Poly(Pyrrole–Phenothiazine) Modified Electrodes. Application as Photoelectrodes *via* a Charge Transfer Complex

Alain Deronzier, Mohamed Essakalli, and Jean-Claude Moutet

Laboratoire d'Electrochimie Organique et de Photochimie Redox (UA CNRS 1210), Université Scientifique, Technologique et Medicale de Grenoble, B.P.68, 38402 Saint Martin d'Hères Cédex, France

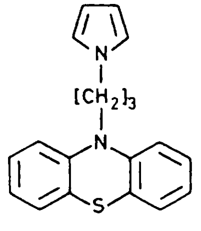
Electrodes modified by a poly(pyrrole–phenothiazine) film are obtained by anodic polymerization of *N*-(3-pyrrol-1-ylpropyl)phenothiazine; they act as photoelectrodes *via* their charge transfer complex with an electron acceptor in solution.

It has recently been established that the electrochemical polymerization of *N*-substituted pyrroles is an attractive means for the elaboration of polymer modified electrodes containing a specific redox centre. Using that method the preparation and behaviour of polypyrrole films covalently bonded to electroactive centres such as polypyridyl complexes of ruthenium(II),[1] rhenium(I),[2] and copper(II),[3] or organic molecules like viologens,[4] nitroxides,[5] and anthraquinones[6] have been reported. This communication describes the modification of metallic electrodes by poly(pyrrole–phenothiazine) films upon anodic polymerization of the monomer PPyr, and their utilization as photoelectrodes *via* irradiation of a charge transfer complex with an electron acceptor such as the tropylium cation.

PPyr† was synthesized in 95% yield by addition of 1 equiv. of pyrrolyl potassium to a tetrahydrofuran (THF) solution of *N*-(3-chloropropyl)phenothiazine. The latter was obtained in 30% yield by addition of a large excess of 1-bromo-3-chloropropane to a solution of the phenothiazine anion[7] in dimethyl sulphoxide (DMSO).

The cyclic voltammogram of PPyr (2×10^{-3} M) in 0.1 M Bu_4NClO_4–MeCN at a platinum electrode shows initially a reversible one-electron oxidation process corresponding to formation of the radical cation $\overset{\bullet+}{\mathrm{P}}\mathrm{Pyr}$ ($E_{\frac{1}{2}}$ 0.40 V)‡ as for a regular *N*-alkylphenothiazine[8] (Figure 1, curve a). On extension of the scan to 1.1 V two combined irreversible anodic peaks with poor reproducibility emerge (Figure 1, curve b), which are due to the oxidation of $\overset{\bullet+}{\mathrm{P}}\mathrm{Pyr}$ and of the pyrrole unit. However their assignment is uncertain since the *N*-alkylphenothiazinium radical cation[8] and *N*-alkylpyrrole[9] are both oxidized around 1 V.

Repeatedly scanning the potential over the range −0.25 to 0.90 V results in a continuous increase in the size of cyclic voltammetric PPyr/$\overset{\bullet+}{\mathrm{P}}\mathrm{Pyr}$ peaks, as shown in Figure 2a, indicating the growth of a poly(pyrrole–phenothiazine) (PPPyr) film on the electrode. The anodic limit of the scanning is a crucial point. Increasing the limit of the potential beyond 0.95 V leads to a lower increase in the PPyr/$\overset{\bullet+}{\mathrm{P}}\mathrm{Pyr}$ peak system while no PPPyr film is obtained on scanning beyond 1.1 V. PPPyr films can also be obtained by controlled-potential oxidation at 0.85 V. If the modified electrode is transferred to clean electrolyte and cycled between −0.2 and 0.8 V the



PPyr

---

† All new compounds exhibited spectroscopic and analytical data consistent with the assigned structure; ^1H n.m.r. of PPyr ($CDCl_3$): δ 2.08 (m, 2 H), 3.71 (t, 2 H, *J* 6 Hz), 3.90 (t, 2 H, *J* 6 Hz), 6.01 (t, 2 H, *J* 3 Hz), 6.43 (t, 2 H, *J* 3 Hz), and 6.56—7.23 (m, 8 H).

