Preparation and characterisation of electrodes modified with iron porphyrins immobilised in a poly(amino acid) matrix

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Controlled reaction of 1-(3-aminopropyl)imidazole with poly(γ-ethyl L-glutamate) leads to conversion of some side-chain ester groups to amides. The functionalised polymer is characterised by ^{1}H NMR spectroscopy. Imidazole complexes have been formed between this functionalised polymer and 5,10,15,20-tetraphenylporphyrin iron(III) chloride and also deuteroporphyrin-IX dimethyl ester iron(III) chloride. Films of the polymer-porphyrin complexes formed on platinum and on tin oxide coated glass show reversible redox activity in acetonitrile and in aqueous electrolytes. Both redox states of iron are characterised as bis-imidazole ligated by their UV–VIS spectra. The influence of the degree of polymerisation of the starting poly(γ-ethyl L-glutamate), the composition of the aqueous electrolyte and the oxidation state of the iron centre on the stability of the hydrogel films towards redox cycling is examined.

Introduction

The deliberate modification of an electrode surface by the immobilisation of electroactive centres on a conducting support continues to be widely investigated.[1,2] In this way, heterogeneous electron transfer can be achieved in a controlled environment. Our group has been interested in the design of modified electrodes based on a poly(amino acid) supporting polymer. Poly(amino acids) are attractive in this respect due to the range of monomeric units available for incorporation and the ability to derivatise these performed polymeric systems with a variety of electroactive groups. This idea was first realised in our reports on the modification of poly(lysine)[3] and poly(ornithine)[4] by the incorporation of 4-nitrobenzoyl groups and of poly(γ-ethyl glutamate)[5] where the side-chain is modified by amide formation with aminomethylferrocene.

Metalloporphyrins are ubiquitous in natural enzyme systems. As a consequence of this biological activity, they have been extensively studied in an effort to elucidate and to mimic their function in enzymes systems.[6] The construction of synthetic systems capable of mimicking the activities of iron porphyrin-containing proteins has been a long sought after goal.[7] Many of the processes that these materials undergo in biological systems require the interconversion of the metalloporphyrin between various oxidation states. There is thus considerable interest in the study of the electrochemistry of simple metalloporphyrins as an aid to understanding the redox activity of the more complex metalloporphyrin-containing proteins and enzymes. Metalloporphyrins are therefore attractive as molecules for the deliberate modification of electrode surfaces. It is hoped that these modified electrodes will display some of the properties associated with porphyrins in a biological environment.

There have been numerous methods reported for the fabrication and subsequent electrochemical characterisation of porphyrin and metalloporphyrin modified electrodes. Many of these studies have focused on the reduction of oxygen in aqueous solution, a process important for fuel cell technology. Early work demonstrated the formation of an adsorbed monolayer of iron or cobalt porphyrins on carbon electrodes which catalysed the reduction of oxygen and hydrogen peroxide.[8] More recently, thiol derivatised cobalt porphyrins have been adsorbed onto gold as orientated monolayers[9] and onto edge plane pyrolytic graphite.[10] A cobalt porphyrin with attached hexacoordinate ruthenium groups can catalyse the reduction of oxygen to water at potentials related to the Ru^{III}/Ru^{II} redox behaviour.[11] Covalent attachment of porphyrins to an electrode surface has been achieved through the hydroxy groups on a superficially oxidised carbon[12] or platinum[13] surface by reaction with an appropriate side chain functional group of the porphyrin. The catalytic reduction of oxygen has also been demonstrated at these modified surfaces.

Other groups have attached porphyrins to a polymer layer coated on the electrode. Physical incorporation into a growing layer of polypyrrole is possible, also porphyrins and metallophyrins containing pyrrole covalently bound to one or more of the *meso*-phenyl groups have been shown to polymerise on oxidation of the pyrrole ring. Derivatives of Fe^{III},[14] Mn^{III}[15] and Co^{II} porphyrins,[16] among others, have been immobilised in this way. The manganese porphyrin modified electrode has been used in the electrocatalytic epoxidation of alkenes,[17] mimicking the action of cytochrome P_{450}. This general methodology may prove a useful alternative[18] to *in vivo* studies of drug metabolism by cytochrome P_{450}.

Polymer supported metalloporphyrins more closely related in design concept to our own have been obtained by the radical polymerisation of an iron tetraphenylporphyrin, modified to contain a 2-methylpropenoyl group. An electrode spin coated with this polymeric material showed the redox behaviour of the Fe^{III}/Fe^{II} system.[19] Copolymerisation of this monomer with *N*-vinylpyrrolidine gave material that could be spin coated onto graphite and where the hydrophilic nature of the pyrrolidone groups ensured sufficient swelling in water that the iron centres gave a reversible redox response. Cyclic voltammetry showed that the iron porphyrin sites in this material were electrocatalytic for the reduction of oxygen in acidic solution.[20]

The efforts of this group have been directed towards the immobilisation of metalloporphyrins in a poly(amino acid) matrix on the electrode surface. This was in an attempt to mimic at the electrode surface, albeit very simply, the biological environment of the metalloporphyrins. Our work has been the subject of a communication in which the spectroelectrochemical UV–VIS and surface-enhanced resonance Raman properties of an iron porphyrin–poly(amino acid) modified electrode were described.[21] This paper will be concerned with the formation of poly(amino acid) supported iron porphyrins which are bis-imidazole ligated, their reversible electrochemical behaviour in both acetonitrile and aqueous electrolytes and characterisation of the iron-centres by UV–VIS spectroelectrochemical methods. In a later paper we will characterise these materials further by resonance Raman spectroscopy.

Results and discussion

Synthesis of polymer supported iron porphyrins

The fabrication of the polymeric support involved the synthesis of a poly(amino acid) which could be further derivatised with suitable ligands capable of co-ordination to metalloporphyrins. Poly(γ-ethyl L-glutamate) (PEG) can be derivatised *via* aminolysis of the γ-ester group. This reaction has been previously used to functionalise the same polymer with an aminoferrocene derivative.[5] In the present work, aminoimidazole derivatives have been utilised for this functionalisation process. Imidazole ligands are known to co-ordinate strongly with iron porphyrins and in many natural enzyme and protein systems, iron porphyrins are immobilised *via* co-ordination to the imidazole nucleus of a histidine amino acid residue.

