Synthesis and Electrochemical Characterization of Bis(fulvalene)diiron Electrode Films†

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Electrochemical reduction of newly synthesised bis(fulvalene)diiron derivatives, $[Fe_2(C_{10}H_8)(C_{10}H_{8-n}R_n)]$ (R = CCl=CHCHO, *n* = 1 or 3), in NBu_4ClO_4–MeCN leads to the deposition of stable electroactive films on glassy carbon and indium–tin oxide coated glass electrodes. The difference in the number of substituents affects the electropolymerization reaction rate and physical and electrochemical properties of the polymer films. The electrode films control the reversibility in redox reactions of organic and organometallic electron acceptors such as *p*-benzoquinones and a cobaltocenium salt in acetonitrile.

Bis(fulvalene)diiron $[Fe_2(C_{10}H_8)_2]$ is a π-conjugated ferrocene dimer with three stable charge states, 0 (II,II), +(II,III) and 2+ (III,III) (numbers in parentheses denote the formal oxidation number of Fe) having curious electrical and magnetic properties.[1–3] The II,III mixed-valence salts, which have been characterized by various physical measurements,[4–8] are involved in the Robin and Day class III compounds,[9] in which extremely rapid intervalence transfer occurs.[7,8] The conductivity is higher for these salts than for the neutral II,II complex.[10,11] In particular, the ionic charge-transfer complex $[Fe_2(C_{10}H_8)_2]$-$[tcnq]_2$ (tcnq = anion of tetracyanoquinodimethane) shows an extremely high conductivity, 10^2 S cm^{-1}, in compressed pellets,[12,13] and a rather high conductivity, (6–9) × 10^{-3} S cm^{-1}, even in a polymer matrix.[14] The III,III dication is diamagnetic owing to both a strong intramolecular interaction through the ligands[15–17] and a direct metal–metal interaction.[18]

Research on polymeric electrode films has lately advanced and a lot of information on the electron-transfer phenomena and conductivity of redox species in polymeric media has been obtained using various electrochemical techniques.[19–25] The use of such techniques is advantageous in a precise control of potentials, and hence the oxidation state of the substances, and in the facile change of counter ions accompanying the redox reactions. We are interested in investigating the relation of electrical properties to the oxidation state and type of counter ions for $[Fe_2(C_{10}H_8)_2]$ and thus commenced a study on the preparation of $[Fe_2(C_{10}H_8)_2]$ electrode films.

We have previously reported the synthesis, properties and utilization of ferrocene and cobaltocenium electrode films formed by electropolymerization of 1-chloro-2-formylvinyl derivatives.[26–33] In this research we have used a similar method to prepare the first example of a $[Fe_2(C_{10}H_8)_2]$ electrode film. This paper describes the preparation of 1-chloro-2-formylvinyl derivatives of $[Fe_2(C_{10}H_8)_2]$, their electropolymerization reaction, electrochemical and spectroelectrochemical properties of the polymer films thus formed, and their characteristics as the charge-transport medium for the reaction of redox solutes. A related study on the electrochemical behaviour of $[Fe_2(C_{10}H_8)_2]$ in polymer electrolytes has been reported.[34]

Experimental

The complexes $[Fe_2(C_{10}H_8)_2]$[4] and $[Co(C_5H_5)_2]PF_6$[35] were prepared by the published methods. Other reagents were obtained from commercial sources and purified by literature methods. A GC-30 glassy-carbon rod was obtained from Tokai Carbon and indium–tin oxide coated glass from Nippon Sheet Glass. Fourier-transform IR, UV/VIS and 400 MHz ^1H NMR spectra were measured with Digilab FTS-65, Shimadzu MPS-2000 and JEOL GX400 spectrometers, respectively. Film thickness was measured with a Tokyo Seimitsu Surfcom surface profilometer.

