

Poly(pyrrole–pyromellitimide) modified electrodes

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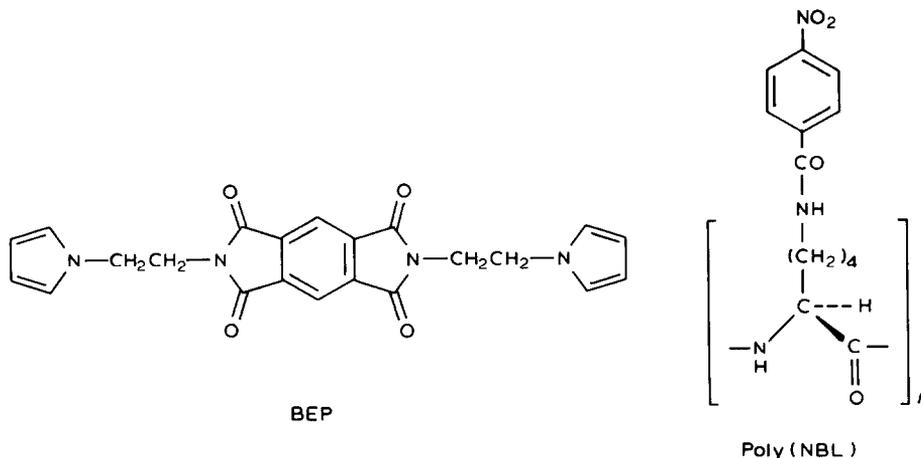
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ABSTRACT

Poly(pyrrole–pyromellitimide) films were prepared by the anodic oxidation of *N,N'*-bis[2-(1-pyrrolyl)ethyl]pyromellitimide (BEP) in acetonitrile media. These films showed a stable redox behaviour in acetonitrile as well as in water media containing 0.1 M tetraalkylammonium salt or LiClO₄, as the supporting electrolyte. Poly(BEP) adsorbed a layer of poly(*N*'-4-nitrobenzoyl-L-lysine) and this bilayer exhibited charging of both electroactive groups.

INTRODUCTION

The electropolymerization of substituted pyrroles containing redox centres [1–6] has received considerable attention recently because of the useful properties of the resulting polymers in electrocatalysis. We have also shown that the electroactive poly(amino acids) bind well to a poly(pyrrole) underlayer [7]. In order to explore this application it is necessary to develop substituted poly(pyrroles) with redox behaviour in an appropriate potential region. In this paper we report the synthesis and electropolymerization of *N,N'*-bis[2-(1-pyrrolyl)ethyl]pyromellitimide, BEP, and the electrochemical behaviour of the resulting polymer.



EXPERIMENTAL

Preparation of monomer

BEP was prepared in 74% yield by the reaction between the dianhydride of pyromellitic acid and 1-(2-aminoethyl)pyrrole [8] in dimethylformamide, according to a procedure [9] used with 2-aminoethanol. *N,N*-Bis[2-(1-pyrrolyl)ethyl]pyromellitimide was recrystallized twice from dimethylacetamide as yellow plates, m.p. 286–289 °C. Found: C, 65.9; H, 4.3; N, 13.7. Calc. for $C_{22}H_{18}N_4O_4$: C, 65.7; H, 4.5; N, 13.9%. 1H NMR, δ (CDCl₃, TMS): 4.05 (4 H, t, $J = 5.9$ Hz, $2 \times$ pyrrole-N-CH₂), 4.22 (4 H, t, $J = 6$ Hz, $2 \times$ N-CH₂), 6.08 (4 H, t, $J = 2.1$ Hz, 4 β -H's of pyrrole), 6.58 (4 H, t, $J = 2.1$ Hz, 4 α -H's of pyrrole), 8.23 (2 H, s, ArH). m/e (%): 402 (M^+ , 30), ν_{max} (KBr): 1712, 1429, 1396 and 1286 cm^{-1} .

Film preparation

All electrochemical studies were performed in a three-electrode, one-compartment cell. The working electrode was a Pt sphere (diameter 1–2 mm), sealed in a glass mounting. A Pt wire was used as the counter electrode. All the potentials are quoted with respect to a saturated sodium chloride calomel electrode (SSCE). The solutions were degassed by bubbling (10–20 min) dry oxygen-free nitrogen. The acetonitrile (Aldrich, HPLC grade) was dried over calcium hydride. Tetrapropylammonium tetrafluoroborate and LiClO₄ were dried under vacuum at 100–120 °C for two days.