Synthesis of poly(γ-ethyl L-glutamate). The most common method for the synthesis of poly(amino acids) involves reaction of the amino acid with phosgene to form the corresponding oxazolidine-2,5-dione, which can be polymerised with loss of carbon dioxide using a range of catalysts. Using this route, a range of poly(γ-ethyl L-glutamate) polymers, differing in molecular weight, have been prepared by modification of the conditions originally reported by Hanby *et al.*[22] After esterification at the 5-carboxylic acid function in glutamic acid, it was convenient to keep the monoester in the form of the hydrochloride salt. Conversion to the 4-(2-ethoxycarbonylethyl)oxazolidine-2,5-dione was achieved by treatment of the γ-ethyl L-glutamate hydrochloride with excess phosgene in dioxane.[23] Reaction of this *N*-carboxy anhydride in dioxane with a catalytic amount of sodium hydride readily afforded poly(γ-ethyl L-glutamate). Sodium hydride has been shown to initiate polymerisation of a number of amino acid *N*-carboxy anhydrides.[24] The polymerisation proceeds by an active monomer mechanism and previous work has suggested that dioxane is a good solvent for this type of polymerisation.[25]

For the purposes of the present study, two samples of poly(γ-ethyl L-glutamate) were prepared having M_v = 13 800 and 120 000 respectively, determined from viscosity measurements in dichloroacetic acid and using the Mark–Houwink relationship established for poly(γ-benzyl L-glutamate).[26] These polymers are designated PED(*l*) and PEG(*h*) respectively. Both samples were prepared from the same batch of *N*-carboxy anhydride using the same ratio of monomer to initiator. The sample of higher M_v was produced from a solution that had been purged with nitrogen both before and during the polymerisation. In general, higher M_v values were found from reactions under nitrogen. Although not investigated any further, a gaseous impurity in the reaction mixture is clearly deleterious to the polymerisation.

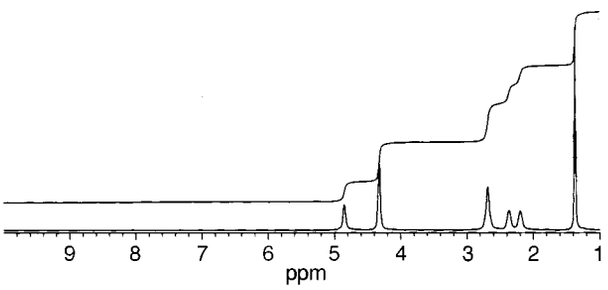
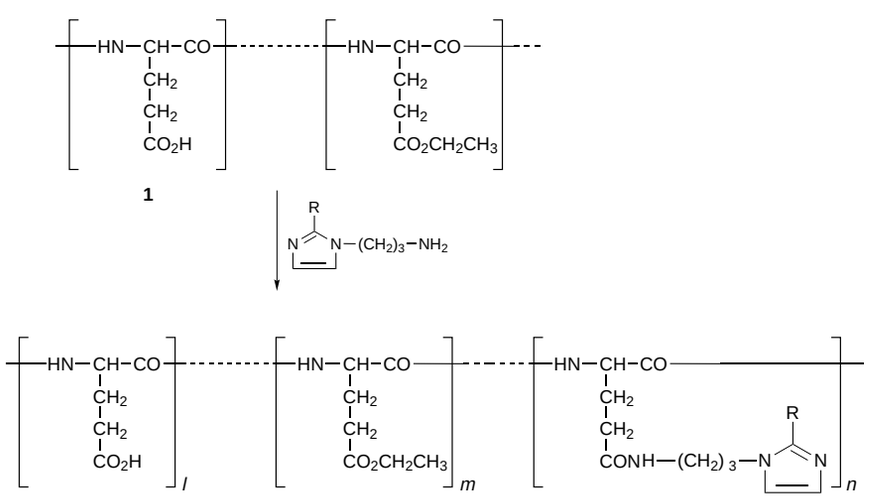


Fig. 1 ^{1}H NMR spectrum of poly(γ-ethyl L-glutamate) recorded in [^{2}H]trifluoracetic acid

^{1}H NMR data for all batches of poly(γ-ethyl L-glutamate), regardless of molecular weight, were identical. Analysis of the ^{1}H NMR spectra from our samples showed that if carboxylic acid groups did exist as a consequence of some ester hydrolysis, their presence accounted for <2% of total structural sub-units in the poly(γ-ethyl L-glutamate) for all samples examined. The analysis was based on a comparison of the integration from the α-CH (δ 4.84) peak, with the peaks due to OCH_2CH_3 (δ 4.32); a typical spectrum is given in Fig. 1.

Imidazole functionalisation of poly(γ-ethyl L-glutamate). The next stage in the synthesis of a suitable polymer involved the introduction of imidazole functionalised groups on the parent structure. These would be capable of co-ordination to metalloporphyrins. The general reaction for the functionalisation of poly(γ-ethyl L-glutamate) is shown in Scheme 1. Poly(γ-ethyl L-glutamate) is illustrated as a co-polymer in which the acidic side groups account for <2% of the total structural sub-units. The reaction involved heating a solution of PEG in the pure aminoimidazole derivative for a period of time. For the imidazole derivatives shown, replacement of approximately 2% of the ester groups with the pendant imidazole arms occurred for every two hours of reaction time at 80 °C using the neat amine solvent. The imidazole functionalised polymers are designated PEG(*l*)-IM and PEG(*h*)-IM respectively. High molecular weight poly(γ-ethyl L-glutamate) was also functionalised with 1-(3-aminopropyl)-2-methylimidazole. The product polymer is designated PEG(*h*)-MeIM.

^{1}H NMR data were used to determine the relative proportions (*l*, *m* and *n* in Scheme 1) of the three sub-units in these functionalised polymers. Results are given in Table 1. Fig. 2 shows the ^{1}H NMR spectrum, in deuterated trifluoracetic acid, of PEG(*h*) functionalised by aminolysis in neat 1-(3-amino-



2a, R = H; **2b,** R = Me

Scheme 1 Modification of poly(γ-ethyl L-glutamate)

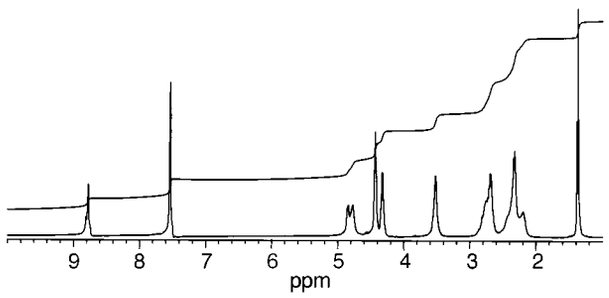


Fig. 2 ^{1}H NMR spectrum of poly(γ-ethyl L-glutamate) doped with 1-(3-aminopropyl)imidazole, recorded in [^{2}H]trifluoracetic acid

Table 1 Composition, determined by ^{1}H NMR spectroscopy, of the functionalised polymers derived from poly(γ-ethyl L-glutamate). Viscosity measurements on the polymers prior to functionalization gave: M_v for PEG(*h*) = 127 900; M_v for PEG(*l*) = 13 400; M_v for PEG = 22 100