Synthesis of $[Fe_2(C_{10}H_8)(C_{10}H_{8-n}R_n)]$ (R = CCl=CHCHO, *n* = 1 *or* 3).—Acetylation of $[Fe_2(C_{10}H_8)_2]$ was carried out by a modified method of Pittman and Surynarayanan.[14] Monoacetyl derivatives (2- and 3-acetylfulvalene)(fulvalene)diiron were prepared as follows. To a mechanically stirred suspension of $[Fe_2(C_{10}H_8)_2]$ (2.0 g, 5.4 mmol) and in dry CS_2 (200 cm^3) cooled in an ice-bath was added dropwise a solution of acetyl chloride (0.42 g, 5.4 mmol) and anhydrous $AlCl_3$ (0.72 g, 5.4 mmol) in CH_2Cl_2 (20 cm^3). After the reaction mixture had been stirred at 0 °C for 1 h, excess of $AlCl_3$ and acetyl chloride were decomposed by adding ice. Extraction with CH_2Cl_2 {0.56 g of $[Fe_2(C_{10}H_8)_2]$ was recovered as an insoluble powder suspended in the water layer} followed by drying with Na_2SO_4 gave a reddish purple solution, which was concentrated by vacuum evaporation and chromatographed on a Merck silica gel 60 column using CH_2Cl_2–ethyl acetate (9:1) as the eluent. Two components appearing as first and second orange bands, a and b, were purified by recrystallization from CH_2Cl_2–hexane. As the resonances of the protons at the 2,5 positions should be found upfield of those at the 3,4 positions,[6,14] components a and b were identified as the 3-acetyl and 2-acetyl derivatives, respectively, from their ^1H NMR spectra. $[Fe_2(C_{10}H_8)(C_{10}H_7$-$COMe$-$3)]$: yield 92 mg (4.1%) (Found: C, 63.95; H, 4.50. $C_{22}H_{18}Fe_2O$ requires C, 64.45; H, 4.40%); ν_{max} 3089, 2924, 1662 (ν_{CO}), 1431, 1352, 1246, 1051, 1031, 810, 505 and 484 cm^{-1} (KBr disc); $\delta_H(CDCl_3)$ 6.2–5.2 (7 H, m, $H^{3,4}$ of ring), 4.5–3.8 (8 H, m, $H^{2,5}$ of ring) and 2.75 (3 H, s, CH_3). $[Fe_2(C_{10}H_8)(C_{10}H_7$-$COMe$-$2)]$: yield 65 mg (2.9%) (Found: C, 64.15; H, 4.35. $C_{22}H_{18}Fe_2O$ requires C, 64.45; H, 4.40%); ν_{max} 3099, 2923, 1665 (ν_{CO}), 1449, 1409, 1358, 1295, 1269, 1236, 1048, 1029, 806, 507 and 484 cm^{-1} (KBr disc); $\delta_H(CDCl_3)$ 6.1–5.3 (8 H, m, $H^{3,4}$ of ring), 4.5–3.6 (7 H, m, $H^{2,5}$ of ring) and 2.34 (3 H, m, CH_3).

A triacetyl derivative, $[Fe_2(C_{10}H_8)\{C_{10}H_5(COMe)_3\}]$ was prepared as follows. Slow addition of acetyl chloride (0.85 g, 10.9 mmol) and $AlCl_3$ (1.45 g, 10.9 mmol) in CH_2Cl_2 (50 cm^3) to a stirred suspension of $[Fe_2(C_{10}H_8)_2]$ (1.0 g) in CH_2Cl_2 (100 cm^3) at 0 °C followed by stirring at 0 °C for 4 h and at room

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† Fulvalene = 5-(cyclopenta-2,4-dien-1-ylidene)cyclopenta-1,3-diene.

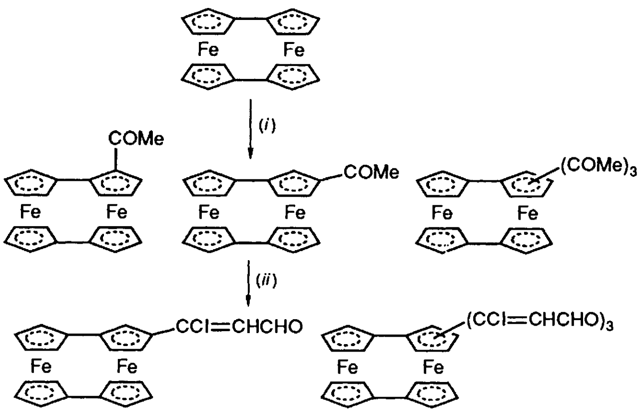
temperature for 1 d gave a dark red solution. Silica gel column chromatography of the concentrated reaction product gave several bands when CH_2Cl_2–ethyl acetate was used as the eluent. The component of the most coloured band was collected and again chromatographed on silica gel with CH_2Cl_2–ethyl acetate–benzene (2:6:2). Recrystallization of the main band component from CH_2Cl_2–hexane afforded an orange-yellow powder, yield 0.28 g (10%) (Found: C, 62.90; H, 4.45. $C_{26}H_{22}Fe_2O_3$ requires C, 63.20; H, 4.50%); ν_{max} 3089, 2923, 1659 (ν_{CO}), 1451, 1357, 1294, 1272, 1237, 1178, 1115, 1050, 966, 900, 856, 829, 622, 509 and 486 cm^{-1} (KBr disc); $\delta_H(CDCl_3)$ 6.2–5.4 (8 H, m, $H^{3,4}$ of ring), 4.7–3.6 (5 H, m, $H^{2,5}$ of ring) and 2.35 (9 H, m, $3CH_3$). These ^1H NMR spectroscopic data indicate that the triacetyl derivative is a mixture of geometric isomers in which all the three acetyl groups were at 2,5 positions (there are seven possible isomers without counting antipodes). We could not separate these isomers by column chromatography and used the material for the electrochemical study without further isolation.