BEP formed a thin polymeric coating on spherical Pt electrodes (diameter 1–2 mm) from 1–2 mM monomer solution in acetonitrile containing 0.1 M electrolyte when oxidized at 1.2 V vs. SSCE. The oxidized polypyrrole structure is bluish black and the reduced form (at 0 V) is yellow.

RESULTS AND DISCUSSION

Behaviour of BEP and of poly(BEP)

Cyclic voltammetry of BEP (2 mM) at a Pt electrode (area = 0.117 cm²) in acetonitrile containing 0.1 M tetrapropylammonium fluoroborate showed two reversible electron transfer reactions with $E^\circ = -0.85$ and -1.45 V for the BEP/BEP⁻ and BEP⁻/BEP²⁻ redox couples respectively (Fig. 1a). The colour of the anion radical (BEP⁻) is pale green while the dianion (BEP²⁻) is reddish pink. An irreversible peak ($E_{pa} = 1.45$ V) with a shoulder ($E_{pa} = 1.27$ V) was observed for the oxidation of pyrrole rings.

In the presence of LiClO₄, BEP showed a different behaviour at negative potentials (Fig. 2a) in acetonitrile solution. An insoluble lithium salt of the reduced BEP was seen as a deposit on the Pt surface and this changed the overall shape of the cyclic voltammetric curve. Similar salt deposition has been observed with benzoquinone [10].

Figure 3 shows the cyclic voltammogram between 0 and -1.8 V of a poly(BEP) film of Pt in acetonitrile containing 0.1 M LiClO₄. During the negative cycle, the

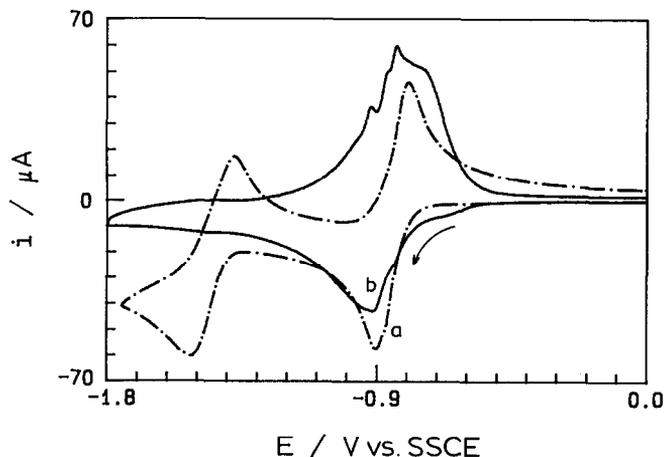


Fig. 1. Cyclic voltammetry in acetonitrile + 0.1 M tetrapropylammonium fluoroborate. (a) BEP (1 mM) at Pt electrode (area = 0.117 cm²), $\nu = 0.15$ V s⁻¹. (b) Poly(BEP) film on Pt (area = 0.135 cm²), $\nu = 0.10$ V s⁻¹. Film prepared by passing 13.7 mC cm⁻² at 1.2 V.

colour of the poly(BEP) film became reddish pink indicating the formation of dianion (BEP²⁻). The cyclic voltammogram of poly(BEP) in acetonitrile with 0.1 M tetrapropylammonium fluoroborate is compared in Fig. 1 with the cyclic voltammogram of the monomer under similar conditions. The polymer no longer shows two well defined single electron transfer waves as observed in the monomer. Similarly, in the presence of lithium ions (Fig. 3), we do not see two well defined single electron transfer waves for poly(BEP). Only the colour of the film provides information

