures that all monomer reaching the electrode is the limiting factor in the electropolymerisation reaction. Electrooxidation of 5CHOI results in the formation of a green film on the electrode surface, accompanied by a small amount of deep red discoloration of the monomer solution. This suggests that the oxidation results in a small fraction of soluble product. A typical current time transient during electropolymerisation is shown in Figure 8.3. The magnitude of the current is comparable to that obtained during electropolymerisation of 5CI and 5CAI under similar conditions. In the initial growth phase of the polymer layer, the current is observed to change with time and in previous studies this was believed to represent the surface being covered in a deposited monolayer of cyclic trimer, formed in the diffusion layer. Subsequently, the current holds an approximately steady state value which indicates that the monolayer acts as a site for steady state polymerisation. These observed steady state current data can be plotted according to the Koutecky-Levich (K-L) equation which separates the observed currents into mass transport dependent and independent terms. Further details on the K-L equation were given in Chapter 7.
Figure 8.2 Plot of the Hammett substituent parameter ($\sigma^+$) against the monomer peak oxidation potential ($E_{pa}$).

Figure 8.3 A typical current time transient for the polymerisation of 5CHOI (30mmol monomer concentration with electrode rotation speed of 4Hz, $E_{pa}$=1.6V).
A Koutecky-Levich plot was constructed the electropolymerisation of 5CHOI data using templates of a preformed 5CI film and also a bare platinum electrode and these are shown in Figures 8.4 and 8.5 respectively. Analysis of the gradients of these graphs allows the determination of the number of electrons (n) passed during oxidation per indole unit. The value of the diffusion coefficient (D) for 5CHOI was assumed to be the same as other indoles as discussed in Chapter 7. The number of electrons passed are all in the range 2.33 > n < 3.00. This is consistent with the polymerisation reaction (as with 5CI and 5CAI) resulting in the formation of oxidised trimer units containing free trimers (n=2.33, Scheme 8.1) with further oxidation to form polymers of linked trimers (n=3.00, Scheme 8.2). The intercept of the graph, is used to obtain \( i_\infty \), which represents the current at infinite concentration and infinite rotation speed when the current is independent of mass transport. The value obtained is between those found for 5CI and 5CAI consistent with the intermediate reactivity of the radical cation expected from Figure 8.2 (also see Chapter 7). The introduction of a template causes a slight increase in \( i_\infty \), although this is of the order of the error limit (±0.7mA)

\[
3\text{In}^{(eq)} \rightarrow \text{In}_3^{+(s)} + 7\text{e}^- + 6\text{H}^+ \quad \text{Scheme 8.1}
\]

\[
n\text{In}_3^{+(s)} \rightarrow \left(\text{In}_3^{+} \right)_{n}^{-(s)} + 2n\text{e}^- + 2n\text{H}^+ \quad \text{Scheme 8.2}
\]

<table>
<thead>
<tr>
<th>Surface</th>
<th>Concentration of monomer solution /mmol</th>
<th>Gradient</th>
<th>n</th>
<th>Intercept ( i_\infty ) ± 0.7 mA</th>
</tr>
</thead>
<tbody>
<tr>
<td>bare platinum electrode</td>
<td>10</td>
<td>0.460</td>
<td>2.56</td>
<td>9.5</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.154</td>
<td>2.55</td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.103</td>
<td>2.29</td>
<td>9.5</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.047</td>
<td>2.51</td>
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</tr>
<tr>
<td>5CI template</td>
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<td>9.5</td>
</tr>
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<td>100</td>
<td>0.047</td>
<td>2.51</td>
<td>11.3</td>
</tr>
</tbody>
</table>

Table 8.1 Data from a Koutecky-Levich analysis for the electropolymerisation of 5CHOI on bare platinum and on templates of 5CI trimers.
Chapter 8 Electrooxidation and Fluorescence Spectroscopy of 5-carboxaldehydeindole

Figure 8.4 Koutecky-Levich analysis of the electropolymerisation of 5CHOI on a 5CI template.

Figure 8.5 Koutecky-Levich analysis of the electropolymerisation of 5CHOI on a bare platinum electrode.
8.3 Characterisation of the oxidation product

8.3.1 Cyclic voltammetry

Cyclic voltammetry of electropolymerised 5CHOI films revealed that the polymers undergo a reversible one electron redox reaction whilst displaying electrochromism by changing colour from green when in the oxidised form to yellow when reduced. A typical CV is shown in Figure 8.6. The oxidation peak was at approximately +400mV and the peak currents were found to be proportional to the sweep rate. This is indicative of rapid redox cycling of a surface bound species. The charge passed during electropolymerisation was calculated by integration and was ratioed to that under the oxidation and reduction peaks of the CV. A ratio of 8:1 was obtained indicating that approximately 8 electrons are passed during film formation if we assume that a one electron redox reaction is taking place when the film is cycled. The expected ratio for the formation of a trimer upon electrooxidation is 7 electrons for a film containing 100% free trimers, however this reaction corresponds to 2.66 electrons per monomer. This is probably because some of the charge passed during polymerisation contributes to generating the fraction of soluble product which is swept away from the electrode and passes into the bulk solution. This has been investigated by RRDE studies.

Figure 8.6 A typical Steady state CV for a 5CHOI film (formed from a 30mmol monomer concentration with electrode rotation at 4Hz). The inset shows a plot of oxidation peak height against the scan speed.
8.2.2 Characterisation of the electrooxidation product at the RRDE

Experiments involving a rotating ring disc electrode, RRDE, were used to characterise the oxidation product generated at the disc electrode. During the experiments, steady state currents were obtained using either a bare platinum electrode or a preformed template of polymerised 5-cyanindole. The disc current was monitored during monomer oxidation at the disc whilst cycling the ring. An electroactive product was observed as a wave at potentials lower than the onset of monomer oxidation. This wave can be attributed to an oxidised species generated at the disc electrode arriving at the ring electrode where it becomes reduced as the ring is swept to more negative potentials. A typical ring polarogram on a bare platinum electrode is shown in Figure 8.7 with and without monomer oxidation occurring at the disc. Assuming that a trimer species is formed, the ring current can be attributed to the reduction of a small soluble fraction of oxidised trimer \((\text{In}_3^+)\) formed at the disc and reduced at the ring according to the reaction in Scheme 8.3.

\[
\text{(In}_3^+ + e^- \rightarrow \text{(In}_3\text{)}
\]

Scheme 8.3

The half wave reduction potential \(E_{1/2}\) of various 5-substituted indole trimers have previously been measured by RRDE experiments and plotted against their Hammett substituent parameter\(^3\). This plot is reproduced in Figure 8.8 with the addition of the half wave reduction potential of the 5CHOI electrooxidation product (+0.65V). It can be seen that the \(E_{1/2}\) is of an intermediate value to that for 5Cl or 5CAI trimers, indicating that this product is most likely the trimer, which has electrochemical properties dependent on the electron withdrawing nature of the substituent. This is also evidence that substituent oxidation does not occur during electropolymerisation.

The soluble fraction \(x\) of the oxidised product that reaches the ring electrode can be calculated using the relationship in equation 8.1 (and equation 8.2). Here \(x N\) is the effective collection efficiency for this reduction wave and can be calculated for each monomer from the mass transport limited disc current, \(i_L\) at various potentials, where \(i_R\) is the ring current, as in equation 8.2. \(N_0\) is the collection efficiency of the RRDE, which has been calculated and measured using the ferrocene / ferrocinium couple to be 0.21\(^5\).
Figure 8.7 Ring polarogram during RRDE studies of 5CHOI with A) the disc potential at 0V and B) with the disc potential at +1.3V.

Figure 8.8 The half wave reduction potential, $E_{1/2}$, against the Hammett substituent parameter ($\sigma^+$) for the 5-substituted indole trimers reproduced from reference 3 with $E_{1/2}$ 5CHOI trimer added. The $E_{1/2}$ for 5Cl and 5NO$_2$ are the lower limits for $E_{1/2}$ as onset of monomer oxidation wave overlaps with the trimer reduction wave.
The data from the RRDE studies is presented in Table 8.2 and a number of points can be noted. Firstly that for both surfaces as the potential increases past the monomer oxidation potential of 5CHOI, \( x \) decreases. This is accompanied by increasing disc currents indicating a more efficient mass transport limited polymerisation at higher potentials. Secondly the use of a template causes reduction in \( x \) and a dramatic increase in disc current. At 1.1 V the potential is just below that of the monomer oxidation peak potential therefore the polymerisation mechanism will be limited by the electrochemical reaction kinetics rather than mass transport. This will hinder the formation of the initial trimer layer and less trimerisation will occur on bare platinum. However on the 5Cl template polymerisation does occur at this potential. This is evidence that surface adsorption is an important mechanism for the growth of the trimer film, and is energetically favourable with respect to the solution coupling reaction.

If the soluble fraction at the polymerisation potential is assumed to be 0.15 then 85% of the electrooxidation product will form a film. If the film consists of only free trimers (7 electrons passed) then the ratio obtained from CV experiments is consistent with the ratio obtained with these RRDE experiments (0.85/7=1:8.2). The large soluble fraction in these experiments indicate that the 5CHOI trimer appears to be much more soluble in acetonitrile than either the 5CAI and 5CI trimers. One of the chief impediments to polymer ECL studies involving polyindoles (described in Chapter 9) was the low solubility of the trimer. The high solubility of the 5CHOI trimer could be exploited in this type of experiment.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Disc Potential / V</th>
<th>( i_{\text{Disc}} ) /mA</th>
<th>( i_{\text{Ring}} ) /( \mu )A</th>
<th>Soluble fraction, ( x )</th>
</tr>
</thead>
<tbody>
<tr>
<td>bare platinum</td>
<td>1.1</td>
<td>2.3</td>
<td>1.6</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>2.8</td>
<td>2.0</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td>1.3</td>
<td>3.4</td>
<td>2.8</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>1.4</td>
<td>3.6</td>
<td>3.0</td>
<td>0.28</td>
</tr>
<tr>
<td>5Cl template</td>
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<td>3.4</td>
<td>2.4</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>4.0</td>
<td>2.0</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>1.3</td>
<td>4.8</td>
<td>2.2</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>1.4</td>
<td>6.6</td>
<td>3.0</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Table 8.2 RRDE data using a bare platinum electrode and a 5Cl template.
8.2.3 Laser desorption / ionisation mass spectrometry

A Laser desorption / ionisation mass spectra, L2MS, of a 5-carboxaldehyde indole film (polymerised from a 20mmol monomer solution at \( W = 16\text{Hz}, 1.5\text{V} \)) was collected over 100 shots using 266nm photoionisation. This is shown in Figure 8.9 and it clearly shows that the major component of the electropolymerised film has a parent ion at 429D. This can be attributed to the cyclic trimer species, which consists of three monomer units with a mass of 145D, minus with 6D due to the loss of 6 protons during coupling as in Scheme 8.1. The fragment peaks present at 401, 373, and 345D. These peaks are separated by 28 mass units representing the successive loss of CO from each of the aldehyde substituents. This peak distribution is consistent with the similar fragmentation pattern observed for 5CAI trimer\(^1\) and 6CAI trimer (Section 5.4) where the separation of fragment peaks is instead 44D representing the sequential loss of \( \text{CO}_2 \). There are no significant peaks below 345D as the resulting indole trimer is an extremely stable species and is not easily fragmented.

![Figure 8.9 L2MS spectra of poly(5-carboxaldehydeindole) produced from a 20mmol solution at \( W = 16\text{Hz}, 1.5\text{V} \).](image)

The characterisation of electropolymerised 5CHOI discussed so far supports the premise that the major oxidation product is a cyclic trimer which has three carboxaldehyde groups as shown in Figure 8.10. This is not surprising perhaps given its similar electrochemical properties to indoles previously studied such as 5CI. As with these indoles it is assumed
Chapter 8 Electrooxidation and Fluorescence Spectroscopy of 5-carboxaldehydeindole

that the trimer is asymmetric as polymerisation follows a similar mechanism. The computational study of the electronic structure of the monomer radical cation in Chapter 4 suggests that the polymerisation mechanism proceeds via an initial 3,3'-dimer linkage in a similar manner to other electron withdrawing group 5-substituted indoles. Drawing a parallel to the computational polymerisation study for 5-cyanoindole as discussed in Chapter 6 it can be assumed that the same spin density distribution will be observed for the dimer radical cation. The films of electropolymerised indoles have been found to be highly photoluminescent and so a fluorescence spectroscopic investigation was carried out to determine the effect of the aldehyde substituent on these properties.

![Figure 8.10 The asymmetric 5-carboxaldehyde indole trimer.](image)

8.4 Fluorescence Spectroscopy

8.4.1 Room temperature fluorescence studies

The excitation and emission spectra of 5CHOI monomer was collected in a range of solvents in order to study the effect of solvent polarity on the emission properties. These are presented in Figure 8.11 and the wavenumbers of the excitation and emission maxima and the Stokes shift are shown in Table 8.3. The fluorescence properties of indole and its derivatives are highly sensitive to the solvent environment as discussed in Section 1.3.4. In polar media a large Stokes shift, calculated as the difference in wavenumbers between excitation maxima and emission maxima, is observed giving rise to a bathochromic shift in the emission wavelength.
This shift increases with solvent polarity, whilst the absorption peak position is much less affected. In order to quantify this relationship of the solvent polarity with the emission wavelength the solvent properties were described by the function, \( f(D,n) \) where \( D \) is the dielectric constant and \( n \) is the refractive index. This function, shown in Equation 8.3, has been used in previous studies\(^4\)\(^6\) to determine if the unusually large Stokes shift in polar media is linked to the solvent dipole relaxation following excitation.

\[
f(D, n) = 2 \left[ \frac{D - 1}{D + 2} - \frac{n^2 - 1}{n^2 + 2} \right]
\]

In these studies the Stokes shift of the emission of indoles in polar solvents has been attributed to the inversion of the two low lying excited states \( ^1L_a \) and \( ^1L_b \). In nonpolar media the emission is from the \( ^1L_b \) which has a lower dipole moment than the \( ^1L_a \) state and is therefore unaffected by the presence of a polar solvent. However in polar media the energy of the \( ^1L_a \) state can be lowered below that of the \( ^1L_b \) via solvent - solute interactions and the \( ^1L_a \) becomes the emitting state.