	Side-chains (%)		
Polymer	Imidazole	Ester	Acid
PEG(*h*)-IM	60	34	6
PEG(*l*)-IM	50	46	4
PEG-MeIM	35	61	4

propyl)imidazole. The signal at δ 1.37 is due to the ester CH_3 group (subunit *m*), signals at δ 3.52 and 4.43 are each due to CH_2 groups in the imidazole side-chain (subunit *n*), while the signal at δ 2.6–2.9 is due to CH_2 groups adjacent to carbonyl functions (subunits *l*, *m* and *n*). Integration of these signals and taking appropriate ratios gave *m* and *n* expressed as a percentage of ($l + m + n$). The value of *l* was obtained by taking $l + m + n = 100$. Analysis of the spectra of the functionalised polymers revealed that some ester hydrolysis as well as aminolysis had occurred. Under the reaction conditions finally adopted, the amount of ester hydrolysis was small and accounted for the presence of <6% of glutamic acid structural subunits in the modified polymers. A decrease in the viscosity of the polymer solutions after the aminolysis reaction was also noted. This is thought to be a result of main chain scission in the presence of the amines. Other workers have also observed main chain scission of poly(γ-methyl L-glutamate) in the presence of primary amines.[27] In some preliminary experiments where *N*,*N*-dimethylformamide was used as a co-solvent much more hydrolysis was detected. Ester hydrolysis has been previously noted by other workers during the aminolysis of poly(γ-methyl L-glutamate) in the presence of anhydrous[28] and aqueous amines.[29] High temperatures and high water content in these reaction mixtures have been shown to favour ester hydrolysis.

The composition of polymers used in this study are listed in Table 1. No attempt has been made to calculate the molecular weight of the functionalised polymers after aminolysis because the structure had departed considerably from the model of poly(γ-benzyl L-glutamate) used in the Mark–Houwink equation for the determination of the molecular weight of poly(γ-ethyl L-glutamate). However, the electrochemical results achieved using modified electrodes prepared from these polymers suggest that absolute differences in the molecular weight of the functionalised polymers are maintained in the same relative order as for the poly(γ-ethyl L-glutamate) starting material.

Preparation of iron porphyrin loaded poly(amino acid) films on electrode surfaces. The metalloporphyrin loaded poly(amino acid) electrode films were prepared *via* a novel method of spray coating. Pre-heated electrode surfaces were sprayed with a solution containing both the functionalised polymer and the metalloporphyrin, from an air brush connected to a compressor.

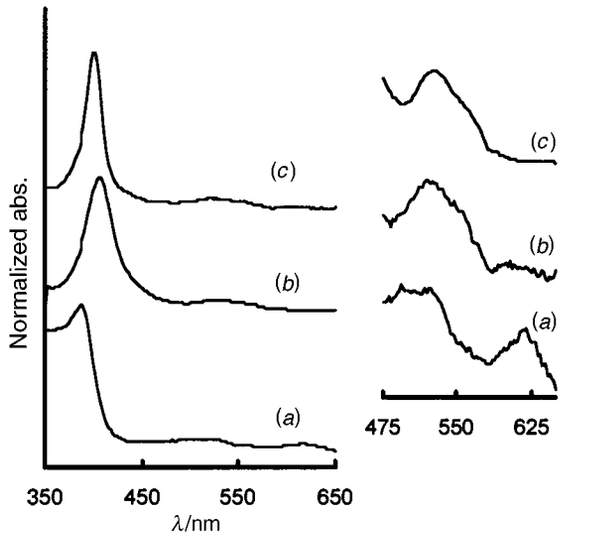


Fig. 3 UV–VIS spectra obtained from a solution of PEG(*h*)-IM (1.0% w/v) and Fe^{III}DPMe chloride (0.2% w/v) in hexafluoropropan-2-ol–dichloromethane (1 : 2 v/v). The system has a five-fold excess of imidazole units over iron porphyrin centres. (*a*) Solution between two glass slides. (*b*) Film deposited onto tin oxide by spray coating from the same solution. (*c*) UV–VIS spectrum of a solution of $[Fe^{III}(DPMe)(IM)_2]^+$ in chloroform. The inset has modified scales so as to display better the absorption between 475 and 625 nm.

This spray coating technique necessitates the use of a low boiling point solvent such that when the sprayed solution hits the moderately heated electrode surface, the solvent readily evaporates, depositing a film of the functionalised poly(amino acid) and iron porphyrin. A solvent mixture of 1,1,1,3,3,3-hexafluoropropan-2-ol and dichloromethane (1 : 2 v/v) was usually used. Hexafluoropropan-2-ol readily dissolved the polymer while dichloromethane ensured complete solubilisation of the iron porphyrin. Solutions were made so as to contain 1% w/v of the functionalised polymer. The amount of the iron porphyrin was varied but was usually in the range of 0.2–0.5% w/v. In all cases quantities were calculated so as to have more than a two-fold molar ratio of imidazole groups (polymer bound) to metalloporphyrin. Thickness was controlled so that the films continued to transmit light at the wavelength of maximum absorption. Optical microscopy showed the absence of any macroscopic pin holes in these films.

Characterisation of the ligand state of iron in the porphyrin loaded PEG-IM films under ambient conditions

In separate experiments, iron(III) tetraphenylporphyrin (FeTPP) and iron(III) deuteroporphyrin IX dimethyl ester (FeDPMe) were examined in the presence of a five-fold excess of polymer bound imidazole ligand. The series of UV–VIS spectra obtained with Fe^{III}DPMe are illustrated in Fig. 3. The spectrum of the film [Soret, 404 nm; Q bands, 526 and 558 (sh) nm] closely resembles that reported[30] for low spin bis-imidazole ligated Fe^{III}DPMe in chloroform (Soret 403 nm; Q bands, 528 and 558 nm) and is distinct from the spectrum of the undiluted solution (Soret, 386 nm; Q bands, 496 and 520 nm) used in the spray coating procedure. In the film the iron centre is predominately bis-imidazole ligated.

The related series of experiments using an Fe^{III}TPP loaded PEG(*h*)-IM electrode film indicates that the iron centre is also predominantly bis-imidazole ligated in the polymer film since the spectrum (Soret, 422 nm; Q band, 554 nm) is similar to that recorded in the literature for a solution of bis-imidazole ligated Fe^{III}TPP in chloroform (Soret, 417 nm; Q bands, 548 and 579 nm).[31] Again, the spray solution showed a distinct spectrum (Soret, 408 nm; Q band, 500 nm).