The 1-chloro-2-formylvinyl group was introduced by use of the Vilsmeire reaction on the acetyl derivatives. To a stirred solution of the 3-acetyl derivative (66 mg, 0.16 mmol) in CH_2Cl_2 (10 cm^3) plus dimethylformamide (dmf) (0.9 cm^3) was added slowly a solution of $POCl_3$ (0.17 g, 1.1 mmol) plus dmf (0.9 cm^3) at 0 °C and stirred at 0 °C for 2 h and then at room temperature for 9 h to give a dark brown solution. Addition of 20% sodium acetate aqueous solution to the reaction mixture, extraction with CH_2Cl_2, drying with Na_2SO_4, and column chromatography on silica gel with chloroform as eluent afforded a 3-(1-chloro-2-formylvinyl) derivative, yield 36 mg (35%) (Found: C, 60.20; H, 3.75; Cl, 8.20. $C_{23}H_{17}ClFe_2O$ requires C, 60.50; H, 3.75; Cl, 7.80%); ν_{max} 3086, 2925, 2852, 1665 (ν_{CO}), 1597 [ν(C=C)], 1426, 1265, 1121, 1046, 1030, 1000, 807, 735, 500 and 482 cm^{-1} (KBr disc); $\delta_H(CDCl_3)$ 10.21 (1 H, d, J_{HH} 7 Hz, CHO), 6.47 (1 H, d, CH=CCl), 5.77–4.77 (7 H, m, $H^{3,4}$ of ring) and 4.64–3.49 (8 H, m, $H^{2,5}$ of ring).

A tris(1-chloro-2-formylvinyl) derivative was prepared from the triacetyl derivative in a similar procedure to that described above, yield 19% (Found: C, 54.60; H, 3.30; Cl, 17.30. $C_{29}H_{19}Cl_3Fe_2O_3$ requires C, 55.00; H, 3.00; Cl, 16.80%); ν_{max} 3097, 2925, 2854, 1685 (ν_{CO}), 1586 [ν(C=C)], 1445, 1399, 1386, 1296, 1262, 1191, 1134, 960, 844, 798, 695 and 508 cm^{-1} (KBr disc); $\delta_H(CDCl_3)$ 10.09 (3 H, m, CHO), 6.40 (3 H, m, CH=CCl), 611–5.30 (8 H, m, $H^{3,4}$ of ring) and 4.58–3.74 (5 H, m, $H^{2,5}$ of ring).

Electrochemical Instrumentation and Procedures.—Cyclic voltammetry was carried out with a Toho Technical Research model 2020 potentiostat, 2230 function generator, and Riken Denshi F-35 X-Y recorder. All experiments were performed using standard three-electrode, one-compartment cells equipped with a platinum-wire counter electrode and an Ag–Ag^+ (10 mmol dm^{-3} $AgClO_4$ in 0.1 mol dm^{-3} NBu_4ClO_4–MeCN) reference electrode.[36] The reference electrode was connected to the cell with a 0.1 mol dm^{-3} NBu_4ClO_4–MeCN salt bridge, positioned with its tip near the working electrode. The glassy-carbon rod (outside diameter 3.0 or 5.0 mm) was embedded in Pyrex glass, and the circular cross-section was used as the working electrode. Its surface was polished with 0.3 μm alumina abrasive, sonicated in distilled water and in acetone, dried, and used for the electrochemical measurements. Indium–tin oxide glass electrodes (2 cm^2) were sonicated in diluted aqueous $HClO_4$, in distilled water, and in acetone, dried, and used for the measurements.

