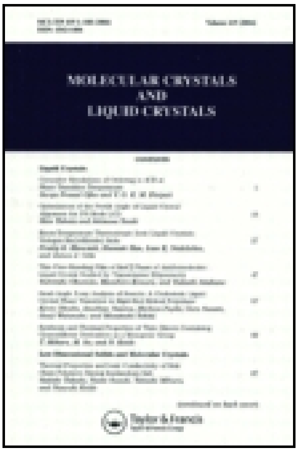

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Oxidative Electropolymerization of Metal Schiff-Base Complexes

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Oxidative Electropolymerization of Metal Schiff-Base Complexes

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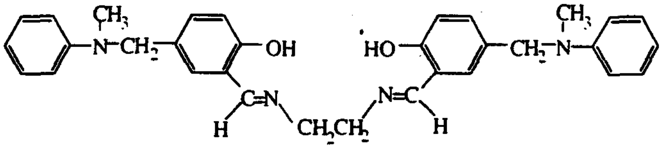
New electropolymerizable metal Schiff-base complexes (M = Ni, Co, or Mn) were prepared for use in polymer modified electrodes by incorporating two N,N-dimethylaniline-like moieties onto the periphery of the *salen* (*salen* = ethylenebis(salicyldiminato)) ligand. Oxidative electropolymerization appears to occur by the tail-to-tail coupling of aromatic amine cation radicals on adjacent molecules near the electrode surface. The electrochemistry of the resulting redox-conductive polymer film in solvent and supporting electrolyte with no monomer present resembles that for the respective monomer in solution. The voltammetric response for the manganese complex polymer is generally poor but can be enhanced by the addition of a redox mediator tetracyanoquinodimethane (TCNQ) to the solution in which the electrode is immersed. Utilizing the mediation reaction approach, approximately twenty five percent of the available manganese in the polymer film was electrochemically active.

The modification of electrode surfaces with polymers containing transition metal complexes is currently an intensive area of chemical research.[2] Potential uses of these redox conducting films include electrocatalysis, solid state devices, and patterning of electrodes among others.[3] Current research on the fundamentals of electrochemical properties of the metal complex polymer films has led to a general understanding of the key factors that govern their electrochemical responses.[2,3] Further advances may be correlated with design and synthesis of additional metal complex polymeric materials.

One of the more successful methods for forming ultra-thin polymeric metal complex films (<<1 μm) is electropolymerization. We have reported a number of electrochemical and synthetic studies of this method that utilized metal complexes containing bipyridine or bipyridine-like ligands.[4] The essential strategy is to incorporate a coupling or polymerizing functional group on the perimeter of the metal complex ligand framework. This functional group is activated toward coupling/polymerization upon electrochemical oxidation or reduction of the metal complex, leading to polymer film formation on the electrode surface. There has been a recent emphasis on extending this strategy to other types of metal complexes for use in polymer modified electrodes. Metalloporphyrins[5] and related macrocyclic complexes[6] have been successfully electropolymerized onto electrode surfaces and some interesting chemistry has emerged.

We report here a further extension of electropolymerization chemistry to the preparation of metal Schiff-base complex polymers as new materials for polymer modified electrodes. There appears to be only one previous report on electrochemistry of a metal Schiff-base complex in a polymer film.[7] A unique aspect to our films is that the polymer film is formed by a series of well defined dimerization reactions upon electro-oxidation. Polymerization is accomplished by incorporating two pseudo dimethylaniline moieties on the Schiff-base ligand's perimeter, as in I; each dimethylaniline can form a tail-to-tail coupled dimer[9] with a dimethylaniline of another complex, forming a polymer in which the metal coordination site is part of the polymer chain. In the present study M = Ni, Co, or Mn.



I

Metal Schiff-base complexes are interesting for use in polymer modified electrodes because they are relatively easy to prepare and derivatize,[9] virtually any transition metal can be incorporated into the ligand, and the complexes have demonstrated catalytic chemistry both in solution and when present in polymer films.[10] Furthermore they complement the metalloporphyrins in that they are strictly planar molecules and can be axially coordinated in some cases. This may for example allow new insight into how the morphology of the metal complex affects film electrochemistry.