The above spectra obtained from solutions in hexafluoropropan-2-ol–dichloromethane were found to be identical to

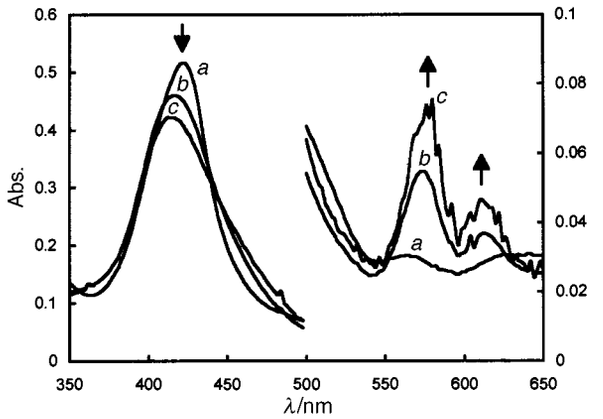


Fig. 4 Evolution with time of the UV–VIS spectrum from a film spray coated onto tin oxide from a solution of PEG-MeIM (1.0% w/v) and Fe^{III}TPP chloride (0.1% w/v) in hexafluoropropan-2-ol–dichloromethane (1 : 2 v/v). The system has a 10-fold excess of imidazole units over iron porphyrin centres. The film was immersed in water and spectra recorded after (*a*) zero time, (*b*) 10 and (*c*) 20 min. Between 500 and 650 nm, the ordinate has been expanded six-fold.

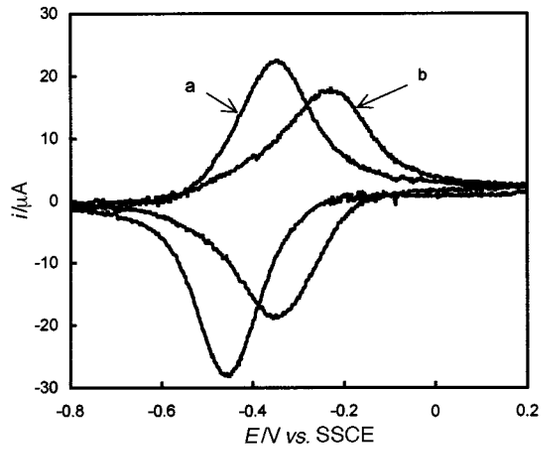


Fig. 5 Cyclic voltammetry of a tin oxide electrode, spray coated with a solution of PEG(*h*)-IM (1.0% w/v) and Fe^{III}DPMe chloride (0.3% w/v) in hexafluoropropan-2-ol–dichloromethane (1 : 2 v/v). The system has a seven-fold excess of imidazole groups over iron porphyrin centres. Curve (*a*) shows the response in 0.1 M aqueous lithium perchlorate; curve (*b*) shows the response in 0.1 M aqueous sodium chloride; scan rate 10 mV s^{-1}.

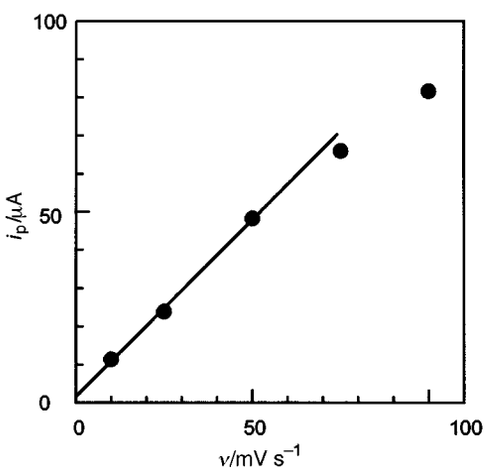


Fig. 6 Cathodic peak response *versus* scan rate (*v*) for a tin oxide electrode, spray coated with a solution of PEG(*h*)-IM (1.0% w/v) and Fe^{III}DPMe chloride (0.3% w/v). The system has a seven-fold excess of imidazole groups over iron porphyrin centres. The electrode was immersed in 0.1 M aqueous lithium perchlorate.

spectra of the porphyrin in the same solvent mixture containing 1 molar equivalent of 1-methylimidazole. Thus monoimidazole ligation is the most likely state for the iron porphyrins in the spray solutions used. The observation of a monoimidazole ligated iron porphyrin species in organic solvents is rare[32] and in this instance seems to be associated with the presence of hexafluoropropan-2-ol since by contrast in chloroform, the addition of aliquots of 1-methylimidazole to either porphyrin followed by spectroscopy showed the formation of low spin bis-imidazole ligated iron(III) porphyrin without evidence for the intermediate monoimidazole species. This reflects the normal situation in organic solvents where there is a larger binding constant for the second imidazole over the first. The mono-imidazole ligated iron(III) porphyrin is high spin and the bis-ligated complex is low spin[32] and a change in spin state is generally accepted as the driving force leading to bis-ligation. In our experiments where solutions are sprayed onto the electrode surface, binding of the second imidazole ligand to the iron porphyrin occurs after evaporation of hexafluoropropan-2-ol.

Characterisation of iron porphyrin loaded PEG-MeIM films under ambient conditions. The PEG-MeIM polymer was prepared in order to have the 2-substituted imidazole as a potential and strongly hindered ligand. However the porphyrin loaded films were not stable and exhibited spectral changes over a period of 24 h in the ambient atmosphere of the laboratory. This sequence of changes occurred more rapidly when the film was immersed in water and is illustrated for Fe^{III}TPP in Fig. 4. The initial spectrum is broad with ill-defined long wavelength bands. The final spectrum is identical with that reported[33] for the μ-oxo dimer of FeTPP.

The behaviour reported for iron(III) tetraphenylporphyrin in the presence of 2-methylimidazole may explain the instability of these films. The iron centre is predominantly low spin in solution and predominantly high spin in the solid state.[34] From analysis of the solid state structure it has been suggested that the steric hindrance between the atoms of the axial ligand and the porphyrinato core does not permit attainment of the short axial bonds required to achieve a low spin state. We suggest therefore that the inability to form a strongly ligated low spin bis-imidazole ligated species in the PEG-MeIM matrix is a result of steric factors associated with the imidazole ligand and the rigidity of the polymer matrix.

Spectroelectrochemical and redox properties of iron porphyrin–poly(amino acid) modified electrodes

No electroactivity was evident for the iron porphyrin loaded PEG-MeIM electrode films where the iron centres are present as μ-oxo dimers. The PEG-IM iron porphyrin modified electrodes show extensive redox behaviour which has been examined in both aqueous and acetonitrile solution. Reversible redox behaviour was observed during cyclic voltammetry in acetonitrile with tetraethylammonium perchlorate as supporting electrolyte and no further comment will be made on experiments in this solvent. For a given film and at the same scan rate, the addition of water to the electrolyte solution increased the area under the redox response. We have concentrated on exploiting the hydrogel nature of these polymers which allows electrochemistry of the water insoluble porphyrins in an aqueous environment.