The $[Fe_2(C_{10}H_8)_2]$ polymer films were prepared by consecutive electrochemical cycling through the reduction waves of the monomer. Following film deposition, the potential was held at −0.5 V until the current decreased to the background level in order that all the sites be in the neutral II,II form. The polymer-coated electrodes thus made were rinsed with acetonitrile and dried in air. When the sites in the polymer are in the neutral form the coated electrodes can be stored in air for at least 1 week without change in electrochemical behaviour.



Scheme 1 (*i*) MeCOCl, $AlCl_3$ in CS_2 or CH_2Cl_2; (*ii*) $POCl_3$, dmf

Results and Discussion

Preparation of 1-*Chloro*-2-*formylvinyl Derivatives of* $[Fe_2(C_{10}H_8)_2]$.—The electrochemically polymerizable substituent 1-chloro-2-formylvinyl was introduced by the Vilsmeire reaction on the acetyl derivatives, as has been used for ferrocene[37] and cobaltocenium derivatives.[28] The acetyl derivatives were prepared from $[Fe_2(C_{10}H_8)_2]$ by a modified method of Pittman and Surynarayanan.[14] We isolated two geometric isomers of monoacetylated $[Fe_2(C_{10}H_8)_2]$ and one triacetyl derivative. It should be noted that the IR and ^1H NMR data which have been reported for the 3-acetyl derivative[14] are for the 2-acetyl derivative according to our assignment (see Experimental section).[6] When the reaction was carried out with 4 equivalents of the acetylating reagents the trisubstituted derivative was obtained in higher yield than the mono-, di- and tetra-substituted derivatives. The trisubstituted derivative was purified repeatedly by column chromatography, but the sample obtained was a mixture of several geometric isomers judging from its ^1H NMR spectrum. This was employed for the following experiment without further purification.

Reaction of the 3-acetyl and triacetyl derivatives with $POCl_3$ and dmf gave the corresponding 1-chloro-2-formylvinyl (R) derivatives, $[Fe_2(C_{10}H_8)(C_{10}H_{8-n}R_n)]$ (n = 1 or 3) (Scheme 1). They were purified by column chromatography and identified by elemental analysis, ^1H NMR and Fourier-transform IR spectra. The ^1H NMR spectrum of the trivinyl derivative showed that the aldehyde proton signal at δ *ca.* 10 was split into nine peaks and that the ratio of the number of $H^{2,5}$ ring protons to that of the $H^{3,4}$ ring protons was 5:8. This indicates that the triacetyl derivative is a mixture in which three 1-chloro-2-formylvinyl moieties are bound at the 2,5 positions of the fulvalene moieties.

Electrode Film Formation.—The 1-chloro-2-formylvinyl derivatives form electrode films by reduction in acetonitrile, as do derivatives of ferrocene and cobaltocenium salts.[21–23] Fig. 1(*a*) and (*b*) show the cyclic voltammograms obtained during the reductive polymerization of $[Fe_2(C_{10}H_8)(C_{10}H_{8-n}R_n)]$ (n = 1 or 3 respectively) at glassy carbon in 0.1 mol dm^{-3} NBu_4ClO_4–MeCN. Both derivatives show two redox waves due to the monomeric II,III–II,II and the III,III–II,III couples in the first scan. The redox potentials are more positive when n = 3 (0.26 and 0.82 V *vs.* Ag–Ag^+) than for n = 1 (−0.01 and 0.53 V) owing to substitution of the larger number of CCl=CHCHO electron-withdrawing groups. The scarce reversibility for the second oxidation when n = 3 indicates the instability of the dication form, III,III, caused by these electron-withdrawing groups. Reduction of the CCl=CHCHO groups occurs at −1.8 and −2.1 to −2.2 V for both n = 1 and 3. When the negative