![Graph showing emission properties of 5-carboxaldehyde indole in different solvents](image)

Figure 8.11 The emission properties of 5-carboxaldehyde indole in different solvents. (A) isopentane, (B) cyclohexane, (C) DMF, (D) EtOH (E) MeOH, and (F) H\(_2\)O (\( \lambda_{ex}=280\text{nm} \)).
Chapter 8 Electrooxidation and Fluorescence Spectroscopy of 5-carboxaldehyde indole

<table>
<thead>
<tr>
<th>Solvent</th>
<th>f(D,n)</th>
<th>Excitation maxima /nm</th>
<th>Emission maxima /nm</th>
<th>Stokes shift Δν_{max} / cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>isopentane</td>
<td>0.030</td>
<td>286 / 289 / 299</td>
<td>307 / 318 / 324</td>
<td>3040</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>0.125</td>
<td>299</td>
<td>308 / 334</td>
<td>3100</td>
</tr>
<tr>
<td>THF</td>
<td>0.885</td>
<td>310</td>
<td>440</td>
<td>9500</td>
</tr>
<tr>
<td>DMF</td>
<td>1.328</td>
<td>304</td>
<td>426</td>
<td>9400</td>
</tr>
<tr>
<td>EtOH</td>
<td>1.329</td>
<td>299</td>
<td>480</td>
<td>12600</td>
</tr>
<tr>
<td>MeOH</td>
<td>1.412</td>
<td>307</td>
<td>500</td>
<td>12600</td>
</tr>
<tr>
<td>MeCN</td>
<td>1.429</td>
<td>292</td>
<td>430</td>
<td>11000</td>
</tr>
<tr>
<td>H₂O</td>
<td>1.516</td>
<td>305</td>
<td>526</td>
<td>14000</td>
</tr>
</tbody>
</table>

Table 8.3 The excitation and emission properties of 5-carboxaldehyde indole monomer in various solvents. The Stokes shift, Δν_{max} is calculated from the difference in wavenumbers of the maximum peaks in the emission and excitation spectra. The values underlined for isopentane are the 0-0 transitions of the \(^1L_b\) state.

The narrowest emission spectra and the shortest emission wavelength for the 5CHOI monomer is observed in isopentane, a solvent which has a low f(D,n) value. This is consistent with emission in nonpolar solvents from the \(^1L_b\) excited state. The excitation and emission in this solvent also have greater vibrational structure from which the \(^1L_b\) 0-0 emission and excitation transition can be located. The difference in wavenumbers between the values for the 0-0 transition of the \(^1L_b\) states, (Δν_{0,0}) in isopentane is 900 cm⁻¹ similar in energy to other indole monomers such as 6-methylindole (700 cm⁻¹) (Section 5.6).

In polar solvents such as ethanol, methanol and water a large bathochromic shift of the emission is observed which leads to an increased Stokes shift, Δν_{max} as has been observed previously for 5-cyanoindole. Broadening with the loss of vibrational structure of the emission spectra may be attributed to strong hydrogen bonding between these protic solvents and the substituent group and acts as to further lower the energy of the excited state and causes a greater shift of the emission to longer wavelength. This has been observed for the previously studied 5-carboxylic acid indole and also for 4- and 6-substituted indole carboxylic acids discussed in Section 5.6 where the broadening of the emission spectrum is much greater than for indoles which have substituents unable to be
involved in hydrogen bonding. However the bathochromic shift observed for 5CHOI in polar solvents is much larger than even the carboxylic acids. The Stokes shift for 5CAI in EtOH is 10500 cm\(^{-1}\) and for 5CHOI in EtOH it is 12600 cm\(^{-1}\). This increase could be due to the increased electron withdrawing nature of this substituent. The increased electron withdrawing effect may contribute towards the first excited singlet, \(S_1\), having a larger dipole and therefore the \(^1L_a\) level is lowered in energy to a greater extent as it experiences a greater solvent - solute relaxation following excitation. The \(^1L_a\) of 5-cyanoindole is not lowered to the same extent, even though the cyano substituent has greater electron withdrawing character than the carboxaldehyde group as it is unable to be involved in hydrogen bonding. Thus it is a combination of the hydrogen bonding ability of the carboxaldehyde group and the electronic effect of the substituent which are responsible for this huge shift in the emission wavelengths in polar solvents.

The fluorescence properties of the electropolymerised 5CHOI were investigated in various different solvents, however this study was limited by the reduced solubility of the trimer in non-polar solvents with respect to the monomer. Electropolymerised films formed from 5-carboxylic acid indole and 5-cyanoindole have a characteristic fluorescence emission in EtOH which is bathochromically shifted with respect to the monomer fluorescence emission. The excitation and emission spectra for 5-cyanoindole polymerisation under conditions favourable for trimer formation are shown in Figure 8.12.\(^4\) This has been attributed to the extremely fluorescent asymmetric cyclic indole trimer.\(^3\) In initial studies of poly(5-carboxaldehyde)indole using ethanol as a solvent this distinctive fluorescence emission was not detected. Instead a broad peak around 540nm was observed as shown in Figure 8.13 and it was initially thought that this was due to a polymer species consistent with the low intensity and broad structureless emission. However this emission was obtained using solutions of films produced from a range of different monomer concentrations and electrode rotation speeds. The effect of solvent polarity on the fluorescence properties is illustrated in Figure 8.13 and the data is summarised in Table 8.4.
Figure 8.12 The fluorescence properties of electropolymerised 5-cyanoindole trimer. (A) the excitation spectrum ($\lambda_{em}$ 430nm) and (B) the emission spectrum ($\lambda_{ex}$ 280nm) in EtOH as reported by Mount and co-workers$^3$.

Figure 8.13 The effect of the solvent on the fluorescence properties of the electropolymersed 5-carboxaldehyde indole films. The excitation spectra in (A) ether ($\lambda_{em}$ 450nm) and (C) EtOH ($\lambda_{em}$ 550nm) and the emission spectra ($\lambda_{ex}$ 320nm, in (B) in ether and D) EtOH.


<table>
<thead>
<tr>
<th>Solvent</th>
<th>Excitation Maxima / nm</th>
<th>Emission Maxima / nm</th>
<th>Stokes shift $\Delta \tilde{\nu}$ / cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ether</td>
<td>333/359/396</td>
<td>429/450</td>
<td>2000</td>
</tr>
<tr>
<td>DMF</td>
<td>336/399</td>
<td>509</td>
<td>5400</td>
</tr>
<tr>
<td>EtOH</td>
<td>335/397</td>
<td>528</td>
<td>6200</td>
</tr>
<tr>
<td>MeOH</td>
<td>295/395</td>
<td>559</td>
<td>9300</td>
</tr>
</tbody>
</table>

Table 8.4 The effect of the solvent on the fluorescence properties of the polymerised 5-carboxaldehyde indole films. The Stokes shift, $\Delta \tilde{\nu}$, is calculated from the difference in wavenumbers between the $S_1$ origin band in the excitation and the estimated $S_1$ origin peak in the emission spectra.

The emission of 5CHOI polymer films is highly dependent on the solvent polarity whilst the position of the excitation maxima does not appear greatly affected. In general, for trimers with other substituents the effect of solvent polarity on trimer emission is much smaller than for their corresponding monomers suggesting that the excited state of the trimer has a lower dipole moment than that of the monomer. This holds true for the 5-carboxaldehyde monomer ($\Delta \tilde{\nu}$ EtOH=12600cm$^{-1}$) and trimer ($\Delta \tilde{\nu}$ EtOH=6200cm$^{-1}$) however the trimer does have an unusually large Stokes shifted emission in polar solvents when compared to other trimers. The solvent environment has little effect on the emission properties of other indole trimers such as the 5CI trimer. The Stokes shift of the emission for the 5CI trimer in EtOH has been observed to be 800cm$^{-1}$ whereas the 5CHOI trimer it is much larger at 6200cm$^{-1}$. In polar solvents the emission is broad and structureless however in ether the emission has increased vibrational structure and under these conditions the peak shape and energy appears to be much more like that of other indole trimers. This suggests that the excited state singlet of the 5-carboxaldehyde indole trimer is a $\pi,\pi^*$ state similar to others studied. The polarity dependence of the 5-carboxaldehyde trimer emission is consistent with the sensitivity of the monomer to the solvent environment however the cause is unclear. The lowering in energy of the $S_1$ state may be contributed to by hydrogen bonding ability of the substituents giving rise to aggregation of trimers in solution however this cannot explain this huge effect of polar solvents. It may be that the excited state of the trimer, $S_1$, has a much larger dipole than other indole trimers and so experiences a greater solvent-solute interaction. This infers that the excited state of the 5-
carboxaldehyde indole trimer has a very different electronic distribution.
In principle the solvent effect on the emission properties of these indole trimers could be
exploited to change the fluorescence emission colour by judicious choice of solvent. This
property can also be exploited to produce copolymers containing this indole unit with
another indole. These would be expected to produce a range of trimers with fluorescent
characteristics intermediate between those of the 5CHOI trimer and other trimers.

8.4.2 Low temperature fluorescence studies

The 5-carboxaldehyde monomer was examined at low temperature by cooling samples to
77K using liquid nitrogen. Ethanol was used as the solvent as it is possible to obtain a
clear glass at these temperatures. As the solvent is frozen in a glass, oxygen is trapped
within the solid matrix. The effect of fluorescence quenching by this species is therefore
reduced. This not only allows a more intense fluorescence emission but also allows
phosphorescence emission to be observed from the triplet state. There are several striking
differences in the emission properties of the monomer in comparison with room
temperature studies. With both solvents the emission was shifted to shorter wavelengths
with greater vibronic structure. Both these effects are the results of the reduction in solvent
relaxation at 77K compared to room temperature. At room temperature the emission was
broad and sensitive to the solvating environment, but at low temperature the solvent cannot
reorganise around the indole molecule as it is trapped in a rigid matrix. The fluorescence
emission was much less intense than for other indoles, however it did show a similar
vibrational structure and this implies that the first excited singlet, $S_1$ results from a $\pi \rightarrow \pi^*$
transition as found for other 5-substituted indole monomers. The vibronic structure is
mirrored in the excitation spectra and this is shown in Figure 8.14. The Stokes shift
between the 0-0 excitation and emission transitions was determined (990cm⁻¹) and found to
be similar to that observed at room temperature (900cm⁻¹) in isopentane. The difference in
wavenumbers between the $^1L_a$ onset and the 0-0 emission transition gives an indication of
the $^1L_a-^1L_b$ separation. The emission is expected to occur from the $^1L_b$ state as solvent
relaxation does not occur to the same extent as at room temperature. The similarity of the
values of both $^1L_a-^1L_b$ separation and $\Delta \tilde{\nu}_{00}$ to those at room temperature in isopentane
infer that the emission is from the $^1L_b$ state.
Table 8.5 The excitation and emission data for 5-carboxaldehyde indole at 77K.

<table>
<thead>
<tr>
<th>Excitation maxima / nm</th>
<th>Emission maxima / nm</th>
<th>Stokes Shift $\Delta \nu_{o,o}$ / cm$^{-1}$</th>
<th>$^{1}L_a^{-1}L_b$ / cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>288 / 291 / 297</td>
<td>306 / 320 / 335</td>
<td>990</td>
<td>2042</td>
</tr>
</tbody>
</table>

Figure 8.14 The A) excitation ($\lambda_{em}$=430nm) and B) emission ($\lambda_{ex}$=280nm) spectra of 5CHOI monomer in EtOH at 77K. The large intensity emission towards at longer wavelengths is due to phosphorescence.

Figure 8.15 5-Carboxaldehyde at 77K. (A) Emission spectrum showing fluorescence and phosphorescence ($\lambda_{ex}$=280nm), and (B) with the fluorescence gated out leaving just phosphorescence observable. The inset shows the fluorescence region magnified. As with other indole monomers further emission was observed at longer wavelengths. This
is due to phosphorescence emission from the first excited triplet, T₁, which is long lived and observable by the naked eye. A typical spectrum is shown in Figure 8.15. However unlike most indoles the phosphorescence is extremely intense and broad with little vibrational structure observed in EtOH. The intensity of the phosphorescence depends on the efficiency of the S₁-T₁ intersystem crossing. Obviously for the 5-carboxaldehydeindole there is some mechanism for spin-orbit coupling to occur which enhances intersystem crossing giving rise to the intense phosphorescence. Both nitro and carbonyl groups are known for having n→π* transitions associated with them. The presence of these substituents causes a greater polarisation of the charge distribution across the conjugated system of the excited state molecule. This has been observed previously for 5-nitroindole which at room temperature is virtually non-fluorescent implying efficient intersystem crossing of energy from the S₁ state to the T₁. At low temperature efficient ISC results in intense broad structureless phosphorescence. This can be attributed to the T₁ having n,π* character due to a low lying n,π* state associated with the nitro substituents. The n→π* transition provides a mechanism for spin orbit coupling which enhances intersystem crossing. A similar case can be inferred for 5CHOI with the n,π* state associated with the carbonyl substituents. However for 5CHOI the triplet must not have pure n,π* character as there is some structure to the phosphorescence in EtOH at 77K and at room temperature fluorescence emission is observable. The S₁-T₁ separation (8580 cm⁻¹) is of comparable magnitude to other indoles.