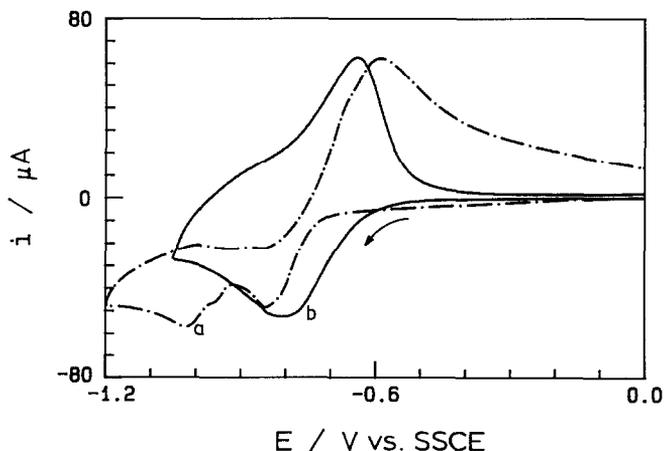


Fig. 2. Cyclic voltammetry in acetonitrile + 0.1 M LiClO₄. (a) BEP (1 mM) at Pt electrode (area = 0.155 cm²), $\nu = 0.10$ V s⁻¹. (b) Poly(BEP) film on Pt (area = 0.112 cm²), $\nu = 0.070$ V s⁻¹. Film prepared by passing 9.5 mC cm⁻² at 1.2 V.

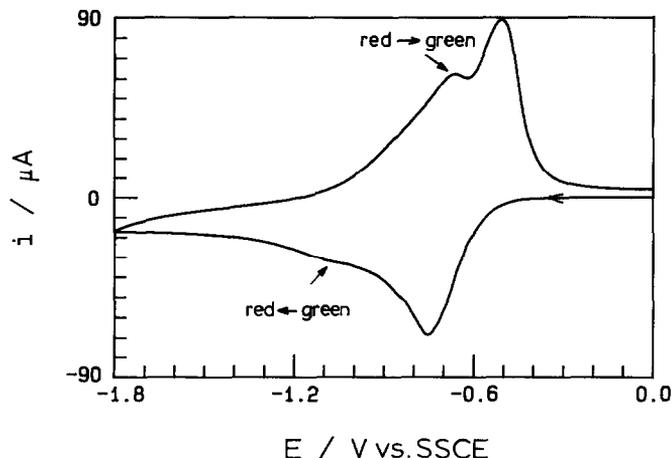


Fig. 3. Cyclic voltammetry in acetonitrile+0.1 M LiClO₄ of a film of poly(BEP) on Pt (area = 0.126 cm²), $\nu = 0.10 \text{ V s}^{-1}$. Film prepared by passing 7.0 mC cm^{-2} at 1.2 V.

about the oxidation state of the redox group (the radical-ion is pale green, the di-anion is reddish pink). These observations suggest that in the case of polymer, the second electron transfer process takes place at a less negative potential than that of monomer. The extent of the second electron transfer process is difficult to estimate because the individual one electron waves are overlapping. Only the colour of the film provides the information about the oxidation state of the redox group.

Oxidation of the polypyrrole backbone occurred at positive potentials (Fig. 4). *N*-substituted polypyrroles are oxidised at more positive potentials than polypyrrole itself and our example shows almost identical behaviour to that of poly(*N*-ethylpyrrole) [11].

Figure 2 compares the cyclic voltammogram of poly(BEP) at negative potentials with that of the monomer in acetonitrile containing 0.1 M lithium perchlorate. The wave for the first electron transfer is very much better defined for the polymer. This shows clearly the difference between mobile redox species in the solution and fixed redox centres in a polymer matrix where the electrochemistry is not complicated by the crystallization of lithium salts as was the case with the monomer.

The polymer shows a reversible wave for the BEP/BEP^{•-} couple when the potential is scanned between 0 and -1.05 V. At potentials less negative than -1.1 V, no pink colouration in the polymer films was observed in the presence of either LiClO₄ or tetrapropylammonium fluoroborate. It is assumed that in this potential region only one electron transfer process takes place to give BEP^{•-}. The cyclic voltammetric data at potentials between 0 and -1.1 V for poly(BEP) film in acetonitrile containing 0.1 M tetrapropylammonium fluoroborate are collected in Table 1. In the film, $E^\circ(\text{BEP}/\text{BEP}^{\bullet-})$ is about -0.92 V with $\Delta E_p < 50 \text{ mV}$ for scan rates less than 100 mV s^{-1} . The value i_{pc}/ν is approximately constant over the scan rates between 10 and 100 mV s^{-1} , suggesting thin layer behaviour, but the peak

