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Electron Transfer in a Novel Synthetic Membrane Analogue for Cytochrome c

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Ester groups in poly(γ-ethyl L-glutamate) were converted to the amide with 1-(3-aminopropyl)imidazole; co-ordination of deuteroporphyrin-IX-$Fe^{III}Cl$ dimethyl ester to the imidazole groups gave a novel electroactive polymer with reversible redox activity in aqueous $NaClO_4$ [$E^\circ = -0.43$ V *vs.* sodium chloride saturated calomel electrode (SSCE)] and in aqueous NaCl ($E^\circ = -0.30$ V *vs.* SSCE).

An iron porphyrin unit functions as the redox site in many electron transfer enzymes. A sub-section of this class of enzymes has the iron with either one or two axial imidazole ligands, in the cytochrome c group the porphyrin is attached to the peptide chain by sulphur bridges between cysteine residues and the two porphyrin vinyl groups.[1] A useful approach to the synthesis of analogues of these natural electron transfer systems is to take poly(γ-ethyl L-glutamate) and modify the ester side chains by attaching groups that can co-ordinate with an iron porphyrin.

In weakly hydrogen bonding solvents, poly(γ-ethyl L-glutamate) spontaneously forms[2] the α-helix characteristic of large sections of enzyme protein chains. Reaction of poly(γ-ethyl L-glutamate),[3] M 5.5 × 10^4,[4] with 1-(3-aminopropyl)imidazole replaced ~50% of the ester groups by the imidazole substituted amide chain to give a polymer whose structural units are summarized in (**1**). A random distribution of ester and amide side chains is assumed. Deuteroporphyrin-IX-$Fe^{III}Cl$ dimethyl ester (**2**) was co-ordinatively attached through the imidazole group to give FeP–EtGlu with $\lambda_{max.}$ [dimethyl sulphoxide solution (DMSO)] at 396 (Soret band), 493, and 611 nm. The subsequent electrochemical evidence indicates that most iron centres in the FeP–EtGlu have one readily exchangeable axial ligand and only one axial histidine group.

We have previously reported[4] on the properties of related electroactive poly(amino acids) where the electroactive group gave reversible behaviour only in aprotic solvents. These were dip-coated onto platinum to form electroactive films. The large body of work from other authors on electroactive polymer films is summarised in ref. 4. Films prepared from FeP–EtGlu show reversible redox behaviour in water.

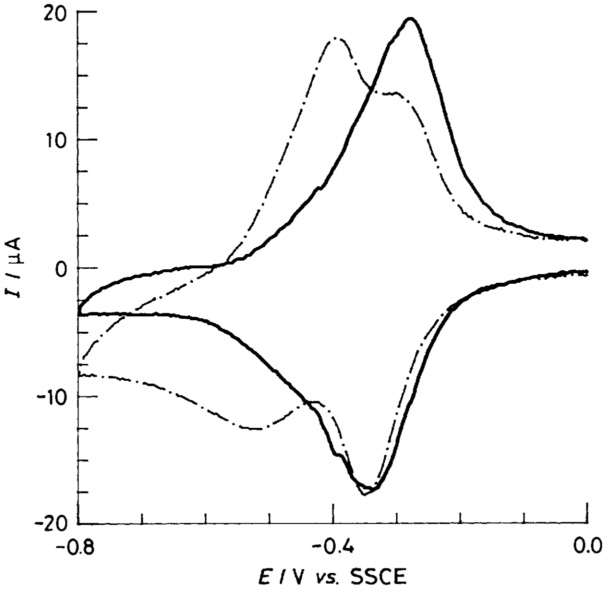
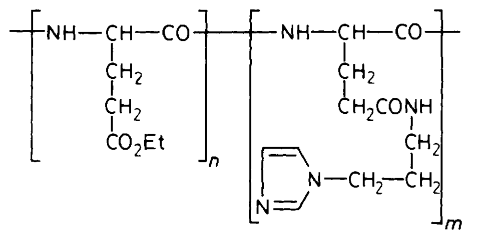
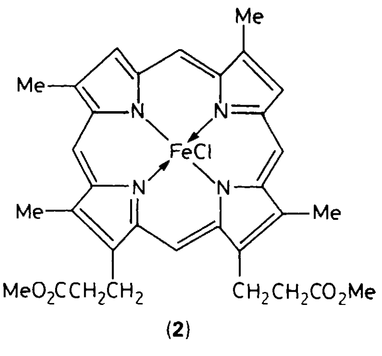