An estimate of the phosphorescence lifetime was determined by installing a time controlled shutter system to the excitation and emission windows of the fluorescence spectrometer sample compartment. Figure 8.16 shows the intensity decay collected with time. At low temperature and these low concentrations (10⁻⁷ M) the phosphorescence is expected to observe single exponential decay kinetics and an estimate of the phosphorescent lifetime can be obtained by fitting a single exponential to the raw data. Due to the high intensity of the phosphorescence emission a decay was easily collected at the maximum emission wavelength (445 nm) and a good fit was possible. The lifetime was determined to be approximately 1.33±0.01 s.
Figure 8.16 The phosphorescence intensity decay for 5-carboxaldehyde indole. The inset shows the log plot of the decay.

The 5-carboxaldehyde monomer has a relatively short phosphorescent lifetime compared to other substituted indole monomers. Indoles such as 5-bromindole a relatively short phosphorescent lifetime due the internal heavy atom effect, a process which allows spin orbit coupling and enhances efficient ISC. In the case of 5nitroindole which also has a short lifetime this is the result of a n→π* transition which is close in energy to the triplet and so promotes intersystem crossing which can effectively compete with other deactivation processes. 5-Carboxaldehyde indole most likely fits into this second category and the existence of a low lying n,π* transition associated with the carbonyl substituent provides an efficient pathway for intersystem crossing leading to not only intense phosphorescence but also short phosphorescent lifetimes. Those indoles that do not have a heavy atom or n,π* state have much longer lifetimes. This short phosphorescent lifetime is consistent with the triplet of 5CHOI monomer having some degree of n,π* character.
Fluorescence emission and phosphorescence spectra of the electropolymerised films of 5CHOI were collected at 77K in EtOH. These are shown in Figure 8.16 with the low temperature spectra of the 5Cl trimer for comparison and this data is summarised in Table 8.5. At 77K increased resolution and a hypsochromic shift of the emission (with a reduced the Stokes shift) was observed as compared to room temperature studies. The fluorescence emission is at a similar wavelength to the 5Cl trimer however the peaks are less well resolved. The vibronic progression observed for 5Cl trimer at 77K has a spacing of 1300cm\(^{-1}\) and can be attributed to a symmetric ring breathing mode\(^7\), this is also observed for the phosphorescence. It appears that the 5CHOI trimer \(S_1\) state has a more complex vibronic system with overlapping modes which gives rise to the less well resolved fluorescence emission at 77K as compared to the 5Cl trimer.

The fluorescence was gated out by means of the shutter system and a phosphorescence spectrum collected using a 15ms delay between excitation and emission shutters. The phosphorescence has well resolved peaks, similar in peak shape and energy to that of other indole trimers indicating that the \(T_1\) has \(\pi, \pi^*\) character. The phosphorescence intensity is of comparable magnitude to the fluorescence emission. This is unlike most other indole trimers where the phosphorescence is difficult to observe as it is weaker and it underlies the vibrational structure of the fluorescence emission. The \(S_1-T_1\) separation (3000cm\(^{-1}\)) for the trimer is smaller than that for the monomer (8580cm\(^{-1}\) ) however is similar in energy to the \(S_1-T_1\) separation of the 5CI trimer. An approximation of the phosphorescence lifetime of the trimer was obtained whilst monitoring the wavelength of maximum emission. When fitted to a single exponential, an estimate of 0.72s was obtained, however a biexponential fit was better (Figure 8.18). It appears that two species contribute to the phosphorescence decay. One of these has a longer lifetime, on the same timescale as the monomer (1.35s). The second species has a bigger contribution (65%) and much shorter lifetime of 0.56s. The greater conjugation of the trimer provides an efficient means of energy dissipation and so the trimer phosphorescence decay is shorter than the monomer. In comparison with other indole trimers the phosphorescent lifetime is fairly short. For 5CAI trimer a much longer lifetime (4.2s) has been determined however for 5BrI trimer the lifetime was estimated to be 0.05s. The 5BrI trimer has available an efficient pathway for intersystem crossing (heavy atom effect) and so phosphorescence is intense and the lifetime short. For 5CHOI timer there are no heavy atoms present, instead the presence of an \(n\) to \(\pi^*\)
transition associated with the carbonyl groups may provide a pathway for intersystem crossing. There is a possibility of other phosphorescent species which have different lifetimes, such as polymers of different conjugation lengths.

These low temperature spectra can be used to construct an approximate energy level diagram. In Figure 8.18 the transitions responsible for the peaks in the excitation and emission spectrum are assigned. This information is useful when choosing candidates for polymer ECL studies which is discussed in Chapter 9.

![Figure 8.18](image-url)

**Figure 8.17** Comparison of electropolymerised 5CI\textsuperscript{7} and 5CHOI. At 77K A) the excitationλ_{ex} 460nm spectrum and B) the full emission λ_{em} 320nm and C) emission spectrum with fluorescence gated out of 5CHOI. D) the excitation spectrum of polymerised 5CI and E) the full emission and F) fluorescence gated out.

<table>
<thead>
<tr>
<th>Trimer</th>
<th>Excitation / nm</th>
<th>Emission / nm</th>
<th>Phosphorescence / nm</th>
<th>S_{0,0}</th>
<th>S_{1} - T_{1} / cm\textsuperscript{-1}</th>
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</thead>
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<tr>
<td>5CHOI</td>
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<td>417/436</td>
<td>447/500</td>
<td>200</td>
<td>3000</td>
</tr>
<tr>
<td></td>
<td>399/412</td>
<td>(470/501)</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>5CI\textsuperscript{7}</td>
<td>275/320/347/363</td>
<td>415/439/466/481</td>
<td>513/550</td>
<td>500</td>
<td>3500</td>
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<tr>
<td></td>
<td>386/407</td>
<td>478/514</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{7}reference 7

**Table 8.5** The fluorescence properties of electropolymerised 5-cyanoidole and 5-carboxaldehyde indole at 77K in EtOH. The S\textsubscript{1}, S\textsubscript{2} and S\textsubscript{3} excitations are underlined and the S\textsubscript{1} and T\textsubscript{1} emission are in bold.
Figure 8.18 The raw data of the phosphorescence intensity decay for film of electropolymerised 5CHOI in EtOH at 77K using an excitation wavelength of 320nm and emission wavelength of 520nm. The inset shows the processed data fitted with a double exponential decay.

Figure 8.18 An energy level diagram constructed using A) excitation $\lambda_{em}$ 460nm and B) emission spectra $\lambda_{ex}$ 320nm and C) emission spectra with the fluorescence gated out.
8.5 Conclusions

5-carboxaldehyde indole can be electropolymerised to form redox active films. These films undergo a one electron redox reaction and the redox active species has been identified as a cyclic indole trimer. The electrochemical properties e.g. the monomer oxidation potential and the halfwave potential \(E_{1/2}\) for trimer reduction suggest that the substituent does not oxidise upon electrooxidation. The electrochemical behaviour of the monomer and trimer are similar to the 5-substituted indoles previously studied, however the photophysical properties are not. At room temperature the monomer and trimer emissions display extreme sensitivity to the solvent environment. Low temperature studies imply that the triplet state of the monomer has some \(\pi,\pi^*\) character, a direct effect of the presence of carbonyl substituents. The trimer has a larger excited state dipole moment than other 5-indoles previously studied due a different electronic distribution in the excited state which may be attributed to the presence of the carbonyl groups. The phosphorescence lifetimes of both monomer and trimer are short indicating some mechanism for intersystem crossing perhaps associated with the substituent. In principle the solvent sensitivity of the 5CHOI trimer emission properties could be used to tune the emission wavelength of indole trimers and produce range a cotrimers containing 5CHOI with fluorescent characteristics intermediate between those of the 5CHOI trimer and others. This could be useful when choosing candidates for polymer ECL applications which are described in Chapter 9.

8.6 References

Chapter 9
Polymer Electrochemiluminescence Studies

9.1 Introduction
In recent years a renewed interest in electrochemiluminescence, (ECL), has been fueled chiefly by the development of conjugated polymers and their potential application in light emitting devices\(^1\) such as light emitting diodes, LEDs, or light emitting electrochemical cells, LECs. In this chapter ECL has been employed as a screening technique to investigate whether or not certain materials are potential candidates as the active species in a light emitting device. Light generation in an ECL reaction occurs when the energy liberated by a redox reaction is sufficient to generate a species in an electronically excited form. The free energy available in this redox reaction, which can be estimated from the standard potentials for the reversible redox couples, determines the amount of energy available to excite the molecule. This in turn determines whether direct (singlet) excitation is possible or multiple redox processes are necessary to produce the excited molecule, which determines the efficiency of the process. It is therefore important to elucidate the pathway that leads to ECL in order to identify potential candidates for incorporation into more efficient devices.

The redox reactions in ECL can be characterised thermodynamically via the standard potentials of the couples involved.\(^1\) The electrochemical reduction and oxidation reactions produce radical ions, usually an electron donor, \(D^-\) and an electron acceptor \(A^{++}\) which are formed from their parent neutral molecules, \(A\) and \(D\) Schemes 9.1 and 9.2.

\[
\begin{align*}
A &\rightarrow A^{++} + e^- & E^0(A^{++}/A) & \text{Scheme 9.1} \\
D + e^- &\rightarrow D^{+} & E^0(D/D^+) & \text{Scheme 9.2}
\end{align*}
\]

These radical species, generated electrochemically, diffuse together and undergo a redox reaction given in Scheme 9.3.

\[
A^{++} + D^{+} \rightarrow A + D
\]

The enthalpy of this one-electron redox reaction can be calculated from the standard potentials of the couples as shown in equation 9.1.
This enthalpy available in a redox process is approximately the energy available for excitation and can be estimated from electrochemical data such as the voltammetric peak potentials, $E_p$ for the electrochemical formation of $A^{*+}$ and $D^*$. The entropy term, $T\Delta S^0$, has been estimated at approximately $0.1\pm0.1\text{eV}^2$ and therefore the uncertainty in the calculation of $\Delta H^0$ is approximately $\pm0.1\text{eV}$. The standard redox potentials can be approximated by the half wave potentials, $E_{1/2}$, of each couple.

Annihilation reactions which form an excited state molecule as a result of electron transfer need to be relatively energetic to populate the triplet or singlet excited state (typically the enthalpy, $-\Delta H^0=2-4\text{eV}$ or $200-400\text{kJmol}^{-1}$) and these occur on a very short time scale (perhaps similar to that for molecular vibration). The equilibrium nuclear configuration changes when the molecule loses or gains an electron. These configuration changes are similar to that from the electronic redistribution that occurs when a molecule absorbs or emits a photon. Both electron transfer and photon transfer processes occur rapidly on the nuclear timescale and so the actual electron transfer will occur at an essentially constant nuclear configuration. This is included in the classical description of electron transfer by considering that the electron transfer occurs at the intersection of the potential energy surfaces for the reactants and products. The Franck Condon principle is obeyed, as the nuclear configurations of the reactants and products are the same at the intersection. This favours excitation in the redox step, as it would be difficult for the molecular framework to accept the large amount of energy in mechanical form on this short timescale and so there is a significant probability that an excited product will be produced$^2$. The species formed by electron transfer can be an emitting excited state singlet, $^1A^*$, or an excited state triplet $^3A^*$ as shown in Scheme 9.4.

\[
\begin{align*}
\text{A}^{*+} + \text{D}^{*-} & \rightarrow ^1\text{A}^* + \text{D} \\
\text{A}^{*+} + \text{D}^* & \rightarrow ^3\text{A}^* + \text{D}
\end{align*}
\]

Scheme 9.4

The energy required to produce an emitting state can be determined from fluorescence spectroscopy studies. The first pathway in Scheme 9.4 has been traditionally referred to as the S-route and ECL reactions which follow this path are known as energy sufficient.
Direct generation of the emitting state by electron transfer occurs because the energy made available by the redox reaction is sufficient to directly produce the excited state singlet. However, where the energy made available by the redox reaction is not sufficient to generate an emitting species, the systems are known as energy deficient. Emission occurs from a state energetically inaccessible to the redox process. In this case an alternative mechanism must be considered, such as energy pooling via triplet - triplet annihilation. This is commonly known as the T-route. Energy pooling takes place as two excited molecules in the triplet state react together with energy transfer, resulting in an excited state singlet molecule and a ground state molecule. This is illustrated in Scheme 9.5.

\[ 2^3A \rightarrow 1A^* + A \]

Scheme 9.5

Reported efficiencies for the T-route are generally a magnitude lower than the S-routes due to the efficient quenching of triplet states and the need for the reaction of two species to form the excited state singlet. The latter results in the efficiency being sensitive to the local triplet concentration. However, the T-route does require less input energy than the S-route which makes it attractive for use in applications. A third route, the ST-route, is also possible where the T-route is available to an energy sufficient system. However, the inefficiencies of the T-route will make it difficult to observe the contribution to emission from this source when in the presence of the more efficient S-route emission.

This is only a basic outline of the possible pathways and omits other complicating processes such as both A and D becoming emitting species, quenching by solvent impurities, and the existence of triplet annihilation pathways other than Scheme 9.5. Crucial to understanding the processes is the need to study the mechanism of ECL production and the energy partitioning into products in these ECL reactions.

Previous polymer ECL systems studied include poly(3-hexylthiophene), and poly(2-methoxy-5-dodecyloxy-p-phenylenevinylene) (MDOPPV) and poly(4-methoxy-2-ethylhexoxy-2.5-phenylenvinylene) (MEHPPV) the last two of which are derivatives of Poly(p-phenylenevinylene). These are \( \pi \)-conjugated polymers that have been extensively studied because they can be incorporated into solid state polymer LED devices. Also studied are a range of polymers with non-conjugated backbones with electroactive and emitting groups covalently attached. One such polymer is poly(vinyl-9,10-diphenylanthracene). In these ECL systems the polymers can act as both the donor and
acceptor species in the redox reaction as they have the ability to undergo both reduction and oxidation.