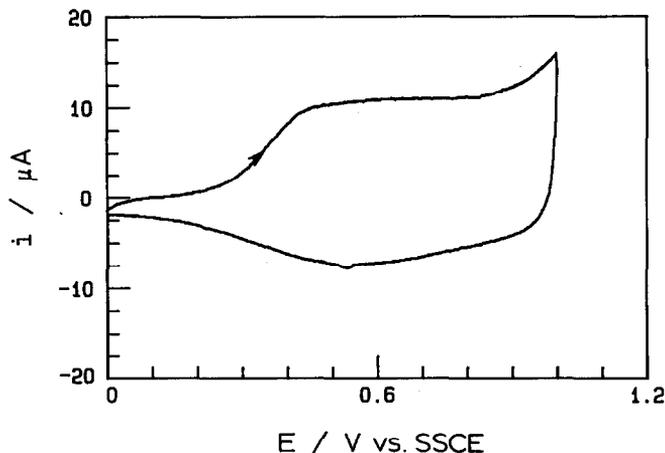


Fig. 4. Cyclic voltammetry in acetonitrile+0.1 M LiClO₄, of a film of poly(BEP) on Pt (area = 0.155 cm²), $v = 0.07 \text{ V s}^{-1}$. Oxidation of the polypyrrole system occurs. Film prepared by passing 7.0 mC cm^{-2} at 1.2 V.

width at half height is about 380 mV, which is much higher than the expected value of 90.6 mV for a single electron transfer process. The peak current does not fall back to the base line because the second electron transfer interferes at negative potentials.

We have attempted to find a relationship between the amount of charge passed during film formation (Q_p) and the charge passed during reduction of the BEP groups (q_c) in the film (see Table 2). Assuming that each pyrrole ring takes 2.25 electrons during incorporation into the polymer film [11], the surface coverage of pyromellitimide units can be calculated from Q_p . The percentage of these units charged on reduction was then found from cyclic voltammetry at negative potentials. Since the cyclic voltammetric waves do not fall to the base line, they do not give the total number of accessible pyromellitimide units. However, it is possible to

TABLE 1

Cyclic voltammetric data from a film of poly(BEP) on Pt (area = 0.112 cm²) in acetonitrile containing 0.1 M tetrapropylammonium fluoroborate. Film prepared by passing 7.5 mC cm^{-2} at 1.2 V. All potentials versus SSCE

$v/\text{V s}^{-1}$	$-E_{pc}/\text{V}$	$-E_{pa}/\text{V}$	$\Delta E_p/\text{mV}$	$-E^\circ/\text{V}$	$i_{pc}/\mu\text{A}$	$i_{pa}/\mu\text{A}$	$i_{pc}v^{-1}/\text{mA s V}^{-1}$
0.100	0.94	0.89	48	0.92	16.0	16.6	0.16
0.081	0.94	0.90	42	0.92	13.1	14.4	0.16
0.064	0.95	0.90	43	0.92	10.5	11.1	0.16
0.049	0.95	0.91	33	0.93	8.2	8.4	0.17
0.036	0.94	0.91	28	0.93	6.1	6.0	0.17
0.025	0.94	0.91	25	0.93	4.4	4.1	0.17
0.016	0.92	0.91	9	0.92	2.9	2.5	0.18

TABLE 2

Comparison between the charge passed during polymerization (Q_p) and the current response during cyclic voltammetry at 0.070 V s^{-1} between 0 and -1.05 V for films of poly(BEP) in acetonitrile

Experiment No.	Electrode area/cm ²	$Q_p/\text{mC cm}^{-2 \text{ a}}$	t_p/s	Electrolyte	$q_c/\text{mC cm}^{-2 \text{ b}}$	$225q_c/Q_p^{\text{ c}}$
SD 273/5	0.112	6.9	30	0.1 M LiClO ₄	0.81	26.4
SD 272/20	0.131	7.6	50	0.1 M LiClO ₄	0.82	24.3
SD 273/20	0.131	14.6	100	0.1 M LiClO ₄	1.1	16.9
SD 273/25	0.162	24.5	200	0.1 M LiClO ₄	1.7	15.6
SD 277/8	0.112	7.5	50	0.1 M TPAB	0.27 ^d	8.1

^a Charge passed during polymerization for time t_p at 1.2 V vs. SSCE of 1 mM monomer solution.

^b Integral under cathodic wave during cyclic voltammetry.

^c % Charging of BEP groups.