‡ All potentials were measured *vs.* an Ag/10^{-2} M Ag^+ reference electrode.

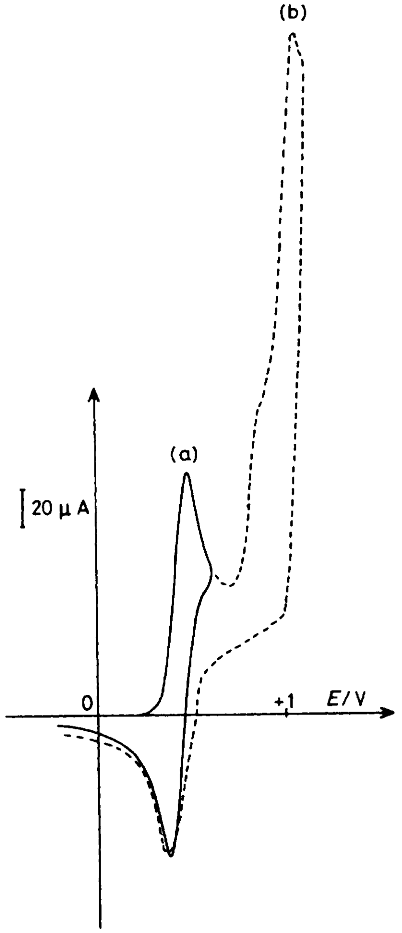


Figure 1. Cyclic voltammograms at a Pt disk electrode (diam. 5 mm) of PPyr (2×10^{-3} M) in 0.1 M Bu_4NClO_4–MeCN; sweep rate v = 0.1 V s^{-1}; (a) (full line), between −0.2 and 0.6 V; (b) (broken line), between −0.2 and 1.1 V.

PPyr/$\overset{\bullet +}{\text{P}}$Pyr peak ($E_{p_a}$ 0.51 V; E_{p_c} 0.42 V at 0.05 V s^{-1}) persists proving the stability of the film (Figure 2, curve b). However the reversibility of the redox system disappears on extension of the cycling up to 1.2 V. At this potential, transformation of $\overset{\bullet +}{\text{P}}$Pyr to its corresponding sulphoxide as for the *N*-methylphenothiazinium radical cation[8] probably occurs in the film. On the other hand the weak pre-peak (E_{p_a} ~0.25 V) at the foot of the PPyr/$\overset{\bullet +}{\text{P}}$Pyr peak system describes the electroactivity of the polypyrrolic chain itself. The absorption exhibited ($\lambda_{max.}$ 515 nm) by the film deposited on an optically transparent doped InO_2 electrode after oxidation at 0.7 V is quite similar to that for the *N*-methylphenothiazinium radical cation species in solution.[8] This absorption is fully restored when the film is reduced back and reoxidized proving the stability of its oxidized form P$\overset{\bullet +}{\text{P}}$Pyr.

It has recently been demonstrated that a photocurrent response can be obtained by visible irradiation of a donor–acceptor charge transfer complex in solution in a photoelectrochemical cell.[10] In that context we have investigated the capability of the PPPyr modified electrode to act as a photoelectrode.§ The presence of the tropylium cation, Tr^+