Figure 1. Cyclic voltammetry at 0.10 V s^{-1} of FeP–EtGlu coated Pt electrode (area 0.152 cm^2) in AN, 0.1 M Pr_4NBF: —— presoaked in aqueous NaCl, ·–·– without NaCl treatment.



(**1**)



(**2**)

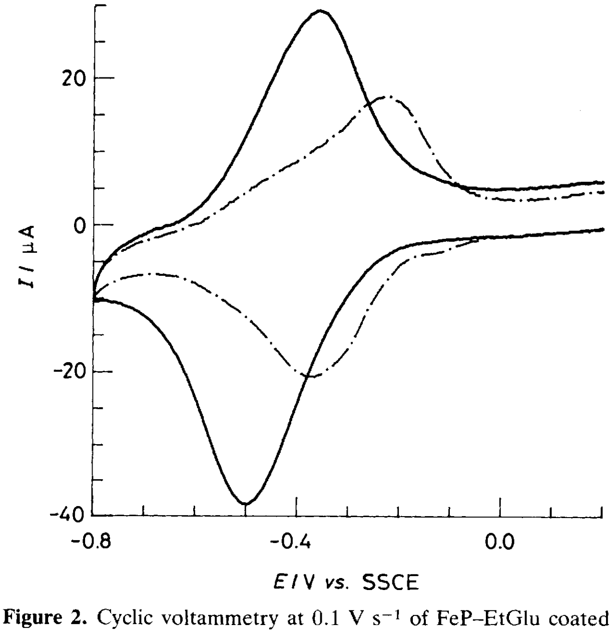


Figure 2. Cyclic voltammetry at 0.1 V s^{-1} of FeP–EtGlu coated Pt electrode (area 0.152 cm^2) in H_2O: —— with 0.1 M $NaClO_4$, ·–·– with 0.1 M NaCl.

FeP–EtGlu was dip-coated onto a clean Pt sphere from 0.3% solution in DMSO and the electrode dried at 50 °C *in vacuo*. This electrode showed two pairs of reversible redox peaks on cyclic voltammetry (CV) in acetonitrile (AN) with 0.1 M Pr_4NBF_4. The relative heights of these two peaks varied with the history of the electrode. Soaking the electrode in aqueous NaCl and then returning to AN caused strong enhancement of one pair of peaks (Figure 1). This behaviour is easily explained if the iron centres have one axial histidine ligand and one other axial ligand, originally Cl^-, but which, in the absence of excess chloride ions, is replaced slowly in solution by a molecule of solvent. The CV behaviour in aqueous solution is shown in Figure 2. In 0.1 M $NaClO_4$ where FeP–EtGlu has one aquo ligand, the system shows $E^\circ = -0.43$ V *vs.* sodium chloride saturated calomel electrode (SSCE). This is reversibly converted in 0.1 M NaCl to the system with one chloro ligand which shows $E^\circ = -0.30$ V *vs.* SSCE.

The redox centre in this poly(amino acid) is very stable and can be cycled more than 100 times in aqueous solution without deterioration. FeP–EtGlu in aqueous $NaClO_4$ shows equilibrium redox behaviour similar to that of cytochrome c peroxidase for which $E^\circ = -0.43$ V *vs.* SSCE at pH 7.[5] The diffusionally controlled heterogeneous electron exchange at a platinum and at a gold electrode has been examined for aqueous solutions of cytochrome c.[6]

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