All films of thickness suitable for spectroelectrochemical experiments showed stable redox behaviour with aqueous sodium or lithium perchlorate as the supporting electrolyte. Films in the high molecular weight matrix again showed stable redox behaviour in the presence of sodium, lithium, potassium or guanidinium chlorides but with less negative peak potentials than in the presence of perchlorate (see Fig. 5). Changing the supporting electrolyte switched between the two cyclic voltammetry responses. The cathodic peak height for these responses varies in a linear fashion with scan rate (*v*) up to 50 mV s^{-1} (see Fig. 6), indicating that at low scan rates the concentration of

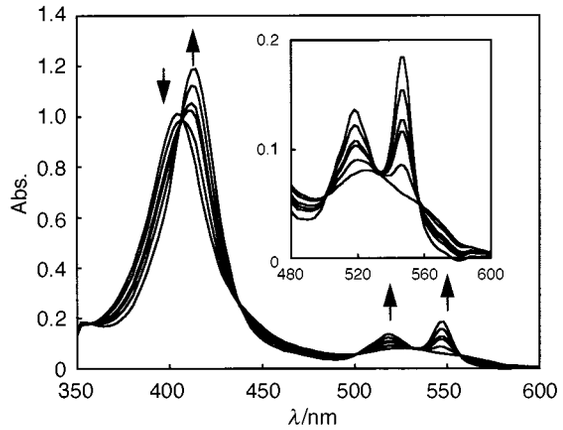


Fig. 7 UV–VIS spectrum of FeDPMe loaded PEG(*h*)-IM film on a tin oxide electrode as a function of applied potential. The film was spray coated from a solution of PEG(*h*)-IM (1.0% w/v) and Fe^{III}DPMe chloride (0.2% w/v) in hexafluoropropan-2-ol–dichloromethane (1 : 2 v/v), then immersed in 0.1 M aqueous $LiClO_4$. The system has a five-fold excess of imidazole groups over iron porphyrin centres. Arrows show the direction of spectral changes on application of increasingly negative potentials of 0, −0.35, −0.39, −0.41, −0.55 and −0.90 V *vs.* SSCE. Inset shows an expansion of the long wavelength region.

Table 2 Electrochemical parameters, determined by slow scan (10 V s^{-1}) cyclic voltammetry, of porphyrin loaded PEG(*h*)-IM spray coated onto a tin oxide surface and immersed in aqueous electrolyte

Porphyrin	Electrolyte/ 0.1 M	$E°$/V *vs.* SSCE[a]	ΔE_p/ mV[b]	Γ/mol cm^{-2}
Fe^{III}TPP	$LiClO_4$	−0.28	130	2.3×10^{-8}
	LiCl	−0.14	140	2.4×10^{-8}
Fe^{III}DPMe	$LiClO_4$	−0.41	110	2.3×10^{-8}
	LiCl	−0.29	120	2.1×10^{-8}

[a] Average of anodic and cathodic peak potentials. [b] Anodic to cathodic peak separation.

reduced species remains uniform across the film. Integration under the cathodic branch of the voltammograms obtained at 10 mV s^{-1} gave values for the surface coverage (Γ) of iron(III) porphyrin given in Table 2 together with redox potentials [$=\frac{1}{2}(E_{pc} - E_{pa})$]. For an ideal thin film $E_{pc} = E_{pa}$ but the literature indicates that non-zero peak splitting for redox polymer modified electrodes is a normal observation.[1] Spectroelectrochemical UV–VIS studies showed that the iron(II) states are also bis-imidazole ligated. Thus the spectrum of the electrochemically prepared Fe^{II}DPMe species (Soret 414 nm; Q bands, 518 and 546 nm) is the same in the presence of either perchlorate or chloride ion and agrees well with the reported spectrum of bis-imidazole ligated low spin Fe^{II}DPMe in chloroform (Soret 413 nm; Q bands, 518 and 546 nm).[30] The spectral changes recorded as a function of applied potential (Fig. 7) show isosbestic points at 406, 436, 500 and 518 nm, indicating the presence of only two absorbing species in the matrix. Construction of a Nernst plot [$E_{applied}$ *vs.* $\log_{10}(Abs_{red}/Abs_{ox})$] yielded a straight line with a slope of 78 mV (Fig. 8). The theoretical value for a one electron process is 59 mV. Similar non-characteristic Nernstian slope values have been observed for other polymer modified electrodes and have been attributed to interactions between neighbouring redox units in the densely populated matrix of the redox polymer modified electrode.[35] Films containing FeDPP in a PEG(*h*)-IM matrix were also reduced to bis-imidazole ligated low spin iron(II) species in the presence of either the perchlorate or chloride ion.

This dependence of the operational formal potential on the electrolyte anion must be connected with the hydration state of this anion within the matrix. An earlier proposal[36] that this dependence is due to changes in the ligation state of the iron centre does not agree with these spectroscopic observations. A

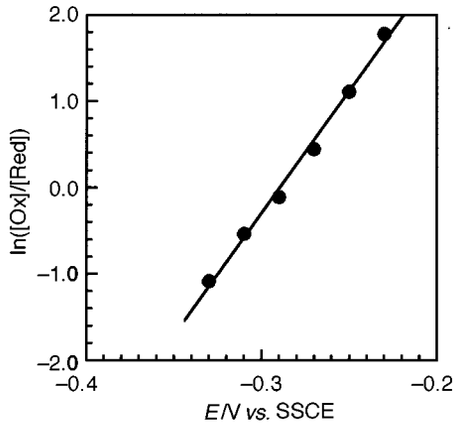


Fig. 8 Nernst plot for the Fe^{III}/Fe^{II}DPMe redox couple immobilised in the PEG-IM matrix and immersed in 0.1 M aqueous $LiClO_4$. Concentrations of the oxidised and reduced forms are obtained from spectra some of which are illustrated in Fig. 7.

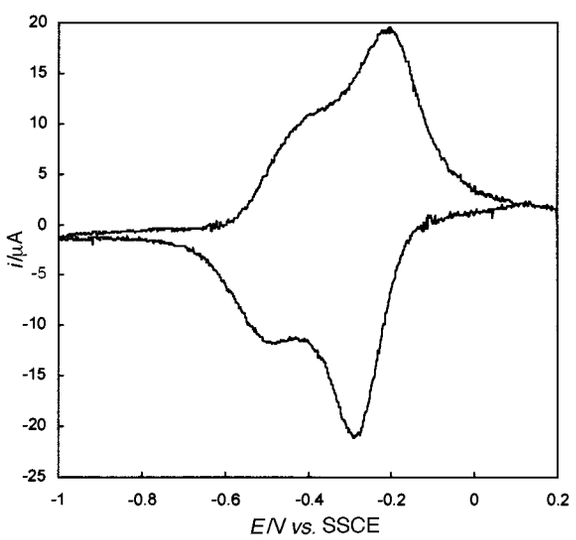


Fig. 9 Cyclic voltammetry of a tin oxide electrode spray coated with a solution of PEG(*l*)-IM (1.0% w/v) and Fe^{III}DPMe chloride (0.3% w/v) in hexafluoropropan-2-ol–dichloromethane (1 : 2 v/v). The system has a six-fold excess of imidazole groups over iron porphyrin centres. Electrolyte: 0.1 M aqueous LiCl; scan rate: 5 mV s^{-1}.

related situation is found in poly(vinylpyridine) redox films where it has been shown by luminescence[37] and electrochemical quartz microbalance[38] techniques that perchlorate, unlike other anions, enters the polymer matrix with no attached hydration sphere. In our films, the non-hydrated perchlorate ion is better able to stabilise the positively charged iron(III) porphyrin compared to the hydrated chloride ion and gives rise to a more cathodic redox response from the iron centre.