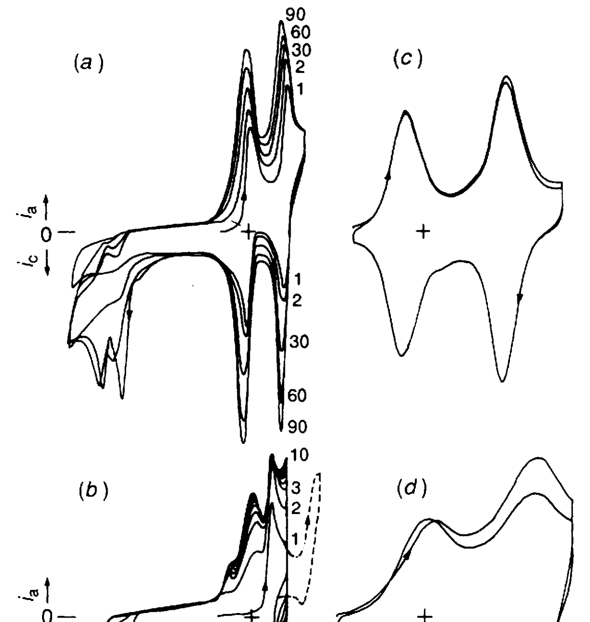


Fig. 1 Reductive cyclic voltammetry of 0.3 mmol dm^{-3} (*a*) [$Fe_2(C_{10}H_8)(C_{10}H_7R)$] and (*b*) [$Fe_2(C_{10}H_8)(C_{10}H_5R_3)$] at a glassy carbon electrode in 0.1 mol dm^{-3} NBu_4ClO_4–MeCN at 0.1 V s^{-1}, and cyclic voltammetry of the corresponding polymer electrode films (*c*) and (*d*) in 0.1 mol dm^{-3} NBu_4ClO_4–MeCN at 0.1 V s^{-1}. Numbers in (*a*) and (*b*) refer to the cyclic scans. The broken line in (*b*) shows a voltammogram when the positive limit of the potential sweep was 0.85 V *vs.* Ag–Ag$^+$. S = 3.53 μA (50 μA cm^{-2})

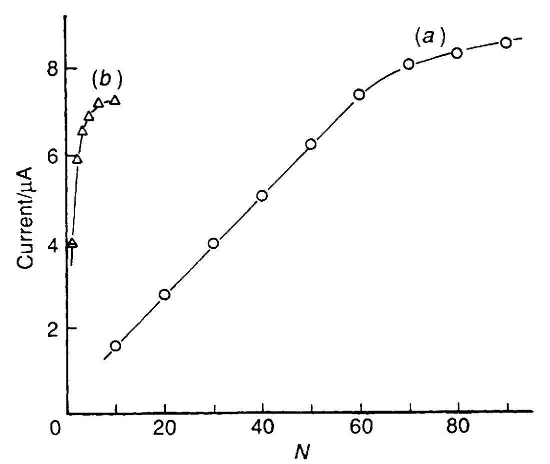


Fig. 2 Dependency of the peak current for the II,II oxidation wave due to the polymer electrode film formed in reductive cyclic voltammetry of 0.3 mmol dm^{-3} (*a*) [$Fe_2(C_{10}H_8)(C_{10}H_7R)$] and (*b*) [$Fe_2(C_{10}H_8)(C_{10}H_5R_3)$] in 0.1 mol dm^{-3} NBu_4ClO_4–MeCN at 0.1 V s^{-1}, on the number of cyclic scans N

limit of the potential scan is more negative than the reduction potential of the CCl=CHCHO groups the peak currents of the two redox waves increase and the peak potentials shift in the negative direction with increase in scan number in the cyclic voltammogram for [$Fe_2(C_{10}H_8)(C_{10}H_7R)$] in Fig. 1(*a*). This indicates the formation of an electroactive film, the redox potential of which is more negative than that of the monomer, on the electrode surface. The negative potential shift can be interpreted in terms of the change in structure of the substituent from CCl=CHCHO to $CCHCH_2OH$ in the electrochemical reduction process, where acetonitrile or a trace amount of water impurity may act as the proton source.[28] The larger number of CCl=CHCHO groups when n = 3 results in a wider separation of redox peak potentials between the monomer and its polymer film as shown in the cyclic voltammogram in Fig. 1(*b*), where the redox wave due to the polymer appears as the new growing anodic and cathodic peaks around 0.01 V, 250 mV more negative than that of the monomer.

The relation between the anodic peak height for the II,III–II,II couple of the electrodeposited polymer with the number of cyclic scans is given in Fig. 2. The polymerization when n = 3 is more rapid than that when n = 1. A similar behaviour has been observed for the ferrocene derivatives [$Fe(C_5H_5)(C_5H_4R)$] and [$Fe(C_5H_4R)_2$].[28] These results are reasonable because the polymerization of a compound with more active sites such as when n = 3 is more rapid than that with fewer sites such as when n = 1. The peak growth with increasing scan number levels off after 60 scans for n = 1 and seven scans for n = 3. This corresponds to the disappearance of the reduction waves for the CCl=CHCHO moieties in the cyclic voltammogram (see Fig. 1). The termination of polymerization by a decrease in the number of pin-holes and/or in permeability of the film formed has often been observed in electropolymerization reactions.[38,39]

