

## Ferrocene-functionalized Polypyrrole Films

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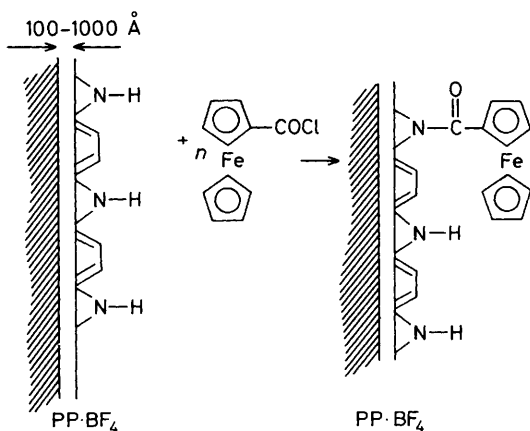
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The reactivity of polypyrrole yields a ferrocene-functionalized conducting polymer.

The electrochemical behaviour of ferrocene has been widely applied in the modification of conducting surfaces.<sup>1</sup> Exploring the chemical reactivity of a proven conducting polymer, polypyrrole, possessing a simple chemical make-up, we have incorporated a ferrocene moiety into the polymer. Functionalization occurs *via* the N-H position which undergoes acylation at monomer units located on the outer surface of the polymer matrix.

The polypyrrole-fluoroborate (PP-BF<sub>4</sub>) films were electro-deposited on optically transparent indium-tin oxide on glass (I.T.O.) as working electrode covering an area of 1.0 cm<sup>2</sup>, with a Pt gauze auxiliary electrode covering an area of 1.0 cm<sup>2</sup>, electrode (s.c.e.) as reference. Films were grown at a constant potential of +0.820 V with current densities of 200 μA/cm<sup>2</sup>. Thickness was monitored by measuring the charge passed (20 mC/cm<sup>2</sup> ≡ 1000 Å as calibrated with a Dektak surface profilometer). The electrolyte-monomer solution was 0.2 M freshly distilled pyrrole in 0.1 M tetraethylammonium fluoroborate-acetonitrile. Solutions were deoxygenated prior to film manufacture. The films were rinsed clean of electrolyte-monomer and placed in a fresh anhydrous acetonitrile solution of ferrocenecarbonyl chloride<sup>†</sup> under nitrogen. The Schotten-Baumann acylation of PP was carried out as shown in Scheme 1. Reaction times ranged from 15 min to 24 h with functionalization occurring to a detectable level after 18 h. Attempts to drive the reaction thermally were unsuccessful owing to the mechanical stress imposed on the film by the boiling solvent. The films were rinsed in a Soxhlet extractor (MeCN) for 3 h prior to analysis.

Cyclic voltammetry of these films in anhydrous deoxygenated 0.1 M Et<sub>4</sub>NBF<sub>4</sub>-MeCN electrolyte (Figure 1) reveals two different redox processes corresponding to the PP moiety and the ferrocene. Values for the redox potentials are: PP, -0.09 V (*E*<sub>pa</sub>), -0.42 V (*E*<sub>pc</sub>); ferrocene, 0.63 V (*E*<sub>pa</sub>), +0.50 V (*E*<sub>pc</sub>), typical of substituted ferrocenes.<sup>2</sup>



Scheme 1. Ferroceneacylation of polypyrrole.

<sup>†</sup> Prepared by treatment of ferrocenecarboxylic acid (Aldrich) with oxalyl chloride in dichloromethane.

The *i*<sub>pa</sub> and *i*<sub>pc</sub> values for both processes are observed to increase steadily for 10–12 full cycles until they stabilize for periods of continuous cycling of more than 50 min at 20 mV/s between +0.8 and -0.8 V. The anodic scan was limited by the instability of PP. Up to this limit, no appreciable decay occurred. It appears that the redox process of the ferrocene partially protects the polypyrrole against irreversible oxidation which occurs at voltages more positive than +0.6 V for unsubstituted polypyrrole.

The *i*<sub>p</sub> values for both redox processes depend linearly on scan rate, although the current values decrease with successive cycles at rates of 100 mV/s or higher, indicating that fewer centres become involved in the redox process.<sup>3</sup> At slower rates, the limiting Δ*E*<sub>p</sub> values obtained (>170 mV) are indicative of slow electron transfer and the broadness of the waves may correspond to different oxidation states present throughout the electroactive surface. Estimation of the Γ ferrocene value from integration of the redox curves is masked by the presence of capacitive currents of PP in the anodic region where this process occurs. Subtraction of these currents leads to an approximate value for Γ ferrocene-ferricinium of 10<sup>-10</sup> mol/cm<sup>2</sup>, *i.e.* the functionalization of PP occurs on the outer surface of the polymer and perhaps only on those sites which are sterically favoured and suitably oriented. An X-ray diffraction spectroscopy study of a 1000 Å/cm<sup>2</sup> functionalized film reveals the presence of Fe. The signal level is low with respect to the background preventing precise quantification but is consistent with monolayer quantities indicating that derivatization occurs on the surface only.

Spectroscopic analysis confirms the presence of the ferrocene moiety which has an absorption band in the visible region peaking at 510 nm for a ferrocenecarbonyl chloride layer on I.T.O. The PP-ferrocene shows the same band at 547 nm measured before the cyclic voltammetric study. After one cycle a film of comparable thickness reveals a red shift of this band as well as a broadening.

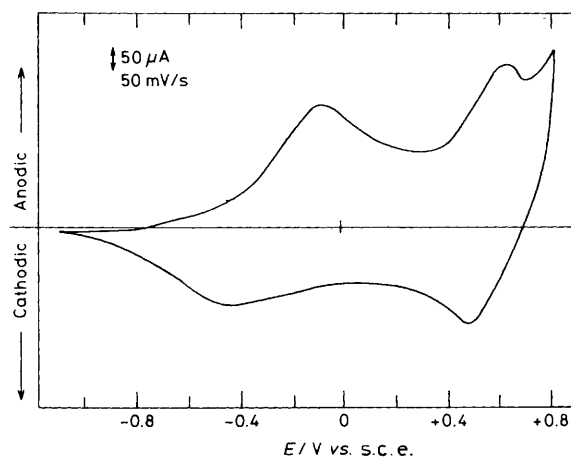


Figure 1. Cyclic voltammogram of a 1000 Å film of PP-ferrocene in 0.1 M Et<sub>4</sub>NBF<sub>4</sub>-MeCN electrolyte.

That it is the N-H function of the pyrrole moiety which is involved in the covalent bonding of carboxyferrocene can be ascertained by performing the same experiment with structurally similar<sup>4</sup> poly(methylpyrrole) films. No ferrocene redox reaction was present in the cyclic voltammetric analysis of those films.

In conclusion, we have found that the amine functionality of polypyrrole is chemically reactive and can generate covalent bonds with suitable groups. The derivatization reaction is limited by steric effects arising from the three-dimensional structure of the polymer and the size of the derivatizing molecule. The process of derivatization does not affect the electrochemical performance of the electroactive species.

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