EXPERIMENTAL

Reagent grade chemicals were used throughout with no additional purification. Solvents were dried over 4A molecular sieves when appropriate and deaerated with argon. The 5-chloromethyl salicylaldehyde,[11] II, was prepared by the method of Wulff and Akelah. All intermediates were characterized by elemental analysis (Galbraith Laboratories, Knoxville, TN), and ^1H NMR (except the Mn and Co Schiff-base complexes which are paramagnetic), IR, and UV-vis spectroscopy; these data are collected in Tables I and II. Metalations were accomplished by reacting the appropriate M(II) acetate salt in refluxing methanol under an inert atmosphere. Manganese(II) was oxidized to Mn(III) by air or with $[CpFe_2][PF_6]$ following initial formation of the Mn(II) Schiff-base complex.

Electrochemical measurements in the three electrode mode were made using locally designed instrumentation. Platinum electrodes were used as working electrodes and all potentials were measured relative to the sodium chloride saturated calomel electrode (SSCE). Supporting electrolyte, $[NEt_4][BF_4]$ was prepared according to Sawyer and Roberts.[12]

RESULTS AND DISCUSSION

Synthesis. The general scheme for synthesizing the derivatized Schiff-base, dubbed *meansalen*, is shown in Figure 1. Preparation of the

TABLE I

Elemental analysis.

		Anal. calcd (found)	
Compound	%C	%H	%N
$C_{15}H_{15}NO_2$ (III)	74.7(73.3)	6.3(6.1)	5.80(5.4)
$C_{32}H_{34}N_4O_2$ (IV)	75.9(74.2)	6.8(7.0)	11.1(10.6)
$C_{32}H_{32}N_4O_2Ni$ (V)	68.2(69.7)	5.7(6.2)	9.9(9.9)
$C_{32}H_{32}N_4O_2Co$ (VI)	68.2(70.1)	5.7(6.1)	9.9(9.8)
$C_{32}H_{32}N_4O_2MnPF_6$ (VII)	54.5(56.0)	4.6(5.2)	7.9(7.3)

TABLE II

^{1}H NMR and UV-vis spectra

Cmpd	Solvent	^{1}H NMR[a] ppm {mult, area, *J*(Hz)}	UV-vis Solvent	 λmax[b](ε)[c]
III	CD_3CN	10.8(s,1); 9.8(*s*,1); 7.45(*dd*,1,J_1=17,J_2=2); 7.21–7.12(*m*,2); 6.92(*d*,1,*J*=8.6) 6.79–6.63(*m*,3); 4.5(*s*,2); 3.0(*s*,3)	CH_3CN 333(3.13)	254(25.8); 309(3.48)
IV	$(CD_3)_2SO$	13.23(*s*,1); 8.52(*s*,1); 7.25–7.07(*m*,4); 6.82–6.55(*m*,4); 4.45(*s*,2); 3.86(*s*,2); 2.94(*s*,3)	CH_3CN	255(50.1); 310(11.1)
V	$(CD_3)_2SO$	7.82(*s*,1); 7.16–7.02(*m*,4); 6.72–6.54(*m*,4); 4.37(*s*,2); 3.34(*s*,2); 2.93(*s*,3)	CH_3CN	258(56.4); 310(11.5); 342(8.8); 410(5.27)
VII			CH_3CN	254(56.4); 284(23.4); 314(13.9); 416(4.42); 359(6.24)

[a] Relative to external Me_4Si.
[b] λmax in nm.
[c] $\epsilon \times 10^{-3}$ M^{-1} cm^{-1}

ligand is relatively straightforward and all reactions yield greater than 75% of product with no apparent contamination from other species. Furthermore, aside from preparation of the species II which requires two days, subsequent reactions can be performed in a matter of a few hours. All of these factors make these Schiff-base complexes highly attractive for use in polymer modified electrode studies.

Electrochemistry. In potential regions more negative than those leading to electropolymerization, the electrochemical responses of the Ni, Co, and Mn metal complex monomer solutions are analogous to data using the unsubstituted Schiff-base ligand *salen* (*salen* = N,N′-ethylenebis(salicyldiminatio)). Table III compares the formal potentials for the metal *meansalen* complexes in $CH_3CN/[NEt_4][BF_4]$ to the values for the complementary *salen* complexes. It is apparent that the presence of the amine substituent has a minor effect on the formal potential of the complex. Shown in Figures 2a, 3a, and 4a are the