Films containing porphyrins supported in a PEG(*l*)-IM matrix showed related but more complicated behaviour in chloride or fluoride ion electrolytes. For the FeDPMe loaded film, the initial cyclic voltammogram (Fig. 9) showed the presence of two redox couples with $E° = -0.22$ and −0.40 V *vs.* sodium chloride saturated calomel electrode (SSCE). The more anodic redox couple is identical to that observed for FeDPMe in a PEG(*h*)-IM matrix and with chloride counter ion. The relative wave heights for the two redox couples was dependent upon the time length for immersion of the Fe^{III} state in the chloride or fluoride electrolyte and eventually the redox couple became broad and ill defined. Reduction of the film at −0.8 V *vs.* SSCE for 5 min and then repetition of the cyclic voltammetry resulted in the reappearance of the two redox couples shown by the virgin film. These results clearly show the importance of specimen pre-history on the redox response of a

polymer modified electrode and this has been emphasised by other workers.[39] Related behaviour was seen for FeTPP films.

The more cathodic redox couple is due to porphyrins that are no longer bis-imidazole ligated and highly aggregated. These states arise by rupture of imidazole–iron porphyrin bonds upon swelling of the polymer matrix due to the ingress of hydrated chloride or fluoride ions. Since perchlorate ions are less hydrated their presence does not distort the matrix.

Pertinent to our work, a difference in behaviour in the presence of either perchlorate or hydrated ions has been noted for other redox polymer modified electrodes.[37,38,40] Also, Bettelheim observed two reversible redox couples for electropolymerised iron *meso*-tetra(aminophenyl)porphyrin on carbon in aqueous acidic electrolytes.[41] The effect was attributed to monomeric and associated porphyrin sites in the film with the more anodic couple attributed to the monomeric porphyrin. Multiple redox couples have also been observed for electropolymerised cobalt porphyrins on graphite electrodes,[42] and interaction of the surface contact cobalt porphyrins with functional groups present on the graphite surface was believed to be the primary reason.

Further papers will characterise these films by Raman spectroscopy and look at their behaviour in the presence of oxygen and carbon monoxide.

Experimental

General

IR spectra were recorded on a Perkin-Elmer 983G spectrometer, linked to a Perkin-Elmer 3700 Data Station for spectral storage and manipulation, FTIR spectra on a Perkin-Elmer 1720X spectrometer and solution UV–VIS spectra on a Perkin-Elmer Lambda 9 spectrometer. ^{1}H NMR spectra were recorded at 300 or 500 MHz using a General Electric QE300 or a GN Ω-500 instrument respectively. *J* Values are given in Hz. Polymers were examined in deuterated trifluoroacetic acid ([^{2}H]TFA) with tetramethylsilane as external standard. Monomers were examined in the usual way with tetramethylsilane as internal standard.

Electrochemical data were obtained using a PAR 173 potentiostat, interfaced with an IBM computer. Spectroelectrochemical UV–VIS experiments were performed using a standard three electrode system placed within the cuvette holder of a Hewlett-Packard 8452(A) diode array spectrophotometer with a resolution of ±2 nm. All potentials quoted are with reference to the sodium chloride saturated calomel electrode (SSCE) unless otherwise stated. A Paasche model VJR#1 air brush, connected to a compressor operating at 15 psi, was used to coat electrode surfaces with a polymer film.

During reactions with phosgene, the excess was destroyed by bubbling through sodium hydroxide solution before venting to the atmosphere.

Syntheses

γ-Ethyl L-glutamate hydrochloride. Glutamic acid (40 g) was added to a solution of dry hydrogen chloride (24.0 g) in dry ethanol (200 ml) at 0 °C, shaken vigorously and the mixture allowed to warm up to room temperature over 5 h when the suspended solid gradually dissolved. The ethanol was removed under reduced pressure to yield a viscous yellow oil which dissolved in diethyl ether (100 ml) to form a cloudy solution. On standing at 0 °C for 12 h, the solution deposited γ-ethyl L-glutamate hydrochloride as a colourless microcrystalline powder (26.0 g, 44%), mp 134–135 °C (lit.[22] mp 134–135 °C) (Found: C, 39.9; H, 7.0; N, 6.5. Calc. for $C_7H_{13}ClNO_3$: C, 39.7; H, 6.7; N, 6.6%); δ_H([$^2H_6$]DMSO) 1.19 (3H, t, *J* 7, OCH_2CH_3), 2.06 (2H, m, CH_2), 2.47 (2H, t, *J* 7, CH_2), 3.91 (1H, t, *J* 6, CH), 4.07 (2H, q, *J* 7, OCH_2CH_3), 8.50 (3H, br, NH_3).

4-(2-Ethoxycarbonylethyl)oxazolidine-2,5-dione. Phosgene was passed for 10 min into a suspension of γ-ethyl L-glutamate hydrochloride (10.0 g) in dioxane (140 ml) at 0 °C. The mixture was slowly warmed to 50 °C over a period of 1 h, during which time the solid dissolved. Unchanged phosgene was removed at 50 °C by passing through the mixture a steam of dry nitrogen for 20 min. Removal of dioxane under reduced pressure gave a viscous oil which was diluted with chloroform (70 ml). Addition of hexane (40 ml) afforded a cloudy solution which was kept at 0 °C for 12 h to yield 4-(2-ethoxycarbonylethyl)-oxazolidine-2,5-dione as colourless cubes. The product was recrystallised from chloroform–hexane as cubes (8.35 g, 87.6%), mp 70–71 °C (lit.[22] mp 71 °C) (Found: C, 47.8; H, 5.6; N, 7.1. Calc. for $C_8H_{11}NO_5$: C, 47.8; H, 5.5; N, 7.0%); $\delta_H(CDCl_3)$ 1.28 (3H, t, *J* 7, OCH_2CH_3), 2.17 (1H, m, $CHCH_aH_b$), 2.37 (1H, m, $CHCH_aH_b$), 4.17 (2H, q, *J* 7.2, OCH_2CH_3), 4.40 (1H, t, *J* 6, $CHCH_2$), 5.53 (1H, br, NH).

