

UV-VIS and Resonance Raman Spectroelectrochemical Properties of Transition Metal Centres Immobilised within a Poly(amino acid) Matrix: Illustrated with an Iron Porphyrin

Steven E. J. Bell,* Martin Devenney, James Grimshaw,* Jadwiga Trocha-Grimshaw and John J. McGarvey

School of Chemistry, Queen's University, Belfast BT9 5AG, Northern Ireland

An iron porphyrin complex has been immobilized on the surfaces of platinum, silver, and indium doped-tin oxide coated glass by using the poly(γ -ethyl L-glutamate)-*N*-(3-aminopropyl)imidazole derivative **1** as a linking agent, thus allowing the surface-enhanced resonance Raman and UV-VIS absorption spectra and electrochemical properties of the porphyrin to be studied in solvents in which it is not normally soluble.

Poly(γ -ethyl L-glutamate) reacts with *N*-(3-aminopropyl)imidazole to give a derivative **1** with terminal imidazole units. The product will coordinate iron porphyrins and the resulting porphyrin-doped polymer can be coated onto an electrode.¹ Using this coated electrode it is possible to explore the surface-enhanced resonance Raman (SERRS) and UV-VIS absorption spectra of the porphyrin in its various oxidation states and using solvents in which the simple porphyrin is not soluble.

In the vast majority of SERRS studies on iron porphyrins, the material has been absorbed directly onto the electrode surface. This procedure can lead to complications both because direct interaction between the adsorbed porphyrin and the electrode is possible,² and because it may be difficult to distinguish between signals due to adsorbed and bulk material.³ Using polymers to immobilise the porphyrins in a matrix which remains electroactive should help to alleviate these difficulties. Numerous systems where porphyrins are attached to a polymer through covalent bonds have been made.⁴ In some cases they have been studied by Raman spectroscopy.⁵ The matrix we describe is fundamentally different from these because the porphyrin is bonded through its iron centre rather than by direct attachment to the ring. Moreover, the polymer **1** does not absorb in the visible region so that porphyrin-doped polymers give SERRS signals dominated by the porphyrin response. We illustrate the potential of this system using the simple iron(III) deuteroporphyrin-IX ester [Fe^{III}(dp)] complex **2**.

The polymer **1** was treated in dimethylacetamide with a deficiency of Fe^{III}(dp)Cl, based on the amount required to form a 2:1 imidazole-porphyrin complex. The complex was precipitated with diethyl ether and then washed with dichloromethane to remove any unbonded porphyrin. The resulting porphyrin-doped polymer was spin-coated onto an electrically conducting support from a 1.2% solution in hexafluoro-

propan-2-ol, followed by evaporation of the solvent. The resulting films did not disintegrate in water or acetonitrile and were characterized as containing Fe^{III}(dp)(imidazole)₂ coordination sites in the following way.

The UV-VIS spectra (Fig. 1) in water and in acetonitrile of a film supported on indium doped-tin oxide coated glass (ITO) are identical (Soret band with λ_{max} 404 nm) with the measured spectrum⁶ of Fe^{III}(dp)Cl in the presence of an excess of *N*-methylimidazole. Films were prepared on roughened silver electrodes[†] which had been dried by soaking with the polymer solution and drying in air. They gave SERRS[‡] (λ_{ex} 488 nm) (Fig. 2) which were dominated by porphyrin skeletal vibrations. The spectra of these films were identical in both aqueous and acetonitrile electrolyte and also identical with the resonance Raman spectrum from a solution of Fe^{III}(dp)Cl in dichloromethane containing an excess of *N*-methylimidazole. The frequency of the skeletal vibrations which act as markers⁷ for the oxidation state, the spin state and ligation of the iron centres were typical for low-spin six-coordinate iron(III) porphyrin (ν_4 1380 cm⁻¹, ν_{11} 1568 cm⁻¹, ν_{10} 1645 cm⁻¹).

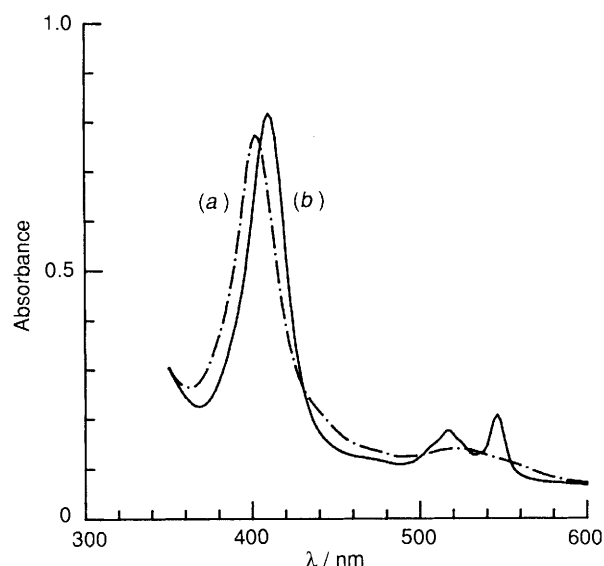
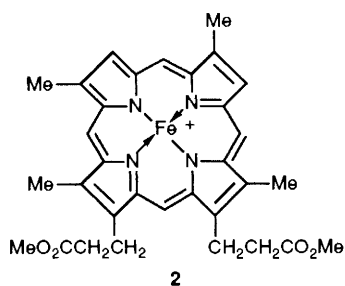
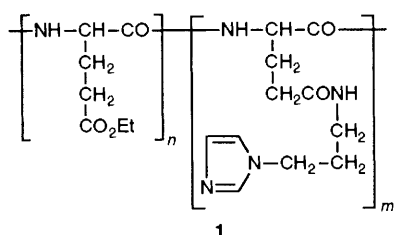