Electrochemical Properties of [$Fe_2(C_{10}H_8)_2$] *Electrode Films.* —Cyclic voltammograms of the electrode films, when n = 1 or 3 formed by the consecutive potential scans as shown in Fig. 1(*a*) and (*b*), in 0.1 mol dm^{-3} NBu_4ClO_4–MeCN, are displayed in Fig. 1(*c*) and (*d*), respectively. When the scan rate is below 0.4 V s^{-1} for n = 1 and 1.0 V s^{-1} for n = 3 the peak-to-peak separation, ΔE_p, remains constant and the peak current varies linearly with scan rate, as expected for the reaction of surface-localized material. The electrochemical properties of [$Fe_2(C_{10}H_8)_2$] films formed at indium–tin oxide are similar to those at glassy carbon. Surface profilometry analysis indicated that both the polymer films on the oxide had smooth surfaces and uniform film thicknesses in the range 200–900 Å. The concentration of electroactive sites in the polymer, c, can be calculated from the film thickness and the surface coverage of electroactive sites, Γ, estimated from the cyclic voltammogram.[28] The electrochemical parameters of the electrode films estimated from the cyclic voltammograms at a scan rate of 0.1 V s^{-1} and the film thicknesses are given in Table 1. The concentration of electroactive sites in the film is 3×10^{-4} mol cm^{-3} when n = 1 and 5×10^{-4} mol cm^{-3} when n = 3, similar to values reported for ferrocene derivatives.[28]

A significant difference is seen in the potential width at peak half-height, $\Delta E_{\frac{1}{2}}$, between the films when n = 1 and 3: the values for the latter are larger than those of the former and all are larger than 90 mV. These values >90 mV (at 25 °C) can be attributed to the high film resistance, repulsive site–site interactions within the film, sluggish charge-transfer reactions at the electrode, and/or a scattered distribution of redox sites with different formal potentials.[40–44] More repulsive site–site interactions when n = 3 can occur judging from the difference in c values (see Table 1). Another possible rationale for the large $\Delta E_{\frac{1}{2}}$ when n = 3 is a distribution of redox sites with various redox potentials because the material is a mixture of geometric isomers as described above.

Spectroelectrochemistry.—Changes in the visible spectrum of the film (n = 3) on an indium–tin oxide electrode in 0.1 mol dm^{-3} NBu_4ClO_4–MeCN with the electrode potential and its

Table 1 Redox properties of $[Fe_2(C_{10}H_8)_2]$ derivatives[a]

	II,III–II,II			III,III–II,III			
Compound	$E^{\circ\prime b}$/V	ΔE_p/mV	$\Delta E_{\frac{1}{2}}$/mV	$E^{\circ\prime b}$/V	ΔE_p/mV	$\Delta E_{\frac{1}{2}}$/mV	c/mol cm^{-3}
$[Fe_2(C_{10}H_8)(C_{10}H_7R)]$	−0.010	60	—	0.053	60	—	—
$[Fe_2(C_{10}H_8)(C_{10}H_5R_3)]$	0.260	80	—	0.820	—	—	—
poly-$[Fe_2(C_{10}H_8)(C_{10}H_7R)]$[c]	−0.110	20	180	0.470	20	160	—
d	−0.120	40	160	0.440	60	160	3.4×10^{-4}
poly-$[Fe_2(C_{10}H_8)(C_{10}H_5R_3)]$[c]	−0.013	25	300	0.610	75	300	—
d	0.050	50	280	0.585	70	290	5.4×10^{-4}

[a] Cyclic voltammetry at glassy carbon in 0.1 mol dm^{-3} NBu_4ClO_4–MeCN at a scan rate of 0.1 V s^{-1}. [b] *versus* Ag–Ag$^+$. [c] At glassy carbon. [d] At indium–tin oxide.