1-(3-Aminopropyl)-2-methylimidazole. This compound was prepared by the literature method[43] and distilled as a colourless oil, bp 96–100 °C at 0.01 mmHg; $\delta_H(CDCl_3)$ 1.85 (2H, m), 2.39 (3H, s), 2.73 (2H, t, *J* 6), 3.94 (2H, t, *J* 6), 6.83 (1H, s, Im*H*), 6.91 (1H, s, Im*H*).

Deuteroporphyrin IX dimethyl ester iron(III) chloride.[44] Hemin (3.0 g) was intimately mixed with resorcinol (9.0 g) and the mixture heated at 155 °C under an air condenser for 45 min. The reaction mixture was washed with ethyl acetate until the extracts were colourless, leaving crude deuteroporphyrin IX iron(III) chloride. This material (2.0 g) was dissolved in methanol (175 ml) containing sulfuric acid (10 g) and left at room temperature for 18 h. Addition of water (200 ml) precipitated the porphyrin ester which was extracted into chloroform. The chloroform extract was washed with ammonia (2 M), sodium hydroxide (1 M) and finally water to convert the product to the μ-oxo dimer form. The chloroform solution was then concentrated to 100 ml and applied directly to a column (1 ft × 2 in) of neutral alumina (Brockmann grade IV). Elution with chloroform afforded first the free base porphyrin followed by the μ-oxo dimer. The μ-oxo dimer-containing solution was evaporated to 10 ml and hydrogen chloride gas passed through for 2 min followed by a stream of nitrogen for 5 min to remove excess hydrogen chloride. The chloroform solution was then allowed to evaporate slowly over 2 days to yield deuteroporphyrin IX dimethylester iron(III) chloride as dark violet crystals (1.4 g, 60.2%), mp 242–244 °C (Found: C, 60.8; H, 5.1; N, 8.5. Calc. for $C_{32}H_{32}ClFeN_4O_4$: C, 61.2; H, 5.1; N, 8.9%).

5,10,15,20-Tetraphenylporphyrin iron(III) chloride.[45] Tetraphenylporphyrin (1.0 g) was dissolved in dimethylacetamide (100 ml) and the solution brought to a gentle reflux. Iron(II) chloride tetrahydrate (800 mg) was added and refluxing continued until the UV–VIS spectrum of a small aliquot showed complete insertion of the iron (10 min). Water (100 ml) was then added and the precipitated product collected by filtration and washed with water until the extracts were colourless. The dried precipitate was dissolved in chloroform (100 ml) and applied to a column (6 in × 1 in) of neutral alumina (Brockmann grade IV). Elution with chloroform recovered the product which moved rapidly off the column, to be followed by a small red band of the unconverted free base porphyrin. This solution of the iron porphyrin in chloroform was concentrated to (40 ml) and saturated with hydrogen chloride gas to ensure conversion to the iron porphyrin chloride. Nitrogen was passed through for 5 min after which the solution was allowed to evaporate over a period of 2 days yielding 5,10,15,20-tetraphenylporphyrin iron(III) chloride as deep violet crystals (0.92 g, 80.3%) (Found: C, 74.7; H, 4.2; N, 7.7. Calc. for $C_{44}H_{28}ClFeN_4$: C, 75.1; H, 4.01; N, 8.0%).

Poly(γ-ethyl L-glutamate) and doping with 1-(3-aminopropyl)imidazole. (*a*) 4-(2-Ethoxycarbonylethyl)oxazolidine-2,5-dione (3.0 g) was dissolved in dioxane (60 ml) and sodium hydride (60% in oil, 0.04 g), previously washed with hexane, was added. The flask was stoppered and the solution stirred for 3 days. Samples were taken at intervals and the extent of reaction monitored by disappearance in the IR spectrum of the charac-

teristic oxazolidinedione bands at 1780 and 1698 cm^{-1}. The reaction volume was reduced to 20 ml and the polymer precipitated by pouring into diethyl ether (250 ml). The polymer was collected as a colourless powder (1.4 g, 71%), M_v 13 400.

1-(3-Aminopropyl)imidazole (1.0 ml) was added to the above polymer (0.3 g). The suspension was heated at 80 °C with stirring and after 15 min the polymer had dissolved. Heating was continued for a total time of 24 h. The solution was allowed to cool to room temperature when diethyl ether (8 ml) was added with stirring, causing the polymer to precipitate. The solution was decanted, and the polymer washed with more diethyl ether (8 ml). After decanting the supernatant liquid, the process was repeated four times. Finally, the polymer was collected by gravity filtration on silicone treated filter paper, and washed well with diethyl ether. The polymer was air dried for 10 min then transferred to a small flask and swelled with ethanol (1 ml) to a soft gel. Diethyl ether (5.0 ml) was added to re-precipitate the polymer which was collected by gravity filtration. The dissolution and precipitation process with ethanol/diethyl ether was repeated up to five times after which the polymer was dried *in vacuo* at room temperature for 24 h. ^{1}H NMR spectra of the polymer in trifluoroacetic acid were used to estimate the extent of replacement of the ester groups with the imidazole functionalised arms, and to ensure that no unreacted imidazole derivative was trapped in the polymer matrix. Unreacted 1-(3-aminopropyl)imidazole was indicated by a sharp triplet at δ 4.54 (CH_2IM). If necessary, the dissolution in ethanol and precipitation with diethyl ether was repeated. This process yielded PEG(*l*)-IM as a pale yellow amorphous powder (0.2 g) (Found by ^{1}H NMR spectroscopy: ratio of $l:m:n = 4:46:50$).

(*b*) 4-(2-Ethoxycarbonylethyl)oxazolidine-2,5-dione (4.0 g) was dissolved in dioxane (60 ml) and nitrogen passed through the solution for 40 min. Sodium hydride (60% in oil, 0.12 g) was washed with hexane and added to the dioxane solution, nitrogen being passed during the course of the reaction. After 4 h, the IR spectrum of a small aliquot from the extremely viscous solution showed the absence of any characteristic oxazolidinedione peaks. The solution was poured into hexane (600 ml) and the fibrous polymer precipitated. The product was collected by gravity filtration, washed well with diethyl ether and dried *in vacuo* at 40 °C for 12 h to yield the polymer as a fibrous mass (3.11 g; 99%) (Found: C, 53.4; H, 6.5; N, 8.6. Calc. for $C_7H_{11}NO_3$: C, 53.5; H, 7.1; N, 8.9%); ν_{CO}(film cast onto KBr disc, solvent removed *in vacuo*)/cm^{-1} 1549, 1656, 1734; δ_H([^{2}H]TFA) 1.37 (3H, t, *J* 7.2, OCH_2CH_3), 2.17 (1H, br, $CHCH_aH_bCH_2$), 2.37 (1H, br, $CHCH_aH_bCH_2$), 2.67 (2H, br, CH_2CO), 4.32 (2H, q, *J* 7.2, OCH_2CH_3), 4.84 (1H, br, HNC*H*CO); M_v = 12 790.