In this chapter preliminary studies are reported of ECL, involving poly(5-substituted indoles) as the emitting species. These have a reversible oxidation couple at positive potentials; however, no reversible reduction couple has been observed at negative potentials within the solvent limit of acetonitrile electrolyte. Consequently a co-reactant must be included in the reaction. Also studied is an ECL system involving poly(2,3-diphenyl-5,8-quinoxaline), PDPQ. This \( \pi \)-conjugated polymer has no observable oxidation at positive potentials and so a co-reactant must also be included. These two systems were studied with the ultimate aim of combining the two polymer species to produce a two-polymer ECL system. The possible pathways for ECL production are discussed and predictions for optimum light production are made.

A pseudoreference electrode (Pt) was used during ECL experiments as a conventional Ag/Ag\(^+\) (0.01M) reference enclosed by a glass frit could not be incorporated into the ECL cell. As both a pseudoreference electrode and a Ag/Ag\(^+\) reference electrode were used, the potentials in this Chapter are all quoted with respect to their particular reference. The position of the redox reaction can be used to determine the potential of the pseudoreference electrode with respect to the Ag/Ag\(^+\) (0.01M) electrode.

### 9.2 ECL experiments between poly(5-cyanoindole) and benzophenone

It was hoped to test the photoluminescent conducting polymers produced from substituted indoles as possible candidates for the active species in light emitting devices. The chief fluorophore formed upon electrooxidation is the asymmetric indole trimer species. The 5-cyanoindole derivative, \((5\text{Cl})_3\), shown in Figure 9.1(a) was chosen as the most promising of the 5-substituted indoles for two reasons. Firstly, the quantum yield of this trimer species in ethanol has been estimated by comparing to that of the unsubstituted indole which is reported to be 0.4.\(^{13}\) It was determined that the quantum efficiency of the trimer is 1.3 times that of indole \(i.e.\ 0.52.\(^{14}\) Secondly, it also has suitable electrochemical properties. With the exception of the 5-nitroindole (5NI) trimer, \((5\text{Cl})_3\) has the highest measured half-wave potential, \(E_{1/2}\), of the previously studied 5-substituted indole trimers.\(^{15}\) However, the 5NI trimer has extremely low intensity fluorescence, as discussed in Chapter 5, and is not
suitable as an emitting species. Using the highest possible $E_{1/2}$ helps to maximise the energy available in the system for excitation of the redox reaction product.

![5-cyanoindole asymmetric trimer and benzophenone](image)

Figure 9.1 (a) The 5-cyanoindole asymmetric trimer and (b) benzophenone.

Benzophenone, (BP), shown in Figure 9.1(b) was selected as a suitable co-reactant for the indole as it has a negative reduction potential at -2.2V vs a Ag/Ag⁺ reference electrode (-1.8V vs SCE) and does not undergo oxidation at positive potentials. Most importantly, its photochemical properties make it attractive for this particular system. Benzophenone has a first singlet excited state, $S_1$, formed from a $n,\pi^*$ transition with the first excited triplet, $T_1$, lying at only slightly lower energy due to small S-T splitting. As a result, BP undergoes rapid intersystem crossing from $S_1$ to $T_1$ with a quantum efficiency of near unity. Thus fluorescence from the $S_1$ state is efficiently quenched and consequently at room temperature BP is not fluorescent.

Films of electrooxidised 5-substituted indoles such as 5NI, 5Cl, 5CAI, 5BrI and also of indole were observed to be unstable when cycled to negative potentials (<-1.5V). In general they dissolve at these negative potentials, with the exception of films of 5CAI which remains intact but loses electroactivity when cycled successively from positive to negative potentials. This suggests that some irreversible process is occurring to the film at these potentials, possibly due to an irreversible rearrangement of the film or chemical reaction. This occurs at potentials within the solvent limit and so it not due to reaction with product from electrolyte/solvent breakdown. Films of (5Cl)₃ are also unstable at negative potentials and so small amounts of trimer were dissolved into dry electrolyte with a few drops of dry DMF. A CV of (5Cl)₃ film is shown in Figure 9.2, showing a decrease in current corresponding to the dissolution of the (5Cl)₃ film.
Figure 9.2 A CV of the (5Cl)$_3$ sweeping from +0.80V to -2.15V with respect to Ag / Ag$^+$. By the fourth cycle no film remained on the platinum electrode. Sweep rate was 50mVs$^{-1}$ and this is used throughout unless where stated.

Figure 9.3 A CV of the (5Cl)$_3$ / BP system. Potentials are with respect to a platinum pseudoreference. Inset shows CV of BP redox couple at the solvent limit.
The (5Cl)$_3$ sample was produced electrochemically under conditions that favour trimer formation (high concentration and high rotation speeds). BP was then added to the solution which was rigorously degassed. A CV of this system in the ECL cell is shown in Figure 9.3. All potentials quoted are with respect to a platinum pseudoreference electrode. The oxidation peak of (5Cl)$_3$ was observed at approximately $+0.60\, \text{V (E}_{1/2} = +0.55\, \text{V vs Pt pseudoref)}$. The current was typically low, reflecting the low solubility of the (5Cl)$_3$ trimer in acetonitrile electrolyte with the added problem that the trimer tended to drop out of solution during degassing. A typical CV of the (5Cl)$_3$ trimer in solution appears to be quite different to that of an immobilised film. The oxidation peak is broad and appears to be accompanied by adsorption of the oxidised trimer. This is followed by a sharp reduction. The reduction of BP was observed at $-2.20\, \text{V (E}_{1/2} = -2.10\, \text{V vs Pt)}$. This couple occurred typically very near the solvent limit, the range of which depends on the purity of both solvent and electrolyte salt. This is possibly why good reversibility of this couple was not often observed. The difference between the standard potentials of the redox couples is $\Delta E^0 = 2.75\, \text{V}$ which is equivalent to the energy available for excitation. The observed $E_p$ values were used to determine the suitable potentials for a double potential step ECL experiment with an overpotential of approximately 200mV (or -200mV) added for each reaction to ensure mass transfer limited oxidation and reduction, respectively. Thus, typically, the electrode was pulsed between $-2.30\, \text{V}$ and $0.90\, \text{V}$. The subsequent current transients were recorded and any ECL emission was measured with a photomultiplier tube. Typical ECL data are shown in Figure 9.4.

The ECL data was analysed for any dependence on the pulse length, the order of pulses and the pulse height. The pulse length did effect the ECL emission and pulses shorter than 2s rarely produced significant emission. Optimum light emission was observed with 2 or 4second pulses usually with an interval of 10 seconds between the pulse pairs. This rest period allowed the solution to regain near-bulk concentrations of parent species near the electrode. The ECL emission during all experiments for this system was observed on the second pulse of the pair, disregarding the sign of the first pulse; therefore no dependence on pulse sign was observed. Pulse height was an important variable in the experiments. Obviously the concentration of the radical ions generated depends on the potential applied. The potentials have to be sufficient to ensure that the reaction is mass transport limited for a consistent radical concentration profile for the electrode. This was investigated by varying the pulse height of both pulses and monitoring the ECL response.
Figure 9.4 ECL data of the (5CI)₃ / BP system with the potential pulsed between +0.90v and -2.30v. A) the potential applied B) is the current transient and C) is the ECL intensity. The BP concentration is 9mmol.

Typical ECL data of this sort are presented in Figure 9.5 and the pulse height variation for this experiment is presented in Table 9.1. The anodic pulse was gradually increased from 0.60V to +1.15V and the cathodic pulse was varied from -2.10V to -2.35V. It can be seen that as the pulse voltages are increased beyond $E^0$ for the redox reactions, ECL becomes apparent. Upon repetition of pulses, the ECL intensity decays with time over approximately 1 minute of continual pulsing (10 pulses). This is attributed to neutral trimer being formed, as a result of the annihilation reaction, and dropping out of solution. This suggests that neutral trimer is less soluble in the electrolyte than the oxidised form. This loss of ECL is shown in Figure 9.6.

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Table 9.1 The potentials for the sequence of increasing pulse heights.
Figure 9.5 ECL data from pulse height experiment for the (5Cl)₃ / BP system. The pulse duration is 2s with 10s rest period. A) The electrode potential is increased in both positive and negative directions, B) the current transient and C) the ECL emission.

Figure 9.6 ECL data from a continuous pulse step experiment. The pulse duration is 2s and pulse heights are +1.15 V and -2.30V. The absence of any ECL emission can be noted when no potential is applied.
Control experiments were carried out with only \((5\text{Cl})_3\) and only BP in solution. The electrode was pulsed in the range of potentials described in the pulse height experiments. During both control experiments ECL emission was not observed from these single-component systems. This is not surprising given that no species was present to provide the oppositely charged radical ion for redox reaction and it confirms that the redox reaction that give rise to ECL must involve species generated from both \((5\text{Cl})_3\) and BP.

The purity of the solvent and the supporting electrolyte is an important factor in determining the quality of the background electrolyte and hence the durability of the ECL reaction. The purity of the electrolyte also has influence over the potential range and the reduction of benzophenone was often observed very near the solvent limit. Thus reactions may occur during the negative pulse with impurities present in the electrolyte. Quenching of the triplet state by oxygen present in solution may occur even after degassing. However, this can be excluded, because rigorous degassing was ensured by several freeze-pump-thaw cycles.

The conditions of the double potential step method (square steps, planar electrode, unstirred solution and diffusion-limited process) permit simplification in interpreting the current data. Mass transport can be restricted to diffusive processes and the planar electrode allows the simplest case of linear diffusion to be applicable. On the first step for a generalised electrode process, Scheme 9.6, the Cottrell relationship (9.2) can be used where \(C_\infty\) is the initial bulk concentration of the ion precursor and \(D\) is the diffusion coefficient, \(i\) is the current, \(A\) is the electrode area and \(D\) is the diffusion coefficient of the reactant. Analysis of the second step is complicated because the homogeneous kinetics produce differential equations which are difficult to solve, even with the aid of digital simulation.\(^2\)

\[
R \rightarrow O + e^- \quad \text{Scheme 9.6}
\]

\[
|i| = \frac{nFAD^{1/2}C_\infty}{\pi^{1/2}A^{1/2}} \quad [9.2]
\]

Where the initial pulse was a positive potential, the anodic current typically shows a peak at the beginning of the pulse which decreases rapidly to a more gentle slope and the current transients were subsequently found not to follow the Cottrell relationship. This most likely reflects the adsorption of the oxidised trimer at positive potentials, possibly followed by
further linking of trimers. The films then appear to dissolve off the electrode at negative potentials when the potential direction is reversed. Where the first pulse in the sequence was negative the cathodic current was analysed. As the data acquisition card cannot measure currents higher than 5mA, a low BP concentration (1.3mmol) was used. This does follow the Cottrell relationship to some extent as illustrated by the relatively constant value obtained by plotting \( \sqrt{it} \) against time in Figure 9.7.

Figure 9.7 The current data from and \((\text{Cl})_3 / \text{BP}\) ECL experiment with A) the system for the first (anodic) pulse corresponding to \((\text{Cl})_3\) oxidation and B) the system for the first (cathodic) pulse corresponding to BP reduction. BP concentration = 1.3mmol.

In order to determine the mechanism of an ECL reaction the energies of the excited states of the species in question must be considered. The 5CI trimer is an extremely efficient fluorophore and its first excited singlet \(S_1\), estimated from fluorescence spectroscopy at \((77K)\) as the shortest emission wavelength, is at 405nm (3.06eV relative to \(S_0\)).\(^{15}\) The first excited singlet of BP is at the higher energy of 370nm, (3.35eV relative to \(S_0\))\(^{16}\) and undergoes rapid intersystem crossing to the \(T_1\), estimated from emission spectra at 77K to be 425nm (2.92eV relative to \(S_0\)). An energy level diagram of these systems is shown in Figure 9.8.
The energy available from the redox reaction is approximately $\Delta E^0 = 2.75\text{eV}$ which is less than that required for excitation to the $S_1$ of either the (5CI)$_3$ or BP (and also the $T_1$ of BP). This is therefore an energy deficient system which does not follow the S-route pathway in order to produce ECL. An alternative pathway for excitation must be found and this most likely involves the first excited triplet of the (5CI)$_3$ which lies at $2.64\text{eV}$ relative to $S_0$ (470nm), which can be estimated from phosphorescence emission spectra at 77K. Triplet-triplet annihilation between (5CI)$_3$ molecules is thought to occur to produce and the electronically excited (5CI)$_3$ $S_1$ state which decays radiatively and gives rise to ECL emission.

![Energy Level Diagram](image)

**Figure 9.8** The energy levels of the 5-cyanoindole trimer estimated from fluorescence spectra showing the phosphorescence and fluorescence emission and the excitation spectra at 77K. The energy levels of benzophenone are included for comparison.

The fact that BP is not fluorescent at room temperature provides indirect evidence that the emitting species is the $S_1$ state of the (5CI)$_3$ trimer. The emission may possibly be due to phosphorescence of BP as the quantum yield of phosphorescence has been measured in solutions of Freon 113 to be $\Phi_p = 0.1^{18}$ at room temperature. This is quite substantial and perhaps some phosphorescence is possible from degassed solutions at room temperature however this is unlikely as quantum yield would be markedly reduced and the $T_1$ of BP is not accessible by the redox reaction. To confirm the emission source of the system an ECL
spectrum must be obtained which requires spectral analysis of the ECL emission. This has not been possible with the present system, due to the inability of the ECL reaction to be stable over sufficient time to enable spectral collection on the Fluoromax spectrometer.