Fig. 1 UV-VIS spectra in water of a film of the porphyrin loaded polymer on ITO: (a) Fe^{III} form at 0 V vs. SSCE; (b) Fe^{II} form at -0.6 V vs. SSCE

[†] The potential of a plate of smooth silver was stepped in aqueous sodium chloride to +0.25 V vs. sodium chloride saturated calomel electrode (SSCE) for 5 s, then to -0.25 V vs. SSCE for 5 s and the process repeated three more times (see R. K. Chang in *Spectroscopic and Diffraction Techniques in Interfacial Electrochemistry*, ed. C. Gutierrez and C. Melendres, Kluwer Academic Publishers, The Netherlands, 1990, p. 155).

[‡] Recorded using a charge-coupled detector (S. E. J. Bell, J. J. McGarvey, S. J. Rigby and D. G. Walmsley, *J. Raman Spectrosc.*, 1991, **22**, 763).

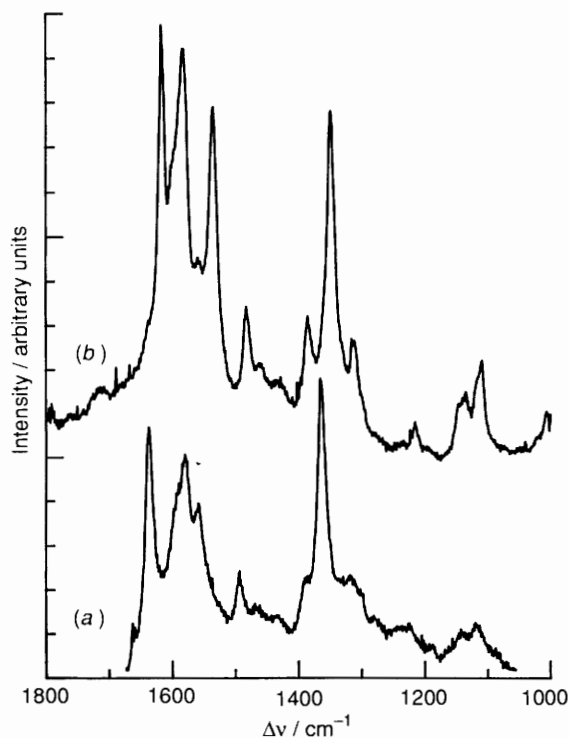


Fig. 2 SERRS in water (λ_{ex} 488 nm) of a film of the porphyrin loaded polymer on silver: (a) Fe^{III} form at 0 V vs. SSCE; (b) Fe^{II} form at -0.6 V vs. SSCE

Cyclic voltammetry of a film on platinum indicated a reversible redox couple with $E^0 = -0.43$ V vs. SSCE in water containing $0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$. In water the position of this couple is dependent on the anion present.¹ No noticeable loss in electroactivity is observed on repeated cycling in water under nitrogen. Qualitatively identical voltammograms were obtained from films deposited on ITO and on a roughened silver electrode. Films prepared on these surfaces were reduced at -0.6 V vs. SSCE and then showed the following characteristics.

The UV-VIS spectra in water and in acetonitrile of a film supported on ITO are identical within experimental error

(Soret band with λ_{max} 414 nm) with the spectrum reported⁶ for $\text{Fe}^{\text{III}}(\text{dp})\text{Cl}$ bis-ligated with a histidine derivative and electrochemically reduced to the Fe^{II} state. On removing the potential, the spectrum reverted over a few minutes to the original Fe^{III} spectrum with no loss in intensity of the Soret band; the system showed good isosbestic points.

The resonance Raman spectra obtained from a coated silver surface at -0.6 V vs. SCE showed the shift in the marker bands expected after conversion to a $\text{Fe}^{\text{II}}(\text{dp})(\text{imidazole})_2$ species (ν_4 oxidation state marker band moved from 1378 to 1362 cm^{-1} ; ν_{10} moved from 1645 to 1624 cm^{-1} ; ν_{11} moved from 1568 to 1546 cm^{-1}). On removing the potential, the original Fe^{III} spectrum was slowly restored. The polymer-porphyrin system described above is an obvious model for natural electron-transfer systems such as cytochrome- b_5 , whose active site is protohaem with two axial histidine ligands coordinating the iron centre. Synthetic modification of the polymer matrix and substitution of other metalloporphyrins are readily achieved. Thus, this general methodology should allow models for the redox-active enzyme systems to be constructed and studied under conditions where interference from surface-porphyrin or porphyrin-porphyrin interactions is minimized.

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