^d Cyclic voltammetry 0 to -1.2 V .

deduce that thin films of poly(BEP) are proportionately more charged on reduction than are thicker films, under the same conditions. Also, the extent of charging of the films is greater in the presence of lithium than tetrapropylammonium counter ions.

Poly(BEP) coated Pt electrodes were fairly stable to continuous cyclic voltammetry between 0 and -1.2 V , and the charge under the cathodic peak decreased slowly (0.4% per cycle). The peak current decayed slightly faster when cycled between 0 and -1.8 V due to the protonation of the dianion.

The electrochemical behaviour of poly(BEP) is quite different to that of poly(4,4'-oxydiphenylenepyromellitimide) films, which showed a poor electrochemical response in non-aqueous electrolyte [12]. The observed electrochemical behaviour of poly(BEP) could be due to the more porous nature of the polypyrrole backbone [13], which facilitates the free cation motion through the film.

The electrochemical behaviour of poly(BEP) films on Pt electrodes was also studied in water containing 0.1 M LiClO_4 . Unlike the poly(pyrrole-anthraquinone) films examined by other workers [4], these poly(BEP) films are fully active in a pure water electrolyte. A typical cyclic voltammogram of poly(BEP) in water containing 0.1 M LiClO_4 is shown in Fig. 5. The behaviour is reversible and E° for the first electron transfer is about -0.84 V . The films were fairly stable to continuous cycling between 0 and -1.03 V , the peak height decreasing slowly (0.4% per cycle).

At potentials more negative than -1.05 V , hydrogen evolution took place in contrast to the reported behaviour of poly(4,4'-oxydiphenylenepyromellitimide) films [12], and the electroactivity of the film decreased substantially on the next scan because gas evolution had loosened the surface adhesion of the film. The observed hydrogen evolution confirms the porous nature of the poly(BEP).

Bilayers from poly(BEP) and poly(N^ε-4-nitrobenzoyl-L-lysine)

The poly(N^ε-4-nitrobenzoyl-L-lysine), poly(NBL), coated Pt electrodes show an "ageing" process and deteriorate rapidly on continuous cycling [14]. The composite bilayer films between polypyrrole and poly(NBL) are found to be more stable than

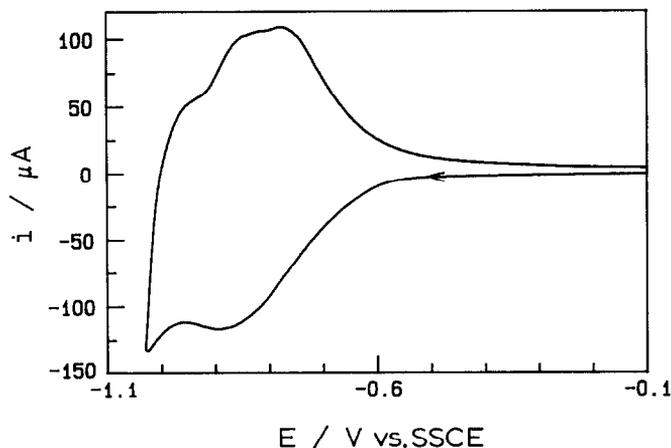


Fig. 5. Cyclic voltammetry in water+0.1 M LiClO_4 of a film of poly(BEP) on Pt (area = 0.124 cm^2), $v = 0.081 \text{ V s}^{-1}$. Film prepared by passing 19.8 mC cm^{-2} at 1.3 V.

poly(NBL) films [7]. In continuing these experiments, poly(NBL) was dipcoated from 0.3% polymer solution in dimethylacetamide onto a poly(BEP) coated Pt electrode. A typical cyclic voltammogram of this Pt/poly(BEP)/poly(NBL) bilayer electrode is compared, in Fig. 6, with the response of poly(BEP) alone in the same electrolyte. The response of the bilayer due to poly(NBL) is the reversible couple at more negative potentials. For the 4-nitrobenzoyl group in this system, $E^\circ = -1.04 \text{ V}$ and the cathodic peak current varied linearly with scan rate.