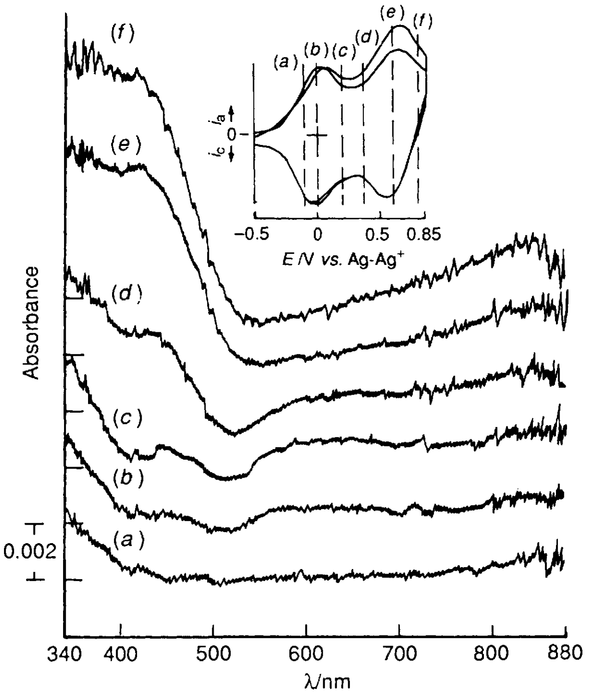


Fig. 3 Differences in the visible spectrum of poly-$[Fe_2(C_{10}H_8)(C_{10}H_5R_3)]$ at indium–tin oxide at −0.1, 0, 0.2, 0.4, 0.6 and 0.8 V *vs.* Ag–Ag$^+$ from that at −0.5 V, and a cyclic voltammogram of the electrode film. Horizontal lines are shifted upwards from (*a*) to (*f*) by 0.002 absorbance units

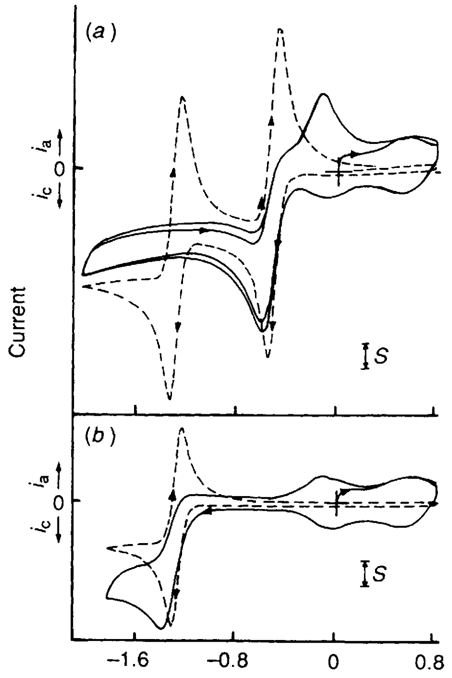


Fig. 4 Cyclic voltammetry of (*a*) dcbq (2 mmol dm^{-3}) and (*b*) $[Co(C_5H_5)_2]PF_6$ (2 mmol dm^{-3}) at poly-$[Fe_2(C_{10}H_8)(C_{10}H_5R_3)]$ coated (——) and uncoated (– – –) electrodes in 0.1 mol dm^{-3} NBu_4ClO_4–MeCN at 0.1 V s^{-1}. S = 10 and 5 μA for the uncoated and coated electrode, respectively

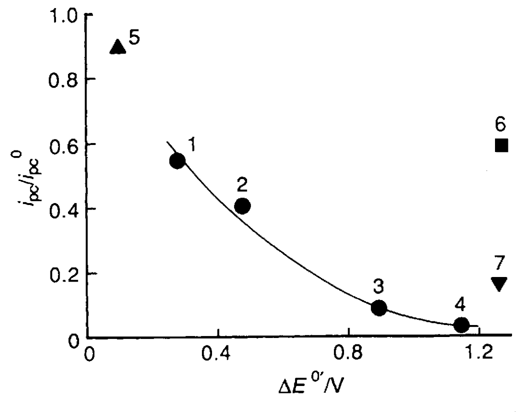


Fig. 5 Plots of i_{pc}/i_{pc}° *vs.* $\Delta E^{\circ\prime}$ for the cyclic voltammograms of redox solutes at a poly-$[Fe_2(C_{10}H_8)(C_{10}H_5R_3)]$ coated electrode; 1, tetrabromo-*p*-benzoquinone; 2, dcbq; 3, 2-methyl-*p*-benzoquinone; 4, tetramethyl-*p*-benzoquinone; 5, tcnq; 6, $[Co(C_5H_5)_2]PF_6$; 7, methyl *p*-nitrobenzoate

cyclic voltammogram are displayed in Fig. 3. In the potential region of the first redox wave (−0.4 to 0.2 V) the absorption at 600 nm increases and that at 520 nm decreases according to the positive potential shift (hence the degree of oxidation). The peak at 600 nm is a typical d–d transition band of the II,III form,[4,13] and that at 520 nm corresponds to the II,II form, and thus the spectral change noted above exactly indicates the oxidation process from the II,II to II,III forms. These changes cease at 0.2 V which is the positive potential edge of the first oxidation wave, as shown in the cyclic voltammogram in Fig. 3. In the potential region of the second redox wave (0.3–0.85 V) the peak at 600 nm decreases and that at 465 nm increases according to the positive potential shift. This change corresponds to the oxidation of the II,III to the III,III form as the peak at 465 nm is due to the latter.[4] Similar spectral changes corresponding to the redox behaviours seen in the cyclic voltammogram were observed when $n = 1$.