If the \((5Cl)_3/\text{BP}\) system does produce ECL via the T-route mechanism, illustrated in Scheme 9.7, then this implies that optimum light production will occur when the concentration of both \((5Cl)_3\) and BP in solution are high. This is due to bimolecular dependence of the T-route, (Scheme 9.7) as it takes two acceptor (A) ions and two donor ions (D) to form a singlet. If the emission arises from the T-route and if the concentration of the donor (BP) is much greater than that of the acceptor ((5Cl)_3), the reaction will exhibit second order behaviour in A^{19}.

\[
(5Cl)_3 \rightarrow (5Cl)_3^{**} + e^-
\]

\[
BP + e^- \rightarrow BP^{**}
\]

\[
BP^{**} + (5Cl)_3^{**} \rightarrow 3(5Cl)_3^* + BP
\]

\[
3(5Cl)_3^* + 3(5Cl)_3^* \rightarrow 1(5Cl)_3^* + (5Cl)_3
\]

\[
1(5Cl)_3^* \rightarrow (5Cl)_3 + hv
\]

Variation of the concentration of \((5Cl)_3^{**}\) is complicated by several factors concerning the solubility behaviour of the parent species. The neutral insoluble trimer is produced as a result of the annihilation reaction and this is indicated by a light green solid which collects at the bottom of the ECL cell. To further complicate the analysis, adsorption occurs during the anodic pulse, creating a thin film of oxidised trimer on the electrode which may be attributed to trimers undergoing further oxidation and becoming linked. This dissolves at negative potentials, as described previously. An approximate control over the concentration of \((5Cl)_3^{**}\) may be achieved by variation of the anodic potential pulse height. A higher potential e.g. +1.10V will ensure that every \((5Cl)_3\) reaching the electrode will become oxidised.

Variation of the BP concentration is easily controlled due to the good solubility in both neutral and reduced forms and at all potentials. Using the same values for pulse height and
the approximate same concentration of \((5\text{Cl})_3\) in each experiment (although in practice difficult to achieve) the concentration of BP in solution was varied. At concentrations of 1.3mmol the maximum intensity was observed to be 0.015V. and at 5mmol the maximum intensity was 0.055V.

An ECL experiment with an electrooxidised film of \((5\text{Cl})_3\) on the working electrode and BP in solution was attempted. Weak ECL was observed, however this disappeared as the \((5\text{Cl})_3\) film dissolved as the potential of the electrode was pulsed to negative values (-2.10V to -2.30V). It is not clear whether the ECL reaction involved \((5\text{Cl})_3\) immobilised in the film or as a dissolving species.

9.3 ECL experiments between poly(2,3-diphenyl-5,8-quinoxaline) and thianthrene.

Poly(quinoxalines) are members of a class of \(\pi\)-conjugated polymers that contain electron withdrawing imine nitrogens, Figure 9.9(a). These polymers have electron accepting properties and are susceptible to electrochemical reduction to generate negatively charged carriers in the polymer chain\(^{20}\). The quinoxaline polymers have two imine nitrogens and this causes their reduction to occur in the potential range (-1.80V to -2.40V vs Ag/Ag\(^+\)). The second important property of poly(quinoxalines) with aromatic substituents such as poly(2,3-diphenyl 5,8-quinoxaline), PDPQ, shown in Figure 9.9(b), is that they exhibit very strong fluorescence in solution and also as films\(^{20}\). PDPQ is therefore an attractive material for ECL reactions.

\[
\text{(a) } \begin{array}{c}
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followed by a second oxidation at the much higher potential of +1.60V vs Ag/Ag⁺. No reduction was observed at potentials more negative than -2.30V in the acetonitrile electrolyte and this is consistent with previous studies⁴¹, however TH has been reported to undergo reduction in DMF electrolyte (0.1M TBAP) at -2.60V vs SCE.⁴²

PDPQ films were drop-coated from solutions of chloroform and cycled in electrolyte containing TH (at a typical concentration of 9mmol). The PDPQ films require a series of potential cycles whilst successively increasing the potential sweep range. This allows ingress of solvent and the movement of counter ions into and out of the film. This preconditioning leads to a more rapid solvation of the film. These films appear to be conducting at positive potentials in the neutral state, as the redox couples of, for example Fc/Fc⁺ and TH/TH⁺, can be observed during cycling to suitable potentials, as illustrated by Figure 9.11. A CV of the PDPQ film and TH in solution is shown in Figure 9.12. The reduction peak of the PDPQ film was observed at Eᵣ = -2.25V vs Pt with the E⁰ estimated at -2.00V. TH is oxidised at Eᵣ⁺ = +1.60V vs Pt with the E⁰ estimated at +1.55V corresponding to the first one electron oxidation.

Figure 9.10 A CV of TH in solution (5mmol). Potentials are quoted with respect to Ag/Ag⁺.
Figure 9.11 A CV of a drop coated film of PDPQ (---) on a platinum electrode. Potentials are quoted with respect to Ag/Ag⁺. Overlaid (---) is a CV of Fc/Fc⁺ (concentration=2mmol) in solution cycled at a PDPQ film on the electrode.

Figure 9.12 A CV of PDPQ film with thianthrene (9mmol) in solution vs Pt pseudoref.
Double potential step ECL experiments were carried out by pulsing the potential between -2.30V and +1.80V and the resultant current transients were monitored and the corresponding ECL recorded. Typical ECL data for this system are shown in Figure 9.13. The ECL experiments were carried out with the pulse sequence first positive then negative (+/-) and light emission was observed always upon the second (cathodic) pulse. In general 2s pulses with 10s rest time between the pulse pairs appeared to give optimum light production. The ECL from this system decreased over time with continuous pulsing. This is due to the PDPQ film dissolving gradually, although the neutral film is stable in acetonitrile for hours, the radical anion form is soluble in this solvent. This results in a thinning film via dissolution and a decrease in peak currents. A CV obtained after the loss of ECL showed no presence of the PDPQ redox couple indicating complete dissolution.

Figure 9.13 The ECL data for the PDPQ film / TH system. A) the applied potential, B) The current transient and C) the corresponding ECL. The electrode was pulsed between +1.68V and -2.20V with 2 s pulse duration and a 10s rest period between.
A control experiment was carried out with TH in solution at the same concentration as a mixed PDPQ / TH system and the same pulse potentials and the intensity of ECL compared. ECL was observed with just TH in solution, although this was weak and never more than one fifth the intensity of the PDPQ / TH ECL. This has been observed before and is thought to be of a preannihilation type\textsuperscript{21,23} ECL involving possibly small amount of products formed from TH\textsuperscript{**}. Preannihilation ECL is observed when the electrode is swept to potentials sufficient only to generate one radical species, either the radical anion or radical cation. Various experiments have been reported\textsuperscript{24, 25} but the mechanism of this phenomenon is still not clear. The general consensus rules out the direct formation of excited states as a result of an electron transfer reaction in favour of a reaction involving an impurity or decomposition products.

The photoluminescence spectra for poly(2,3-diphenyl-5,8-quinoxaline), PDPQ, which exhibits strong fluorescence, is shown in Figure 9.14E). The multicomponent nature of this chemically polymerised linear polymer is illustrated by the excitation spectra obtained at the emission wavelengths of C) 520nm and D) 540nm. This PDPQ sample very likely contains various polymer chain lengths which have differing number of monomer units. A measurement of the fluorescence emission intensity was performed on a solution containing an equimolar mixture (10\textsuperscript{-5}M) each of PDPQ and TH. The fluorescence intensity was compared to their single component solutions and it was observed that the emission due to TH cannot be observed because of the overlap of the extremely intense PDPQ fluorescence. Thus PDPQ fluorescence emission is essentially unchanged by the addition of TH.

The spectroscopic properties of the PDPQ and TH were studied in order to determine the energy levels of the excited states. The fluorescence spectrum of PDPQ at 77K is shown in Figure 9.10. This allows the first excited singlet state, \( S_1 \) to be located at approximately 2.60eV relative to \( S_0 \) (473nm).\textsuperscript{20} This is consistent with a previous study which determined the \( S_1 \) from the onset of the excitation in solution at room temperature.
Figure 9.14 The A) excitation ($\lambda_{em}$ 440nm) and B) emission spectra of TH in EtOH and C) excitation ($\lambda_{em}$ 520nm), D) excitation ($\lambda_{em}$ 540nm) and E) emission spectra of PDPQ in EtOH at room temperature.

Figure 9.15 The energy level diagram of TH estimated from the emission spectra showing A) phosphorescence and B) the fluorescence emission and C) excitation spectra at 77K and the energy levels of PDPQ estimated from D) the emission and E) excitation spectra at 77K.
The fluorescence of TH in ethanol is characterised by a large Stokes shift, with a wavelength of maximum excitation at 258nm and maximum emission at 434nm. Excitation of TH generates an increased dipole moment and interaction with the polar solvent results in a lowering of the excited state energy and so the emission is observed at longer wavelengths. A previous study estimated the $S_1 \rightarrow S_0$ energy from the maximum emission peak (2.84eV)\textsuperscript{21}. However, the emission maximum generally corresponds to the maximum of the Franck-Condon envelope of vibronic transitions and will give an underestimation of $S_1 \rightarrow S_0$ energy. A more accurate value can be obtained by estimating the wavelength at half peak height which is approximately 415nm (3.02eV) or from the emission spectrum at 77K in a frozen EtOH glass, which is shown in Figure 9.15. This indicates that the $S_1$ is approximately at 417nm (24200cm\textsuperscript{-1}, 3.00eV relative to $S_0$). The first excited triplet, $T_1$, of TH determined from the phosphorescence peak in the emission spectrum obtained at 77K in EtOH at 475nm (2.59eV relative to $S_0$) which is consistent with a previous study.\textsuperscript{21,26}

The energy available from the redox system is 3.50V and consequently the system is energy sufficient with respect to both TH and PDPQ, as both the singlet states are accessible by the energy made available by the redox reaction Although weak ECL is observed with TH alone the emission of the mixed system is likely to come from the lowest lying singlet of the PDPQ. This is supported indirectly by the photoluminescence spectra of the equimolar solution of PDPQ and TH. Also accessible are the triplet states of both species so a mixed S-T-route may be possible, especially since the quantum yield for phosphorescence of TH has been measured at 0.94\textsuperscript{21}.

### 9.4 ECL experiments between poly(5-cyanoindole) and poly(2,3-diphenyl-5,8-quinoxaline)

The conducting nature of the PDPQ film allows the addition of a second layer of polymer by cathodic polymerisation. 5-cyanoindole was found to electropolymerise on top of a RDE with a drop coated PDPQ film with a current comparable to that on a bare platinum electrode (if perhaps slightly lower) to produce a PDPQ / (5Cl)\textsubscript{3} polymer bilayer. The reduction peak of PDPQ was observed at -2.08V (E\textsubscript{1/2}=-1.90V) and the (5Cl)\textsubscript{3} was observed to undergo oxidation at +0.55V (E\textsubscript{1/2} +0.40V). A CV is shown in Figure 9.16 ECL experiments were unsuccessful with these bilayers, most probably due to insufficient energy for either the S or T routes, with the added complications of solubility problems.
The energy available from this redox reaction, $\Delta E$, calculated from the $E_{1/2}$ for each couple, is approximately 2.30eV. This is insufficient to excite either the $S_1$ of $(5\text{Cl})_3$ (3.06eV relative to $S_0$) or the $S_1$ of PDPQ (2.60eV relative to $S_0$). There is also insufficient energy to produce the first excited triplet, $T_1$, of $(5\text{Cl})_3$ (2.60eV relative to $S_0$). Moreover, the $(5\text{Cl})_3$ film dissolves at the negative pulse potentials (approximately -2.10V vs Pt) and the reduced form of PDPQ is also soluble. These solubility problems are illustrated in the CV Figure 9.16 by the decrease in currents. Other factors such as the film thickness and possible quenching of ECL by extremely conducting films must also be considered.

Figure 9.16 A CV of a PDPQ / $(5\text{Cl})_3$ bilayer potentials are with respect to Ag/Ag+ reference electrode. The peak currents for both peaks change with time. The currents due to the $(5\text{Cl})_3$ couple are observed to decrease dramatically due to the dissolution of the $(5\text{Cl})_3$ film. The sweep rate is 100mVs$^{-1}$. 

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9.5 Conclusions

ECL from $(5\text{Cl})_3$ and PDPQ can be obtained by double potential step electrolysis of solutions of $(5\text{Cl})_3$ trimer and films of PQ in electrolyte. The $(5\text{Cl})_3$ / BP system is inferred to follow a T-route pathway. To produce ECL emission involving the more efficient S-route with electropolymerised indoles energy input greater than 3.06eV is required to be made available by the redox reaction. This can be achieved in two ways. Firstly by replacement of BP by a species which will produce radical anions at a more negative potential. This will be difficult because the BP reduction is very near the solvent limit in this system, which is critically dependent on the purity of solvent / electrolyte purity. Secondly the oxidation potential of the indole trimer could be increased by substitution or dissubstitution with electron withdrawing groups.

An alternative route is to manipulate the electronic structure of the indole trimer to produce a lower $S_1$ energy. However, the majority of the indole trimer species studied so far appear to have very similar $S_1$ energies. The exception is the 6CAI trimer; from emission spectra at 77K, the $S_1 - S_0$ energy difference was estimated at 2.89eV and the $T_1$ estimated at 2.44eV relative to $S_0$ (see Figure 9.17). Both $S_1$ and $T_1$ would be lower in energy if the 6CAI trimer replaced $(5\text{Cl})_3$ and less input energy would be required to give rise to ECL via the T route.

Employing indole trimer species with lower $S_1 - S_0$ energies must, however, be balanced by the amount of energy made available by the redox reaction, which depends on the redox potentials. The carboxylic substituent has less electron withdrawing character than the cyano group and, as a result, the 6CAI trimer has lower $E_{1/2}$ of 600mV vs Ag /Ag$^+$ (Section 5.3.1) than $(5\text{Cl})_3$ (estimated at >650mV). Consequently, in a BP / (6CAI)$_3$ ECL system it can be predicted that there will be insufficient energy made available by the redox reaction to access the $S_1$ of either species or for that matter the $T_1$. 
Films of DPPQ have been shown to be an excellent choice of redox polymer which are capable of reduction and are highly luminescent and so can take part in an ECL system as the emitting species. The conducting nature of the neutral form makes it attractive because bilayers of polymers can be formed by electropolymerisation of a second polymer film on top of a drop coated PDPQ film. Bilayer ECL involving PDPQ / (5C1)_3 were unsuccessful as there is insufficient energy in this system to access the excited state of either of the species. However, this maybe rectified by modification of the electrochemical or fluorescence emission properties of the indole trimer as described above.