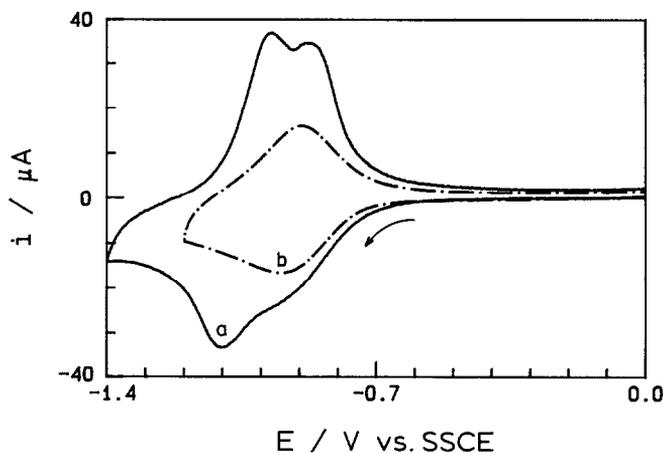


Fig. 6. Cyclic voltammetry in acetonitrile+0.1 M tetrapropylammonium fluoroborate, $v = 0.10 \text{ V s}^{-1}$. (a) Pt/poly(BEP)/poly(NBL) modified electrode (area = 0.182 cm^2), poly(BEP) film was prepared by passing 4.17 mC cm^{-2} at 1.2 V. (b) Pt/poly(BEP) modified electrode (area = 0.155 cm^2), film prepared by passing 7.47 mC cm^{-2} at 1.2 V.

The region where poly(BEP) exchanges electrons with the electrode overlaps the first electron transfer region for poly(NBL) completely. Thus electron transport to and from poly(NBL) through a segregated layer of poly(BEP) is possible. In such a situation we cannot readily distinguish between electron transport to poly(NBL) in this way or through defects in the poly(BEP) layer which allow direct interaction between poly(NBL) and the electrode. Murray has studied bilayers with more widely separated electroactive regions [15]. Unfortunately this poly(BEP)/poly(NBL) bilayer electrode was found to be less stable than the poly(BEP) electrode to continuous cyclic voltammetry between 0 and -1.4 V. The area under the cathodic peak decreased gradually (3.4% per cycle) probably due to the protonation of both nitrobenzoyl radical anion and BEP^{2-} . Both cathodic and anodic peaks retained their normal shape during the gradual decrease in height. Thus the typical ageing phenomenon of poly(NBL) on platinum is not observed and we conclude that adhesion between the two polymers is maintained during continuous cyclic voltammetry.

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REFERENCES

- 1 L. Coche, A. Deronzier and J.-C. Moutet, *J. Electroanal. Chem.*, 198 (1986) 187.
- 2 A. Deronzier, M. Essakalli and J.-C. Moutet, *J. Chem. Soc., Chem. Commun.*, 1987, 773.
- 3 A. Deronzier, D. Limosin and J.-C. Moutet, *Electrochim. Acta*, 32 (1987) 1643.
- 4 P. Audebert and G. Bidan, *J. Electroanal. Chem.*, 238 (1987) 183.
- 5 S. Cosnier, A. Deronzier and J.-C. Moutet, *Inorg. Chem.*, 27 (1988) 2389.
- 6 J. Grimshaw and S.D. Perera, *J. Electroanal. Chem.*, 2265 (1989) 335.
- 7 J. Grimshaw and S.D. Perera, *J. Chem. Soc., Perkin Trans. II*, (1989) 1711.
- 8 I. Jirkovsky and R. Baudy, *Synthesis*, (1981) 481.
- 9 J.A. Cowan and K.M. Sanders, *J. Chem. Soc., Perkin Trans. I*, 1985, 2435.
- 10 K.J. Stutts and G.W. Eastland, *J. Electroanal. Chem.*, 235 (1986) 357.
- 11 A.F. Diaz, J. Castillo, K.K. Kanazawa and J.A. Logan, *J. Electroanal. Chem.*, 133 (1982) 233.
- 12 K.J. Krause and J.L. Bales, *J. Electrochem. Soc.*, 135 (1988) 1137.
- 13 R.A. Bull, F.R. Fan and A.J. Bard, *J. Electrochem. Soc.*, 129 (1982) 1009.
- 14 A.M. Abeysekera, J. Grimshaw, S.D. Perera and D. Vipond, *J. Chem. Soc., Perkin Trans. II*, 1989, 43.
- 15 H.D. Abruna, P. Denisevich, M. Vmana, T.J. Meyer and R.W. Murray, *J. Am. Chem. Soc.*, 103 (1981) 1.