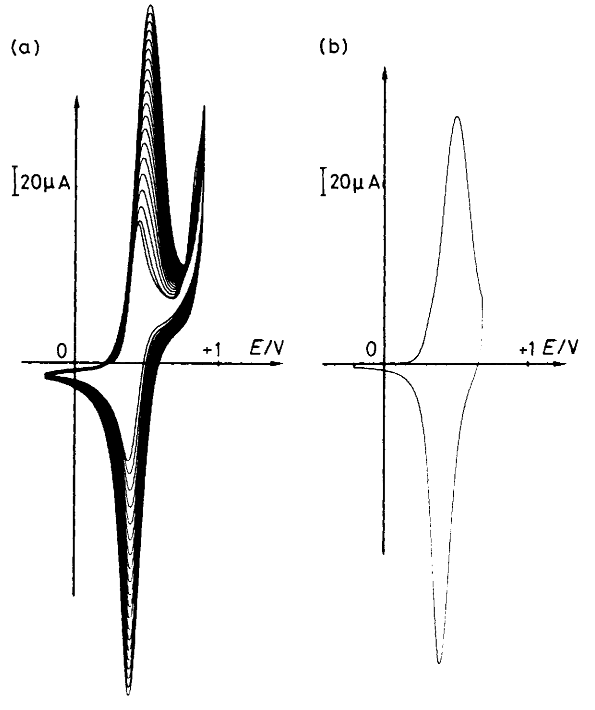


Figure 2. (a) Oxidative electropolymerization of PPyr (2×10^{-3} M) by repeated potential scans at a Pt disk electrode (diam. 5 mm) in 0.1 M Bu_4NClO_4–MeCN; sweep rate v = 0.05 V s^{-1}. (b) Cyclic voltammogram of a Pt/PPPyr electrode ($\Gamma = 3.4 \times 10^{-8}$ mol cm^{-2}) in 0.1 M Bu_4NClO_4–MeCN; sweep rate v = 0.05 V s^{-1}. The electroactivity has a 6% drop after 50 cycles between −0.2 and 0.7 V.

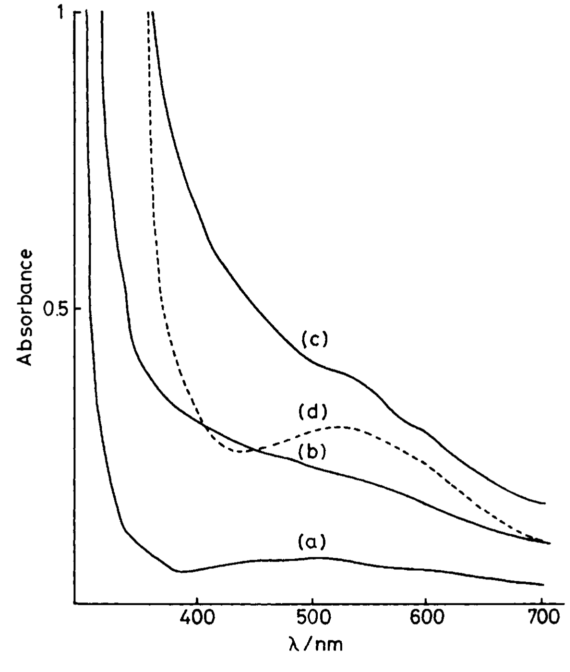
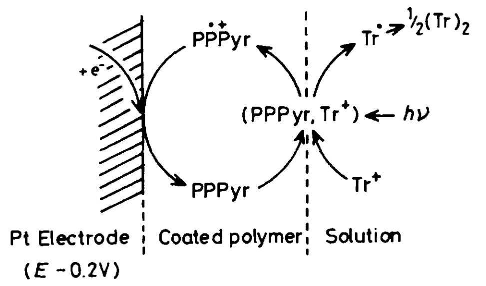


Figure 3. Spectral change accompanying the complexation of a PPPyr film ($\Gamma = 6.5 \times 10^{-9}$ mol cm^{-2}) by Tr^+ in 0.1 M Bu_4NClO_4–MeCN. (a) no Tr^+; (b) 5×10^{-2} M Tr^+; (c) 10^{-1} M Tr^+; (d) charge-transfer complex in 0.1 M Bu_4NClO_4–MeCN solution between *N*-methylphenothiazine (2×10^{-3} M) and Tr^+ (10^{-1} M).