Polymers formed from indole derivatives are novel materials for light emitting devices and ECL techniques have provided preliminary results which suggest that further research would be profitable in developing these materials for light emitting applications. ECL can be used to test potential materials for the fabrication of light emitting devices. By selection of suitable reactants, the free energy of a redox system can be tuned to obtain the lowest energy required for electronically exciting the emitting species. This is advantageous as minimising the turn-on voltage of a light emitting devices makes it more economical. The colour of emission can, in principle, be tuned by careful selection of materials, although
this is limited for indole polymers at present. In this study only the 6CAI trimer or the 5-carboxaldehydeindole trimer have significantly differing emission properties from the other indoles suggesting that a greater range of substituted indoles need to be investigated.

9.6 References


Chapter 10
Conclusions

This thesis has presented a computational and electrochemical study of a range of electropolymerised 4-, 5-, 6-, and 7-substituted indoles. This chapter contains a summary of the chief findings of this research with some final comments on the implications of this work.

A combination of computational quantum chemical methods with electrochemical techniques has been employed to explore the electronic structure of the 5-substituted indoles. Correlation of the energy differences between neutral and radical cation indoles with the Hammett parameter was found to be similar to that of experimentally measured oxidation potentials. This suggests that the anomalous oxidation potentials of 5-methoxyindole, 5-hydroxyindole and 5-aminoindole actually have their origin in the fundamental electronic structure of these indoles and are not due to specific substituent / electrode surface interactions as previously proposed.

Density Functional Theory and semi-empirical calculations have shown that it is possible to predict oxidation potentials. The DFT calculations showed a good agreement between the theoretical values and those observed experimentally. A greater discrepancy was found with the less rigorous semi-empirical calculations and so the level of accuracy is important. Prediction of DFT redox potentials reveals that the substituent nature does have an effect and this can be determined computationally. This method can be used to predict the oxidation potentials of as yet unstudied substituted indoles before synthesis. This would be extremely useful in the development of novel indole conducting polymers as it would also make possible the screening of indole radical cation for their potential to form asymmetric trimers.

Calculation of the electronic structure of the monomer radical cation, the species involved in trimer formation, has shown significant differences in the calculated $\pi$-spin density distribution between indoles with electron withdrawing substituents and indoles with electron donating substituents. For those with electron withdrawing groups the unpaired
electron is located at the 3-position which is consistent with the formation of a dimer via 3,3'-linkage in the initial stages of polymerisation. For indoles with electron withdrawing substituents the chief location of the unpaired electron in the radical cation is near the substituent consistent with previous experimental observation that trimerisation of these indoles will only occur on a surface of a preformed trimer film.

The electronic structure of the indole radical cation has been probed by studying the effect of substituent nature and position. Electrooxidation of a various 4-, 6- and 7-substituted indoles result in redox films consisting of novel indole trimers. The monomers and electropolymerised films are photoluminescent and the indole trimer was inferred to be the chief fluorophore. Quantum chemical methods predict oxidation potentials of these indoles in good agreement to experimental values. The transmission of electronic substituent effects through the aromatic system of the indole radical cation was again different for electron withdrawing and electron donating substituents. This was realised after a DFT study of placing an electron donating group in different positions and the effect this had on the radical cation spin density distribution. Disubstitution with electron donating groups also has a dramatic effect.

Computational methods were used to elucidate the polymerisation mechanism. Thermodynamic control over the polymerisation process involving the most stable product has been shown to be unlikely. This has been discounted on the basis of DFT calculations. Calculation of the theoretical oxidation potentials gives an indication of the dimer oxidation potentials which suggest that if the dimer species could be isolated then different connectivities may be distinguished by electrochemical methods. Consideration of the π-spin densities of the dimer radical cation species reveals that a 3,3'-linkage is most likely for indoles with electron withdrawing groups and other indole radical cations with the spin density near the C3 position. In the 3,3'-dimer radical cation a redistribution of the spin density over the C3-C2 bond is consistent with the formation of the asymmetric trimer. For indole radical cations with the spin density at the C2 position, such as 5,6-dimethoxyindole, an alternative mechanism of trimerisation is likely via the 2,2'-dimer. This type of calculation can help elucidate the polymerisation mechanism of indole monomers already studied and is also is a useful predictive tool to screen novel monomers.
before experimental investigation and so be used in the design of novel conducting polymers.

The stability of the oxidised indole and 5-cyanoindole asymmetric trimer can be explained by the location of the spin density which is chiefly located around the central benzene ring with substantial spin density spread over the whole system. The asymmetric distribution of the spin density is directly due to the asymmetric nature of the trimer species.

Koutecky-Levich analysis for the polymerisation surface reaction of 5-substituted indoles at a template reveals that the rate determining step is most likely the coupling reaction of the indole radical cations on the polymer film surface. The coupling reaction rate appears to correlate with the monomer radical cation reactivity and so this work validates previous assumptions. A major implication of this work is that if we can probe the coupling rate of a range of substituted indoles by using a template then it would be possible to produce a whole range of cotrimers for which we can predict and quantify the copolymerisation products. By ensuring there is a high enough electrode potential applied we can expect to produce a statistical distribution of cotrimers from known mixtures of indoles with different monomer radical cation reactivities.

5-Carboxaldehyde indole can be electropolymerised to form redox active films. These films undergo a one electron redox reaction and the redox active species has been identified as a cyclic indole trimer. The electrochemical properties of both monomer and trimer suggest that the substituent does not alter upon electrooxidation. Whilst the electrochemical behaviour is similar to 5-substituted indoles such as 5CI or 5CAI the photophysical properties are not. At room temperature both the monomer and trimer display extreme sensitivity to the solvent environment. Low temperature studies infer that the triplet of the monomer has some n,π* character, a direct effect of the presence of carbonyl substituents. The trimer appears to have a larger excited state dipole moment than other trimers previously studied most likely due to a different electronic distribution in the excited state. The phosphorescence lifetime of both monomer and trimer are relatively short perhaps indicating some mechanism for intersystem crossing. In principle the solvent sensitivity of the 5CHOI trimer emission properties could be exploited to produce range of copolymer trimers with fluorescent characteristics intermediate between those of the 5CHOI trimer and others. This could be useful when choosing candidates for polymer ECL studies.
ECL from (5Cl)$_3$ and PDPQ can be obtained by double potential step electrolysis of solutions of (5Cl)$_3$ trimer and films of PQ in electrolyte. The (5Cl)$_3$ / BP system was inferred to follow a T-route pathway. To produce ECL emission involving the more efficient S-route with electropolymerised indoles energy input greater than 3.06eV is required to be made available by the redox reaction. At present few of the indole trimers studied have different emission properties. Films of DPPQ can take part in an ECL system as the emitting species.

Polymers formed from indole derivatives are potential materials for light emitting devices. ECL techniques have provided preliminary results which suggest that further research would be profitable in developing these materials for light emitting applications. ECL can be used to screen potential materials for the fabrication of these devices as tuning the free energy of the redox reaction and the emission properties can be tested.

The information in this thesis can be used to devise a methodology for understanding indole based polymers. Significant understanding of the polymerisation process, the properties and behaviour of monomer and electrooxidation product is now possible. We can now understand the electronic effect of substitution on electrochemical properties and it is possible to relate electrochemical behaviour to the electronic structure of the radical cations. We can calculate the theoretical oxidation potentials for these species and potentially for any other molecule with similar behaviour. The research has shown that a much wider range of trimer functionality is possible and an even larger range can be predicted. We can also determine if the monomer will undergo trimerisation and so consequently screen for novel monomers.

The proposed polymerisation mechanism has been corroborated and this work has shown that there may be two pathways of trimerisation which are dependent upon substitution. This implies that by judicious substitution we can choose the polymerisation pathway. We can now understand the surface coupling reaction and the factors which effect the coupling rate of radical cations and a theoretical basis for predicting the products of a novel copolymerisation has been provided.
It has been shown that indole polymers can be used in ECL applications and it is possible to tune the emission properties by prudent functionalisation. Using a combination of the fundamental information described above, an informed search for an indole polymer species, with specific electrochemical properties is possible. This could be employed to find other indole conducting polymers suitable for ECL and perhaps other light emitting applications.

Finally, this research provides a theoretical underpinning of the electrochemical aspects of indole conducting polymers. The obvious future direction of research in this area will be to gain a theoretical understanding of the fluorescence properties. Mount and co-workers have begun to do just this by a computational study of excited state species. This would ultimately allow indole monomers and electropolymerised indoles to be screened for both electrochemical and fluorescence properties before experimental investigation.
Appendix 1

A.1.1 Postgraduate Courses and Lectures

Colloquia and Physical Chemistry section meetings
Research Councils Graduate School Management Training course (CRAC)
Transferable Skills
Basic HTML Programming
Programming Concepts
Electrochemical Techniques

A.1.2 Conferences and Meetings

Butler Meeting, Glasgow Calidonian University 1997
Butler Meeting, Newcastle University 1998
Electrochem '98, Liverpool University, September 1998
Butler Meeting St. Andrews University 1999
Royal Society of Chemistry, Materials Chemistry (MC⁴), Trinity College Dublin 1999
Physical Chemistry Section Meetings Firbush 1997 -1999
Appendix 2

A.2.1 Reprints of Publications
Calculations of the electronic structure of substituted indoles and prediction of their oxidation potentials

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Density functional theory (DFT, DMol) and semi-empirical (PM3) calculations have been used to determine theoretical values for the standard redox potentials for the oxidation of substituted indoles. The calculations have been corrected for solvation (COSMO) and for thermal effects (zero point energy and temperature variations in enthalpy and entropy) using frequency calculations. Good agreement between these theoretical values and those observed experimentally are found for the DFT calculations. The less rigorous semi-empirical calculations produce a reasonable estimate of the redox potentials but show a greater discrepancy between experiment and theory. Quantum chemical DFT calculations on indole radical cations indicate that electron withdrawing 5-substituents show a similar spin density distribution in the aromatic system, whereas electron donating substituents show a different distribution. This could explain the observed differences in the oxidation and subsequent coupling reactions of indole radical cations with electron donating and those with electron withdrawing 5-substituents. Significant differences are observed in the spin density distribution between these and previous semi-empirical calculations. This further emphasises the sensitivity of these calculations to the level of accuracy of the computational method.

Introduction

Polymeric indole films have been proposed as potential candidates for fast response potentiometric sensors and for direct oxidation and reduction of biomolecules. For many of these applications it is desirable to produce electroactive indole layers with a wide variety of substituents. The most obvious method for achieving this has been the electrooxidation of a wide variety of substituted indoles. The electrochemical polymerisation process of these indoles has been a subject of debate in the past. In previous papers we have shown that electropolymerisation of a series of 5-substituted indoles at platinum electrode results in the formation of a redox active film. The redox active species present in the film have been characterized as the asymmetric trimer (I) by spectroscopic and electrochemical methods. This is in contrast to the proposed structures for the electropolymerised film of Billaud et al. They postulate that the "polymer" consists of linear chains with regular 2,3-linkages. However it is important to note that their experimental results are consistent with the formation of (I), which we have isolated and fully characterised.

Computational methods have now become valuable tools for simulating the electronic structure and energies of molecules, capable of providing insight into the electronic effect of the substituent and hence the oxidative polymerisation process of substituted indoles. However few quantum chemical studies have been carried out on these systems and those that have been published recently are of a solely semi-empirical nature. In fact in the oldest study, all molecular geometries were rigid, a direct consequence of the relative computational expense of performing geometry optimisations fifteen years ago. Two of these studies have considered the polymerisation process in terms of reaction between an indole radical cation and a neutral indole. This is in contrast to experimental observation that polymerisation involves the coupling of radical cations.

In this paper we investigate the electronic effect of the indole substituent and how this affects the energy and electronic distribution in the neutral monomer and the monomer radical cation and hence the observed redox potential and the radical cation coupling process. We calculate the electronic structure and energy of indole neutral monomers and radical cations using two theoretical methodologies: semi-empirical and DFT. This is because ab initio post-SCF calculations on molecules of this size are currently impractical. This information is then used to calculate theoretical oxidation potentials of substituted indoles, which are compared with experimental data in order to test the accuracy of the calculations. In this work the stabilising effects of the solvent are taken into account. This is crucial as it allows comparison with solution electrochemical measurements to be made. The reasons for presenting our own semi-empirical results here are twofold. Firstly, they serve as a direct comparison to other published data calculated using the less rigorous semi-empirical methods, as well as an assessment of the reliability of these semi-empirical methods compared to more accurate DFT calculations.
approaches. Secondly, they form a reference point for calculations of larger, more complicated systems such as dimer and trimer species, which we report elsewhere and which become computationally expensive using quantum chemical methods. A good example is provided by the asymmetric trimer which comprises 42 atoms when \( R = H \) (I) and more for other substituents, making full quantum chemical calculations highly computationally demanding. Semi-empirical methods would allow a far greater throughput of calculations, as long as there is no drastic compromise of accuracy. It is this question of accuracy that these reference calculations assess.