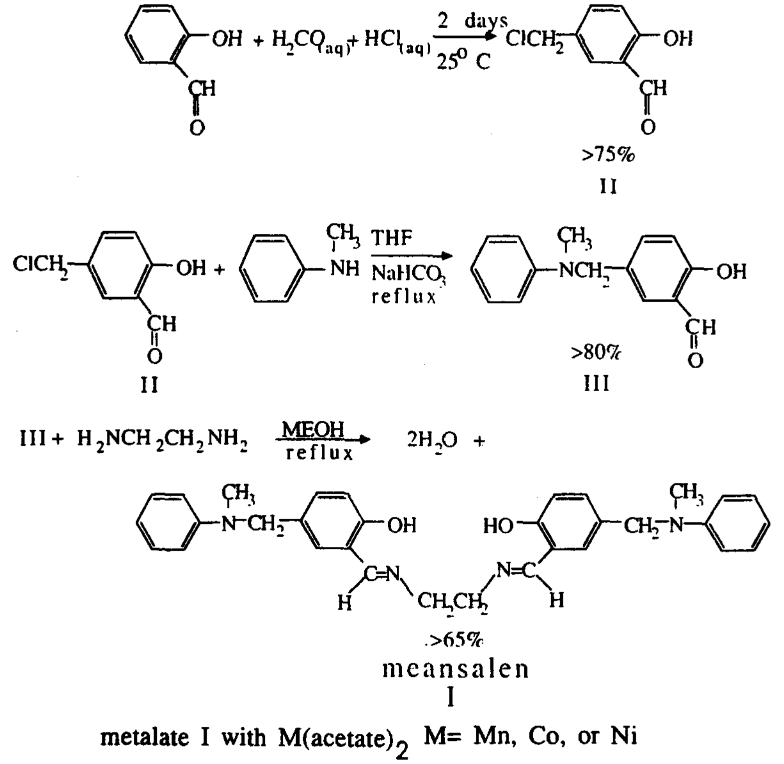


FIGURE 1 Synthetic scheme for preparation of the ligand *meansalen*.

TABLE III

Electrochemical data[a,b]

Compound	Electrolyte	E^0(V)	ΔE_p(mV)	Couple
Ni(meansalen)	$[NEt_4][BF_4]$	−1.69	60	Ni(II/I)
Co(meansalen)	$[NEt_4][BF_4]$	−1.30	55	Co(II/I)
		0.21	160	Co(III/II)
$[Mn(meansalen)][PF_6]$	$[NEt_4][BF_4]$	−0.24	160	Mn(III/II)
Ni(salen)	$[NEt_4][BF_4]$	−1.72	61	Ni(II/I)
Co(salen)	$[NBu_4][ClO_4]$	−1.23[c,d]	—	Co(II/II)
	$[NEt_4][ClO_4]$	0.20[e]	—	Co(III/II)
$[Mn(salen)][PF_6]$	$[NEt_4][ClO_4]$	−0.25	130	Mn(III/II)

[a] CH_3CN solution.

[b] *vs* SSCE reference (sodium chloride saturated calomel electrode).

[c] G. Costa, A. Puxeddu and E. Reisenhofer, *J. Chem. Soc., Dalton Trans.*, 2034 (1973).

[d] DMF solution.

[e] R. P. Hanzlik and D. F. Smith, Jr., *J. Chem. Soc., Chem. Commun.*, 528 (1974).