---

§ A previous attempt[11] using an electrode modified by plasma polymerized vinylferrocene film complexed with CCl_4 showed the value of this type of design as photoelectrode, despite its short lifetime (20—60 min).



Scheme 1

(0.1 M), in 0.1 M Bu_4NClO_4–MeCN induces a strong increase in the film absorption resulting from the formation at the interface of a charge transfer complex between the phenothiazinyl group and Tr^+. The charge transfer transition extends from 700 nm to the u.v. region with a shoulder at around 525 nm¶ (Figure 3). Irradiation by visible light of the PPPyr—Tr^+ system induces quite a stable photocurrent I_l (no loss after 20 min of irradiation) if the modified electrode is potentiostated at −0.2 V. $I_l = 0.54\ \mu A\ cm^{-2}$ for an apparent surface concentration of electroactive species of 3.6×10^{-8} mol cm^{-2}. The mechanism for this cathodic photocurrent generation can be represented as in Scheme 1.

Photoexcitation induces the electron transfer leading to $\dot{\mathrm{P}}\overset{+}{\mathrm{P}}\mathrm{Pyr}$ and $Tr^{\cdot}$, the latter dimerizing rapidly to give bitropyl.[12] PPyr regenerated by the electrode is complexed again by the excess of Tr^+ and is ready for participation in another photoredox cycle.

The authors are grateful to Professor G. Cauquis for his interest in this work.

Received, 27th January 1987; Com. 099

¶ The charge transfer complex in 0.1 M Bu_4NClO_4–MeCN solution between *N*-methylphenothiazine (2×10^{-3} M) and Tr^+ (10^{-1} M) exhibits a band centred around 520 nm (see Figure 3, broken line).

References

1 G. Bidan, A. Deronzier, and J.-C. Moutet, *Nouv. J. Chim.*, 1984, **8**, 501; S. Cosnier, A. Deronzier, and J.-C. Moutet, *J. Electroanal. Chem.*, 1985, **193**, 193; J. G. Eaves, M. S. Munro, and D. Parker, *J. Chem. Soc., Chem. Commun.*, 1985, 684.

2 S. Cosnier, A. Deronzier, and J.-C. Moutet, *J. Electroanal. Chem.*, 1986, **207**, 315.

3 F. Daire, F. Bedioui, J. Devinck, and C. Bied-Charreton, *J. Electroanal. Chem.*, 1986, **205**, 309.

4 G. Bidan, A. Deronzier, and J.-C. Moutet, *J. Chem. Soc., Chem. Commun.*, 1984, 1185; L. Coche, A. Deronzier, and J.-C. Moutet, *J. Electroanal. Chem.*, 1986, **198**, 187.

5 G. Bidan and D. Limosin, *Ann. Phys. (Paris)*, 1986, **11**, 5.

6 P. Audebert, G. Bidan, and M. Lapkowski, *J. Chem. Soc., Chem. Commun.*, 1986, 887.

7 P. Hanson and R. O. C. Norman, *J. Chem. Soc., Perkin Trans. 2.*, 1973, 264.

8 G. Cauquis, A. Deronzier, J.-L. Lepage, and D. Serve, *Bull. Soc. Chim. Fr.*, 1977, 295, and references therein.

9 A. Diaz, J. Castillo, K. K. Kanazawa, J. A. Logan, M. Salmon, and O. Fajardo, *J. Electroanal. Chem.*, 1982, **133**, 233.

10 B. P. Sullivan, W. J. Dressick, and T. J. Meyer, *J. Phys. Chem.*, 1982, **86**, 1473; A. Deronzier and F. Esposito, *Nouv. J. Chim.*, 1983, **7**, 15.

11 M. F. Dautartas, K. R. Mann, and J. F. Evans, *J. Electroanal. Chem.*, 1980, **110**, 379.

12 J. M. Leal, T. Teherani, and A. J. Bard, *J. Electroanal. Chem.*, 1978, **91**, 275; A. Deronzier, *Tetrahedron Lett.*, 1984, **25**, 2867.