The above polymer (0.3 g) was cooled in liquid nitrogen and powdered with a glass rod. It was suspended in 1-(3-aminopropyl)imidazole (3.0 ml) and heated at 85 °C for 60 h. The resulting solution polymer was cooled to room temperature and diluted with diethyl ether (8 ml) when the polymer precipitated as a gel. The supernatant liquid was decanted and the residue washed three times with diethyl ether (8 ml). This process was repeated using small volumes of a mixture of diethyl ether (95 ml) and methanol (5 ml) until the ^{1}H NMR spectrum showed the absence of unreacted imidazole and the polymer, PEG(*h*)-IM, formed a pale yellow powder (0.28 g) (Found by ^{1}H NMR spectroscopy: ratio $l:m:n = 6:34:60$).

Characterisation of the polymers

Specific viscosity [η_{sp}] of the polymer solutions at various concentrations (*c*) in dichloroacetic acid was measured using an Ubbelhode viscometer. The intercept of a graph of [η_{sp}/c] *vs.* *c* gave the intrinsic viscosity [η]. The intrinsic viscosity is related to the molecular weight (M_v) of poly(γ-ethyl L-glutamate) by the appropriate Mark–Houwink equation.[26]

The ^{1}H NMR spectra of imidazole doped polymers in [^{2}H]-trifluoroacetic acid were used to determine relative values of ($l + m + n$) and of *m* and *n*. Percentage values for *l*, *m* and *n* were calculated on the basis of $l + m + n = 100$. Spectral assignments for PEG-IM are as follows: δ_H 1.37 [t, *J* 7.2, OCH_2CH_3, (*m*)], 2.2–2.5 [$CHCH_2$ (*l*, *m*, *n*) and CH_2CH_2IM, (*n*)], 2.6–2.9 [CH_2CH_2CO, (*l*, *m*, *n*)], 3.52 [br, $CONHCH_2$, (*n*)], 4.32 [br, OCH_2CH_3, (*m*)], 4.43 [br, CH_2IM, (*n*)], 4.47–4.9 [br, NHC*H*CO, (*l*, *m*, *n*)], 7.54 [br, IMH_2, (*n*)], 8.77 [br, IM*H*, (*n*)].

Doping with 1-(3-aminopropyl)-2-methylimidazole

Poly(γ-ethyl L-glutamate) (0.5 g, M_v = 22 100) was dissolved in 1-(3-aminopropyl)-2-methylimidazole (3.0 ml) and the solution heated at 80 °C for 24 h. The reaction mixture was worked up as in the example (*a*) above using 1-(3-aminopropyl)imidazole to yield PEG-MeIM as a pale yellow powder (0.34 g), δ_H([$^2H_6$]TFA) 1.38 [t, *J* 7, OCH_2CH_3, (*m*)], 2.2–2.5 [$CHCH_2$, (*l*, *m*, *n*), CH_2CH_2IM (*n*), CH_3IM (*n*)], 2.6–2.8 [br, CH_2CH_2CO, (*l*, *m*, *n*)] 3.63 [br, $CONHCH_2$, (*n*)], 4.35 [br, OCH_2CH_3, (*m*), CH_2IM, (*n*)], 7.39 [br, IM*H*, (*n*)] (Found by ^{1}H NMR spectroscopy: ratio $l:m:n = 4:61:35$).

Preparation of electrodes

Platinum bead electrodes were prepared by heating a length of platinum wire (0.56 mm diameter) in a hydrogen–oxygen flame to form a sphere, typically 2 mm in diameter. The wire was silver soldered to a copper wire, then fused into a glass support so that only the working platinum was exposed.

Platinum flag electrodes were prepared by spot welding a platinum plate (typically 0.25 cm^2) onto a platinum wire of length 2.0 cm. The platinum wire was soldered onto copper wire and then sealed into a glass support leaving only the platinum exposed.

Transparent indium doped tin oxide (ITO) electrodes (typically 1.6 cm^2) were prepared as follows. Silver wire (0.1 cm diameter) was silver soldered onto copper wire. A length of the end of the silver wire (1.0 cm) was hammered flat and the conducting side of the glass electrodes attached to the flattened silver using silver loaded epoxy resin. The silver–copper connector was then fused into a glass support. A suitable electrode area for cyclic voltammetry and chronoamperometry experiments was achieved by masking part of the electrode with Teflon tape. During these experiments the connecting wire and the upper part of the teflon tape were not exposed to the solution. After use the electrodes were cleaned by addition of dichloromethane, followed by wiping the polymer film with a soft tissue. The electrodes were then sonicated in water and further washed with hexafluoropropan-2-ol and dichloromethane.

Polymer coating of electrodes. Films on platinum bead electrodes were prepared by the method of dip-coating the electrode in a solution of the polymer-porphyrin (typically 0.3% w/v) in dimethylacetamide or dimethyl sulfoxide. After 20 min, the electrode was removed and dried *in vacuo* at 50 °C for 20 min.

The majority of the cyclic voltammetry, chronoamperometry and spectroelectrochemical UV–VIS experiments were carried out on metalloporphyrin loaded, functionalised PEG films, formed by a method of spray coating. This was accomplished by loading a solution of the polymer (*ca.* 1% w/v) and metalloporphyrin (*ca.* 0.1–0.3%) in hexafluoropropan-2-ol and dichloromethane into an artist's air brush and spraying onto the flat electrode surface heated to around 80 °C so that the solvent flashed off. The amount of film deposited on the surface could be controlled by the spraying time, typically 3–5 s.

Electrochemical measurements

Cyclic voltammetric and chronoamperometric experiments were conducted in a standard three electrode cell system. The working electrode was either platinum or indium doped tin oxide-coated glass and the counter electrode was platinum wire. The reference electrode was a sodium chloride saturated calomel electrode (SSCE), separated from the main compartment

by means of a salt bridge containing the electrolyte solution used in the cell. The reference electrode and the salt bridge were connected *via* a solution of 1.0 M $NaNO_3$. A quasi-reference silver wire electrode was sometimes used in order to minimise resistance drop across the cell. This consisted of a silver wire fused in glass, dipping directly into the electrolyte solution in the main compartment.

Spectroelectrochemical measurements

The cell was a standard 1 cm path length Pyrex cuvette with the working ITO electrode (area 1.3 cm^2) clamped at the front face of the cell. The counter electrode of platinum wire (4.0 cm; 0.5 mm diameter) and a quasi-reference silver wire electrode were attached to a Teflon frame and clamped inside the cell. Electrical connections were made through soldered and insulated copper leads. The working electrode potential was controlled using a PAR 273 potentiostat, under manual operation. Data acquisition time for each spectrum was 1 s.

Acknowledgements

A studentship from the Department of Education for Northern Ireland (to M. D.) is gratefully acknowledged.

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Paper 7/06863H
Received 22*nd September* 1997
Accepted 2*nd February* 1998