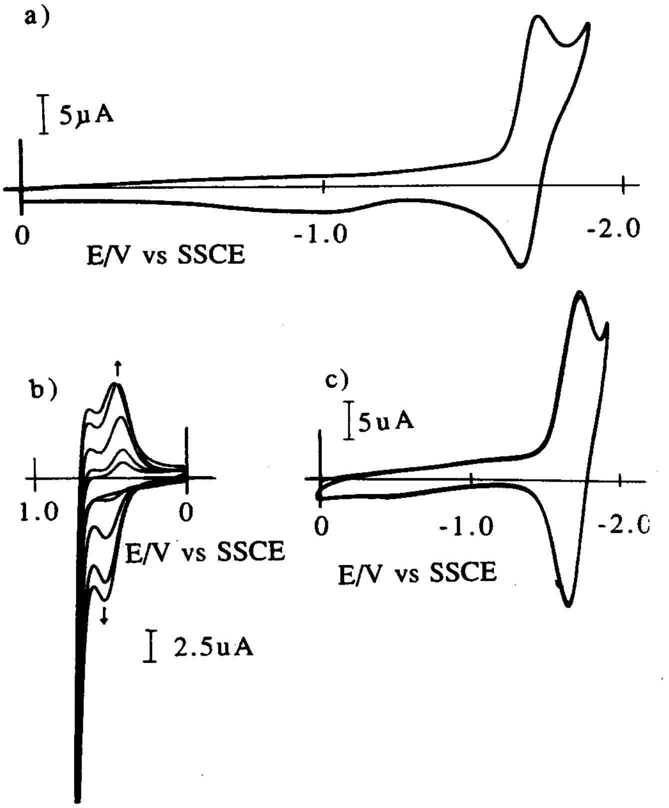


FIGURE 2 Curve a) Cyclic voltammogram of a 1.0 mM solution of Ni(meansalen). Curve b) Electropolymerization of a 1.0 mM solution of Ni(meansalen). Scans 1, 2, 5, 10 and 15 are shown. Curve c) Voltammetric response of a poly-Ni(meansalen) film in solvent and supporting electrolyte with no monomer present. $\Gamma_{app} = 2.0 \times 10^{-9}$ mole/cm^2. All voltammograms on Pt electrodes at 100 mV/s in 0.1 M. [NEt$_4$][BF$_4$]/CH$_3$CN vs. SSCE reference.

cyclic voltammograms of the metal complexes Ni(meansalen) IV, Co(meansalen) V, and [Mn(meansalen)][BF$_4$] VI, respectively.

Electropolymerization. The oxidative coupling of the radical cations of N,N-dimethylaniline (DMA), VII, which leads to the formation of the dimer N,N,N'N'-tetramethylbenzidine[8] (TMB), VIII, Eq. 1, should represent a model for oxidative coupling of I. The electrochemistry of DMA is shown in Figure 5. It can be seen that the formal potential, E°, for the TMB$^{+/o}$ couple appears at 0.45 V. There is also a cathodic peak for the reduction of TMB^{++} to the monocation at 0.6 V but the complementary oxidation peak is obscured by oxidation

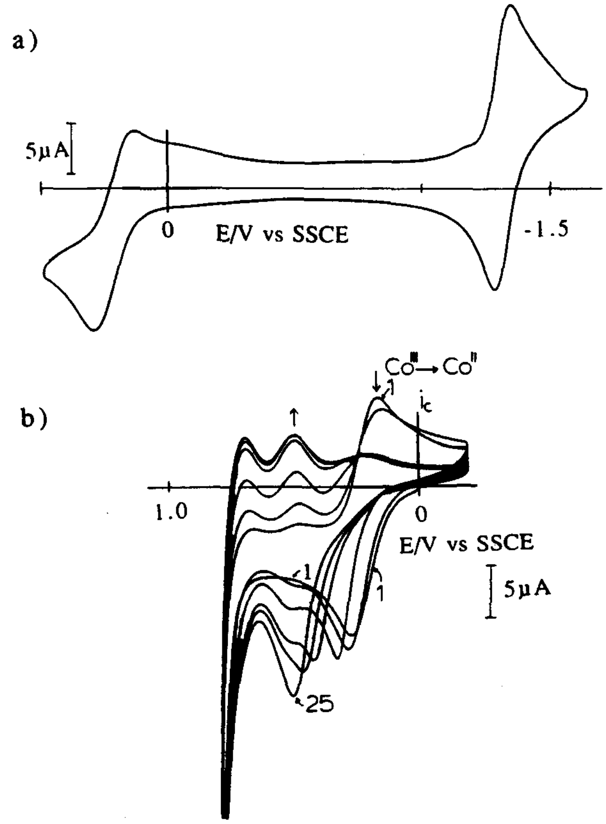


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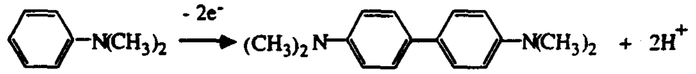
FIGURE 3 Curve a) Cyclic voltammogram of a 1.0 mM solution of Co(meansalen). Curve b) Electropolymerization of a 1.0 mM solution of Co(meansalen). Scans 1, 4, 10, 19, 22, and 25 are shown. Curve c) Voltammetric response of a poly-Co(meansalen) film in solvent and supporting electrolyte with no monomer present. $\Gamma_{app} = 1.8 \times 10^{-9}$ mole/cm^2. See text for details regarding the current burst observed in the scan labeled 1. Curve d) Voltammetric response of a poly-Co(meansalen) film that had been initially reduced at negative potentials as in curve 3c) and then scanning was initiated to positive voltages (scan 1). All voltammograms on Pt electrodes at 100 mV/s in 0.1 M $[NEt_4][BF_4]/CH_3CN$ vs SSCE reference electrode.

of the DMA monomer. Thus we will rely on the appearance of the peak corresponding to the $TMB^{+/0}$ couple to aid in determining if the oxidized Schiff-base complexes form an analogous dimer.