**Experimental and computational methods**

All chemicals used in these experiments were of AnalR grade or equivalent. Electrochemical control of the rotating disc electrode (RDE) studies was by a standard three electrode potentiostat (Oxford Electrodes), with the data being collected by means of a multifunction data collection card (Intelligent Instruments) and a PC. A 2 cm squared platinum gauze electrode was used as a counter electrode and the working electrode was a Pt RDE disc area of 0.387 cm². The reference electrode was made in house and consisted of a silver wire dipped into a reference solution of silver perchlorate (0.01 mol dm⁻³) in electrolyte (0.1 mol dm⁻³). All potentials have been converted with respect to the standard redox potential of the ferrocene/ferrocenium, (Fc/Fc⁺) couple, measured by linear sweep voltammetry in the electrolyte solution. The electrolyte consisted of 0.1 mol dm⁻³ lithium perchlorate, LiClO₄ (Acros) in acetonitrile (Fisons, dried, distilled). The acetonitrile was refluxed over CaH₂ and distilled to further dry the solvent and the LiClO₄, was dried in vacuo at 60 °C for two days before use.

The CAChe program suite from Oxford Molecular was used for the semi-empirical calculations, which employ MOPAC as the compute engine. We have used the PM3 Hamiltonian. For DFT calculations, the DMol³ and Amsterdam Density Functional (ADF) packages were used under license from Molecular Simulations Inc. Both of these are based on a density functional theory (DFT) approach for the solution of the electronic structure of atoms and molecules. The DMol³ program uses a double-numerical basis set augmented by polarisation functions on all atoms. ADF uses a basis set comprising Slater-type orbitals of double zeta quality with polarisation functions on all atoms (DZ + P). The core 1s electrons of all non-hydrogen atoms were frozen in the ADF calculations. For all DFT calculations, gradient corrections (GGA) to the local density approximation were used via the PW91 functionals. Gradient corrections generally provide improved predictions of bonding energies and electronic spectra compared to the local density approximation.

Using two different DFT calculation packages enables us to assess their 'off the shelf' performance to predict the structure and energetics of substituted indole monomers. We have also performed some basic 'confidence tests' using both packages, which are briefly discussed. Both packages are capable of predicting the gas phase heterolytic bond dissociation energy of small OH-containing molecules (e.g. CH₃OH, HCO₂H, H₂O) to within ±0.1 eV of the experimentally determined values. We have also compared the predicted optimised geometry of 5-hydroxyindole (3) with that determined from X-ray crystallography (Table 1).

![Image](image_url)

**Table 1** DFT (DMol³/ADF, PW91) and semi-empirical (MOPAC, PM3) gas phase and X-ray crystallographic structural data (bond lengths, \( r \), in Å, bond angles, \( \theta \), in degrees)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>DMol³</th>
<th>ADF</th>
<th>MOPAC</th>
<th>Molecule A</th>
<th>Molecule B</th>
<th>Molecule C</th>
</tr>
</thead>
<tbody>
<tr>
<td>r(N1-C1-C2)</td>
<td>1.381</td>
<td>1.362</td>
<td>1.407</td>
<td>1.357(6)</td>
<td>1.372(7)</td>
<td>1.370(8)</td>
</tr>
<tr>
<td>r(N1-N1-C1-C9)</td>
<td>1.385</td>
<td>1.366</td>
<td>1.410</td>
<td>1.370(6)</td>
<td>1.377(6)</td>
<td>1.382(8)</td>
</tr>
<tr>
<td>r(C2-C3-C4)</td>
<td>1.378</td>
<td>1.366</td>
<td>1.381</td>
<td>1.349(6)</td>
<td>1.344(7)</td>
<td>1.356(8)</td>
</tr>
<tr>
<td>r(C3-C4-C8)</td>
<td>1.433</td>
<td>1.416</td>
<td>1.436</td>
<td>1.420(5)</td>
<td>1.430(5)</td>
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<tr>
<td>r(C4-C5-C6)</td>
<td>1.392</td>
<td>1.375</td>
<td>1.388</td>
<td>1.368(4)</td>
<td>1.362(6)</td>
<td>1.359(6)</td>
</tr>
<tr>
<td>r(C5-C6-C7)</td>
<td>1.413</td>
<td>1.398</td>
<td>1.421</td>
<td>1.392(6)</td>
<td>1.394(7)</td>
<td>1.393(6)</td>
</tr>
<tr>
<td>r(C6-C7-C8)</td>
<td>1.380</td>
<td>1.357</td>
<td>1.372</td>
<td>1.395(5)</td>
<td>1.395(5)</td>
<td>1.394(6)</td>
</tr>
<tr>
<td>r(C7-C8-C9)</td>
<td>1.390</td>
<td>1.375</td>
<td>1.377</td>
<td>1.373(7)</td>
<td>1.376(5)</td>
<td>1.383(8)</td>
</tr>
<tr>
<td>r(C8-C9-N1)</td>
<td>1.399</td>
<td>1.384</td>
<td>1.404</td>
<td>1.393(5)</td>
<td>1.377(6)</td>
<td>1.378(8)</td>
</tr>
<tr>
<td>r(C8-C9-N1-C9)</td>
<td>1.409</td>
<td>1.394</td>
<td>1.402</td>
<td>1.403(6)</td>
<td>1.399(5)</td>
<td>1.417(7)</td>
</tr>
<tr>
<td>r(C8-C9-N1-C9)</td>
<td>1.423</td>
<td>1.409</td>
<td>1.421</td>
<td>1.414(6)</td>
<td>1.406(6)</td>
<td>1.399(6)</td>
</tr>
</tbody>
</table>

*See 3 for atom numbering. Labels A, B and C refer to the three different indole environments in the crystal.*
denoted as A, B and C in Table 1). In absolute terms, bond lengths are generally predicted to within ±0.02 Å and bond angles to within ±1 degree of the experimental values. These are typical of the general accuracy of gradient-corrected DFT calculations. Of course, we cannot automatically assign discrepancies between calculated and experimental parameters to the inadequacy of the DFT method. The H-bonding interactions present in the crystal, together with the fact that the structure was determined at 210 K will result in inherent structural differences compared to our calculations. (In particular, thermal vibrations associated with experimentally determined positions can lead to a bond length shortening.16) Given these effects, we conclude that the DFT calculations give an accurate description of the structure of 5-hydroxyindole.

In Table 1, we have also included the structural data for a PM3 optimisation of 5-hydroxyindole. The table shows that the semi-empirical method predicts bond angles of comparable quality to the DFT results. The maximum deviation is approximately 1.5 degrees compared with the experimental data and the bond lengths show slightly larger deviations than their DFT counterparts, particularly around the N atom, where PM3 calculations predict the N-C bonds to be 0.03 Å longer than experimental value.

The MOPAC and DMol³ programs have the facility to include the effects of solvation in the calculations, clearly important in trying to predict the experimentally observed oxidation potentials. The COSMO solvation model of Klamt and Schuurmann17 is used, which treats the solvent as a polarisable continuum of relative permittivity, ε. The details of the implementation are reported elsewhere.19,20 Relative permittivities of 78.5 and 37.5 were used for water and acetonitrile, respectively.21 In the following sections, we present results for the gas phase calculation of energy differences between neutral and radical cation indole monomers, together with a discussion of the trends we observe. We investigate the effects of substituent character and substituent position. We then consider the effects of solvation and temperature on the calculated results, followed by a comparison of experimental measurements and values predicted from these calculations. Finally, we consider the calculated electronic distribution in the monomer radical cation, and the effect this has on the observed redox potentials and the mechanism of radical cation coupling.

Results and discussion

We have recently shown from electrochemical studies using a RDE2 that the observed peak oxidation potential of 5-substituted indoles shows a good correlation with Hammett substituent parameter, σ⁺, with the notable exception of hydroxy and methoxy substituents. The Hammett parameter which is found to be most appropriate is that for a para substituent (with efficient electronic conjugation of the substituent into the aromatic system). This suggests that there is good conjugation of the 5-position substituent into the indole aromatic system and that we can use σ⁺ as a means of describing the substituent effect on the electronic structure of indole. A major component of these observed oxidation potentials is the energy difference between radical cation and neutral 5-substituted indoles, which we have calculated using the computational methods described in the previous section. Whilst this calculation is for the gas phase molecules at 0 K and therefore neglects the effects of solvation and temperature, the energy differences may be expected to show a similar trend to the peak potentials when plotted against σ⁺, and this is indeed the case (Figs. 1 and 2).

The calculated ADF and DMol³ energy differences are similar and energy differences are of the order of 0.1 eV, which is relatively unsurprising given their common methodology and choice of functional (PW91).22 All subsequent DFT calculations were therefore carried out using DMol³ and the PW91 functional. However, the semi-empirical energy differences are consistently larger than the ab initio values. It is interesting to note that the calculations predict a similar departure of the 5-methoxy, 5-hydroxy and 5-amino substituents from the regression line of the Hammett plot produced from the electron withdrawing substituents. When experimentally observed these anomalies were previously attributed to aggregation in solution or electrode surface interactions3 but calculations suggest that the cause is intrinsic to the electronic structure of the 5-hydroxyindole, 5-methoxyindole and 5-aminoindole molecules. This is further borne out in the calculations corrected for thermal and solvation effects (vide infra).

In addition to investigating the effect of changing the nature of the substituent, we have also performed calculations to investigate the effect on the energy difference of changing the position of a given substituent by studying a variety of indole carboxylic acids and methyl indoles. In Table 2 we present the results of DFT gas phase calculations using PW91, to investigate the variation of the neutral–radical cation energy difference, ΔE, for 4,5,6 or 7-methyl and carboxylic acid substituted indoles along with the experimentally observed half wave potentials, E₁/₂. The calculated effect of substituent position is found to be relatively small, which is consistent with the experimental data and it is encouraging that the order of ΔE and E₁/₂ data correlate well. However, the effect of substituent position is rather small and could be comparable in magnitude to the error associated with the calculation method (±0.1 eV).

![Fig. 1](image1.png)

**Fig. 1** Energy differences, ΔE, between 5-substituted neutral and radical cation indoles in the gas phase vs. the Hammett substituent parameter, σ⁺, as calculated using different theoretical methodologies/packages of; (■) PM3, (●) ADF, (▲) DMol³. The substituent, R, is shown for each point. The gradients of the lines of best fit (calculated without the OH, OMe and NH₂ data points) are (■) 0.642 eV⁻¹, (●) 0.783 eV⁻¹, (▲) 0.872 eV⁻¹.

![Fig. 2](image2.png)

**Fig. 2** The experimentally observed half wave potentials, E₁/₂, with respect to the ferrocene/ferrocinium couple, Fe/Fe⁺, plotted against σ⁺. All redox potentials are quoted with respect to the Fe/Fe⁺ couple unless otherwise stated.

In order to determine values for solution oxidation potentials, the inclusion of solvation effects in the calculations is necessary. This has a dramatic effect on these calculated energy differences. Figs. 3 and 4 shows results for semi-empirical (PM3) and DFT (PW91) calculations of the radical cation-neutral energy difference, performed using COSMO with acetonitrile and water as solvents. The gas phase energy differences are added to these figures as a comparison. The inclusion of a solvent environment has led to marked reduction in energy of the radical cation solution species relative to the neutral molecule. This is because the screening charges which are set up in the solvent have most effect on stabilising the charge on the radical cation and reduce the energy between neutral and radical cation species. It is interesting to note that the gradients and intercepts of the plots for

![Fig 3 PM3 energy differences, ΔE, between 5-substituted neutral and radical cation indoles vs. σ⁺ in the (□) gas phase, (●) with acetonitrile solvation, (▲) with water solvation. The gradients of the lines of best fit (calculated without the OH, OCH₃, and NH₂ data points) are (□) 0.042 eV⁻¹, (●) 0.246 eV⁻¹, (▲) 0.220 eV⁻¹.](image)

![Fig 4 DFT energy differences, ΔE, between 5-substituted neutral and radical cation indoles vs. σ⁺, (□) gas phase and (●) acetonitrile solvation. The gradients of the lines of best fit (calculated without the OH, OCH₃, and NH₂ data points) are (□) 0.872 eV⁻¹, (●) 0.509 eV⁻¹.](image)

### Table 2 Gas phase energy differences, ΔE, between neutral and radical cation species and observed halfwave potential, E1/2, relative to Fc/Fc⁺, for 4,5,6 or 7-substituted indole carboxylic acids and methyl indoles (calculated using DMol³, PW91)

<table>
<thead>
<tr>
<th>Substituent position</th>
<th>ΔE/eV</th>
<th>E1/2/V</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 COOH</td>
<td>7.87</td>
<td>0.94</td>
</tr>
<tr>
<td>5 COOH</td>
<td>7.92</td>
<td>0.94</td>
</tr>
<tr>
<td>6 COOH</td>
<td>7.93</td>
<td>0.95</td>
</tr>
<tr>
<td>7 COOH</td>
<td>7.89</td>
<td>0.94</td>
</tr>
<tr>
<td>4 CH₃</td>
<td>7.42</td>
<td>0.70</td>
</tr>
<tr>
<td>5 CH₃</td>
<td>7.51</td>
<td>0.74</td>
</tr>
<tr>
<td>6 CH₃</td>
<td>7.41</td>
<td>0.69</td>
</tr>
<tr>
<td>7 CH₃</td>
<td>7.47</td>
<td>0.72</td>
</tr>
</tbody>
</table>

*See 3 for atom numbering.