The amount of $[Fe_2(C_{10}H_8)_2]$ sites in each film, Γ, was evaluated from the spectral changes shown in Fig. 3 and the absorption coefficient, ε (dm^3 mol^{-1} cm^{-1}), assuming that the values of ε are similar to those of unsubstituted $[Fe_2(C_{10}H_8)_2]$: 370 at 600 nm for II,III and 2755 at 475 nm for III,III. The Γ values thus obtained were 2.5×10^{-9} and 2.8×10^{-9} mol cm^{-2} for peaks at 600 and 475 nm, respectively. These values are consistent with the value, 2.5×10^{-9} mol cm^{-2}, obtained from the cyclic voltammogram.

Charge-transport Properties of the $[Fe_2(C_{10}H_8)_2]$ *Polymers.*—In Fig. 4 are displayed cyclic voltammograms of 2,6-dichloro-*p*-benzoquinone (dcbq) and cobaltocenium tetrafluoroborate $[Co(C_5H_5)_2]PF_6$ at poly-$[Fe_2(C_{10}H_8)(C_{10}H_5R_3)]$ coated and uncoated glassy carbon electrodes in 0.1 mol dm^{-3} NBu_4ClO_4–MeCN. Only a cathodic wave is seen at the formal potential of the solutes at the coated electrode, although they undergo reversible redox reactions at the uncoated electrode. A small anodic wave is observed at *ca.* −0.2 V *vs.* Ag–Ag$^+$, the negative limit of the oxidation wave of the II,II form, indicating that the oxidation of solutes is mediated by the oxidation of the latter. It should be noted that the second reduction peak of dcbq due to dcbq$^-$–dcbq^{2-} does not appear at the coated electrode [Fig. 4(*a*)]. Similar voltammograms can be observed for organic electron acceptors such as other *p*-benzoquinones, methyl *p*-nitrobenzoate and tcnq. We have previously reported this kind of charge-transport control by electrodeposited polyferrocene[26,28] and polycobaltocenium films.[27] A kinetic study of the poly[1,1′-bis(chloromethyl)-ferrocene] system has suggested that these irreversible charge-transport phenomena are not caused by charge-controlled selective permeation within the film but by rate-limiting electron transfer between the film-surface electroactive sites and the redox solutes by way of charge-transfer complexation.[29] The fact exhibited in Fig. 4 that similar electrochemical behaviours are observed for both *neutral* benzoquinones and *cationic* cobaltocenium salt at the poly-$[Fe_2(C_{10}H_8)(C_{10}H_5R_3)]$ coated electrode again deny the possibility of the permeation mechanism.

The relation between the normalized peak current for the reduction of redox solutes, $i_{pc}/i_{pc}{}^{\circ}$, where i_{pc} and $i_{pc}{}^{\circ}$ represent the cathodic current for the reduction of solutes at a poly-$[Fe_2(C_{10}H_8)(C_{10}H_5R_3)]$ coated and uncoated glassy carbon electrode, respectively, and the difference in formal potentials, $\Delta E^{\circ\prime} = \{E^{\circ\prime}(\text{II,III–II,II})$ in poly-$[Fe_2(C_{10}H_8)(C_{10}H_5R_3)] - E^{\circ\prime}$(solute)$\}$, is displayed in Fig. 5. A gradual decrease with negative shift of the formal potential is observed for *p*-benzoquinones. This indicates that the current value (hence the reaction rate) is governed by the thermodynamics of electron transfer between the solutes and poly-$[Fe_2(C_{10}H_8)(C_{10}H_5R_3)]$. Data for solutes other than *p*-benzoquinones such as $[Co(C_5H_5)_2]PF_6$, methyl *p*-nitrobenzoate and tcnq lie apart from the curve for *p*-benzoquinones. This indicates that not only the electron affinity relating to the formal potential but also the structures of the electron acceptors are important in determining the electron-transfer rate. It is concluded that the kinetics of reduction of the organic and organometallic electron acceptors at the poly-$[Fe_2(C_{10}H_8)(C_{10}H_5R_3)]$ coated electrode are controlled by the electron-transfer reactions between the surface complex sites in the film and the redox solutes, which occurs probably *via* charge-transfer complexation.[45]

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