### Table 3 Semi empirical (PM3) redox potential data. $E_{300,e}$ is the calculated solvated redox potential at 300 K. $E_{0,K}$ is the difference in the calculated redox potentials at 300 K and 0 K, $E_{corr} = E_{300,e} - E_{9,e}$

<table>
<thead>
<tr>
<th>Substituent</th>
<th>$E_{300,e}$/V</th>
<th>$E_{0,K}$/mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₂</td>
<td>1.25</td>
<td>4.6</td>
</tr>
<tr>
<td>CN</td>
<td>1.02</td>
<td>11.2</td>
</tr>
<tr>
<td>CHO</td>
<td>0.98</td>
<td>9.6</td>
</tr>
<tr>
<td>COOH</td>
<td>1.02</td>
<td>3.2</td>
</tr>
<tr>
<td>Br</td>
<td>0.98</td>
<td>9.7</td>
</tr>
<tr>
<td>Cl</td>
<td>0.96</td>
<td>13.3</td>
</tr>
<tr>
<td>H</td>
<td>0.87</td>
<td>8.4</td>
</tr>
<tr>
<td>CH₃</td>
<td>0.89</td>
<td>-22.9</td>
</tr>
<tr>
<td>OCH₃</td>
<td>0.91</td>
<td>4.3</td>
</tr>
<tr>
<td>OH</td>
<td>0.89</td>
<td>-3.6</td>
</tr>
<tr>
<td>NH₂</td>
<td>0.37</td>
<td>-4.2</td>
</tr>
</tbody>
</table>

In the case of the DFT calculations, the characterisation of stationary points by vibrational analysis is a computationally intensive task. DMol³ evaluates frequencies by finite differences of analytic gradients and a complete set of frequency calculations for all the range of substituents presented here would be a huge undertaking. (We estimate it would take approximately 1000 CPU hours on a Silicon Graphics O2 (R5000) workstation.) Instead, we have used the semi-empirical correction terms described above to convert our 0 K DFT energy differences into values of free energy differences ($ΔG_{300}$). While this is not strictly accurate, we note that the corrections due to thermal enthalpy and entropy are in general very small and are of the order 3–15 meV (with the exception of the 5-methyl substituted indole which is slightly larger, 22 meV, Table 3). We have also evaluated the applicability of this approach by performing a 'spot check', to compare the magnitude of the correction terms determined from semi-empirical and DFT calculations. We performed DFT frequency analyses of the neutral and radial cation of

water and acetonitrile are very similar, even though their relative polarities, $e_s$, differ by nearly a factor of two (78.5 and 37.5, respectively). In fact the introduction of 0.1 mol dm⁻³ LiClO₄ as background electrolyte will be expected to slightly change the relative permittivity of acetonitrile. Although there is no published value for the relative permittivity of this electrolyte, $e_s$ for acetonitrile containing 0.1 mol dm⁻³ tetraethyl ammonium tetrafluoroborate, TBABF₄, has been measured as 38.8 at 25 °C²³ and the value of $e_s$ for 0.1 mol dm⁻³ LiClO₄ would be expected to be similar. However these results suggest that such a relatively small change in permittivity will cause little change in the measured difference in the energies of the radical cation and neutral species, and hence that the value of relative permittivity of acetonitrile is appropriate for use in these calculations.

All the calculation results we have reported thus far relate to total energies calculated at 0 K. To observe room-temperature, solution-phase free energy differences ($ΔG_{300}$), with which we may then calculate oxidation potentials, $E_{300,e}$ we must include corrections for the zero point energies and the differences in enthalpy and entropy of the neutral and radical cation species between 0 and 300 K. Such thermodynamic terms are readily obtained from a frequency analysis of the stationary point geometry. In the case of the semi-empirical calculations, this took around 2 GPU hours per molecule on a desktop PC. All structures were confirmed as true minima on the potential energy surface (with no negative vibrational frequencies). These results are presented in Table 3. The calculated oxidation potentials, $E_{300,e}$ were referenced to the potential of the Fc/Fc⁺ value, calculated in a similar manner to the indole oxidation potentials, using PW91, COSMO and frequency analysis for zero point energy, enthalpy and entropy corrections. The Fc/Fc⁺ energy difference was used as the constant reference for all calculations.

In the case of the DFT calculations, the characterisation of stationary points by vibrational analysis is a computationally intensive task. DMol³ evaluates frequencies by finite differences of analytic gradients and a complete set of frequency calculations for all the range of substituents presented here would be a huge undertaking. (We estimate it would take approximately 1000 CPU hours on a Silicon Graphics O2 (R5000) workstation.) Instead, we have used the semi-empirical correction terms described above to convert our 0 K DFT energy differences into values of free energy differences ($ΔG_{300}$). While this is not strictly accurate, we note that the corrections due to thermal enthalpy and entropy are in general very small and are of the order 3–15 meV (with the exception of the 5-methyl substituted indole which is slightly larger, 22 meV, Table 3). We have also evaluated the applicability of this approach by performing a 'spot check', to compare the magnitude of the correction terms determined from semi-empirical and DFT calculations. We performed DFT frequency analyses of the neutral and radial cation of

![Table 3 Semi empirical (PM3) redox potential data. $E_{300,e}$ is the calculated solvated redox potential at 300 K. $E_{0,K}$ is the difference in the calculated redox potentials at 300 K and 0 K, $E_{corr} = E_{300,e} - E_{9,e}$](image)
5-cyanoindole and from these determined the magnitude of the DFT correction terms to be 11.4 meV. This is in comparison to the semi-empirical value of 11.2 meV. The similarity of these values leads us to conclude that this approach gives an order of magnitude estimate of the corrections due to these effects, at a fraction of the computational cost.

In Fig. 5 we have plotted the corrected PM3 and PW91 redox potentials against $\sigma^+$ of the substituents. These data show that both the semi-empirical and DFT redox potentials predict a good correlation between $\sigma^+$ and the redox potential, with the exception of hydroxy, methoxy and amino substituents. They also highlight differences between these calculations, in that PM3 calculations consistently produce $E_{000}^a$ values which are greater than those calculated by PW91, and the gradients of the semi-empirical and DFT lines are different.

In order to quantify which of the calculations is the more accurate, it is necessary to compare these values with experimental data. To do this, it is necessary to obtain standard redox potentials from experimentally determined peak oxidation potentials. The shapes of these peaks are complicated by the coupling reaction at relatively high concentrations, but all monomer oxidation peaks show a shape characteristic of electrochemical reversibility at low concentrations (1 mM or less) as judged by the convenient diagnostic for a Nernstian linear sweep voltammetric (LSV) response ($E_{LSV} - E_{1/2} = 1.09 \frac{RT}{nF} = 59.2 \text{mV at } 25 \degree C$ for a 1-electron redox reaction)26 where $E_{LSV}$ is the LSV peak potential and $E_{1/2}$ is the half wave potential. This indicates that the effect of coupling reactions of the radical cations at the electrode on the measurement of the standard redox potentials, $E^{o}_{298}$, is small at these low concentrations. If we assume as before that the neutral and radical cation species have equal diffusion coefficients in solution, $E_{1/2}$ is equal to the standard redox potential, $E^{o}_{298}$. Fig. 6 shows these experimental values, $E_{298}^{o}$ plotted against the calculated values, $E_{298}^{o}$, for semi-empirical and DFT (PW91) calculations. A good correlation between calculated and experimental data corresponds to a straight line of gradient unity and zero intercept (neglecting the small error introduced by the slight difference in temperature between the two data points).

![Fig. 5](image1)

**Fig. 5** Plot of calculated standard redox potentials, $E_{298}^{o}$, using (A) semi-empirical (PM3), (B) DFT and (C) experimental redox potentials, $E_{298}^{o}$.

![Fig. 7](image2)

**Fig. 7** Spin density distribution mapped onto a 99% electron density isosurface for the radical cations of (a) indole, (b) 5-carboxylic acid indole, (c) 5-aminoindole, (d) 5-hydroxyindole. (The colouring is schematic and is as follows: red indicates a positive spin density, whilst blue is zero. The same range of spin density was used for all four plots.)

![Table 4](image3)

**Table 4** Comparison of method and location of spin density in order of decreasing spin density distribution for indole radical cation

<table>
<thead>
<tr>
<th>Method</th>
<th>Spin density distribution (in order of decreasing spin density)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental</td>
<td>$p$-CIDNP</td>
</tr>
<tr>
<td>Semiempirical</td>
<td>Mulliken</td>
</tr>
<tr>
<td>DFT</td>
<td>Mulliken</td>
</tr>
<tr>
<td>Hybrid</td>
<td>Mulliken</td>
</tr>
<tr>
<td>DFT</td>
<td>Spin density map</td>
</tr>
</tbody>
</table>

* Determined by photochemically induced dynamic nuclear polarisation spectra ($p$-CIDNP)28,30 * Ref. 7. * Density functional theory with the LDA SVWN and the GGAmethod BLYP.28 * Hybrid H-F/DFT (B3LYP).28 * This paper.

sets). It is clear that the DFT data in Fig. 6 fit the experimental data more closely than the semi-empirical data. (This is to be expected, as the DFT quantum chemical method is more rigorous.) It is also highly satisfying that (from Fig. 5) this method is able to predict the oxidation potentials of hydroxy, methoxy and amino substituted indoles more accurately than \( \sigma^+ \) (ref. 3 and Fig. 5). The DFT-calculated oxidation potentials for all 5-substituted indoles predict absolute values within \( \pm 0.1 \) V of the experimental values, which is the approximate error of the DFT method and we have added this notional value of \( \pm 0.1 \) V as error bars to the calculated data on Fig. 6.

Given the close fit of PW91 calculation to experiment, it is informative to look at the calculated variation in electron density in these molecules. Since the coupling reaction involves radical cations, we have concentrated on the electron density of the indole radical cations. Previous work has considered charges derived from a Mulliken population analysis on each atom in the indole molecule. This is an arbitrary scheme for assigning charges, which divides the orbital overlap equally between two atoms involved in a bond and which can lead to unrealistic charges, for example when the bond is polar. Indeed, all such charge partitioning schemes are ultimately arbitrary since the atomic charge, unlike the charge density, is not a quantum mechanical observable and is not unambiguously predicted from first principles. Thus Mulliken population analysis may lead to a distribution far from the actual electronic distribution in the molecule.

As coupling of the radical cations would be expected to occur by pairing of the radical spin from each radical cation to form a bond, we have chosen to calculate the spin density for each indole radical cation. We have mapped this spin density onto the 99% electron density isosurface of the radical cation. This gives us a pictorial representation of the distribution of the spin density (the unpaired electron) in the radical cation. The larger the value of the spin density is at a given point, the more likely bond formation via radical pairing would be as it is at this point where the electronic orbitals of neighbouring radical cations would begin to overlap. Fig. 7 shows representative spin density distributions for four 5-substituted indole radical cations, one with an electron withdrawing substituent (\( \sigma^+ \) greater than zero), the unsubstituted indole radical cation (\( \sigma^+ \) equal to zero) and two with electron donating substituents (\( \sigma^- \) less than zero). It is clear from these (and other) data that all electron withdrawing substituents show similar spin density distribution around the aromatic system, with the greatest spin density being found in the 3-position. This indicates that the spin density distribution is insensitive to the nature of the electron withdrawing substituent. Also, significant spin density is observed around the aromatic system, indicating good conjugation between the aromatic ring and the substituent. Both these observations explain the correlation of the energy of the radical cation (and hence the oxidation potential) with \( \sigma^+ \). In contrast, the electron donating groups show a different distribution, with the most significant spin density being observed in and around the substituent. This is the most likely origin of the deviation of these energies (and the oxidation potentials) from the Hammett relationship. Table 4 presents a comparison of the locations of maximum spin density of our calculated spin density distribution of the indole radical cation and previous determinations. It is interesting that these calculations produce significant differences in the locations of maximum spin density from those calculated previously. This indicates the sensitivity of these systems to the level of calculation and further illustrates the danger of using approximate computational methods. Finally, it is satisfying that in contrast to previous work the locations of maximum spin density predicted by the DFT calculations agree with experimentally measured spin densities.

### Conclusion

The results presented in this paper have shown that DFT calculations on the neutral and radical cationic forms can be used to determine the redox potential for the oxidation of 5-substituted indoles. This means that the effect of changing the nature and location of substituents on the redox potential can be determined. Furthermore, calculations of the spin density of the monomer radical cations give insight into the origins of observed differences in the redox potentials of electron withdrawing and electron donating substituents. There are significant differences in the calculated energies and electronic distributions when compared to those obtained using previous semi-empirical techniques. Even the most recent semi-empirical parameterisation gives an increased error over DFT methods, but this is to some extent counterbalanced by a significant increase in the speed of computation, particularly for large systems. Care must be taken to quantify these errors if semi-empirical methods are to be used for analysis of experimental data. It is interesting to speculate on the effect that the calculated spin density distribution of the indole radical cation has on trimer formation. We have already suggested that the formation of the asymmetric trimer could be achieved by the initial coupling of two monomer radical cations to form a 3-dimer. Further oxidation and coupling of this dimer with a monomer radical cation would then lead to the asymmetric trimer (I) rather than a symmetric trimer. These calculations lend support to this hypothesis, as they confirm that those indoles with electron withdrawing substituents would be expected to couple at the 3 position (the position of maximum radical electron concentration). We have also shown that indoles with electron donating substituents do not readily form asymmetric trimers, unless oxidised on a predeposited film or template of indole trimers with electron withdrawing substituents. This result can now be explained by coupling in solution being due to an alternative mechanism in this case. This would arise from the observed difference in spin density distribution, which would lead to a product different from (I). However, asymmetric trimer formation can occur as adsorption of the radical cations onto a predefined and preoriented template overcomes this problem. We are presently investigating this coupling reaction and the energy, structure and reactivity of (I) by performing calculations. This will be the subject of a future paper.

### Acknowledgements

We thank Enterprise Ireland and the British Council (Grant no BC/99/001) for travel funding and EPSRC for financial support.

### References

The ADF energy differences were calculated relative to the constituent atoms in their ground states, rather than the atomic "fragments" used by default in ADF.

Note that here we are forced to use a DFT calculated value of the FeFc+/Fc oxidation potential as a reference for the semi-empirical calculations. This is clearly not ideal, but having pursued all options, we found no alternative. The MOPAC programme is not parametrised for transition metals. The SPARTAN package, which does include parameters for first row transition metals, does not allow for solvation of these systems.
“Of all the things I have lost, I miss my mind the most.”

*Steve Tyler*