Eq. (1)

The oxidative electropolymerizations of the Ni, Co, and Mn com-

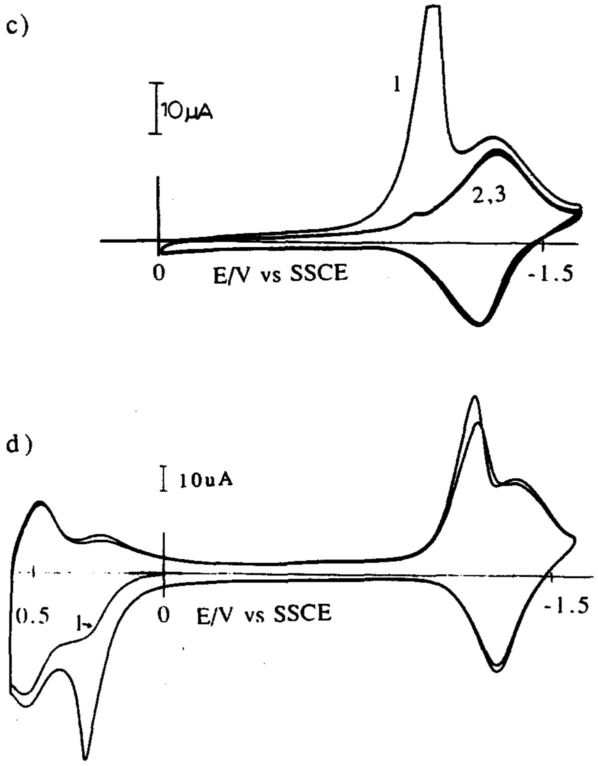


FIGURE 3 CONTINUED

plexes are shown in Figures 2b, 3b, and 4b with data summarized in Table IV. The non-metallated ligand itself shows no electrochemical waves except at positive potentials where the DMA-like substituent is oxidized but this reaction interestingly does not yield a polymer film. The metallated complexes do form electroactive polymers as evidenced by the growing current-potential patterns as the electrode potential is repetitively scanned as in Figures 2b, 3b, and 4b. The nickel and cobalt complexes are electropolymerized by extending the potential scan to 0.8 V while a slightly more positive potential (0.9 V) is required for the manganese complex. The more positive potential for the manganese complex probably arises from the cationic nature of this complex.

It is significant that all the voltammograms exhibit during electropolymerization, peaks at about 0.5 V (Table IV) which is very close to the value (0.45 V) for the $TMB^{+/o}$ couple discussed above. We

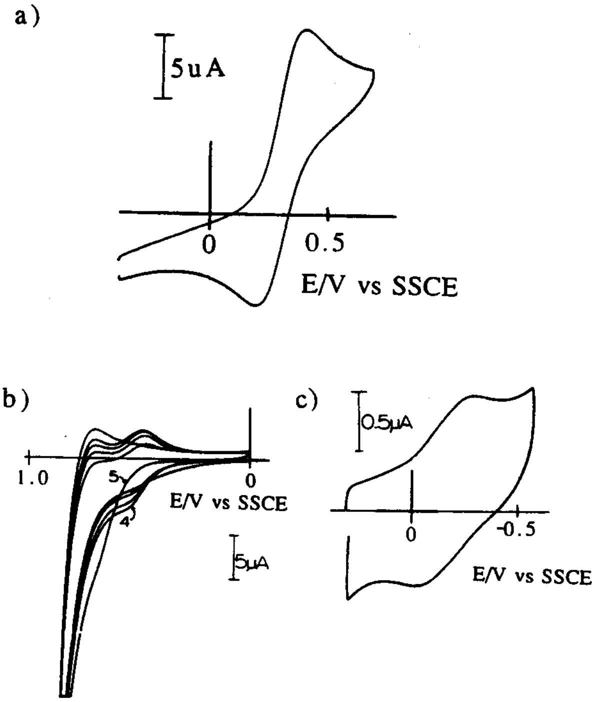


FIGURE 4 Curve a) Cyclic voltammogram of a 1.0 mM solution of [Mn(meansalen)][BF_4]. Curve b) Electropolymerization of a 1.0 mM solution of [Mn(meansalen)][BF_4]. Scans 1 through 5 are shown. Curve c) Voltammetric response of a poly-[Mn(meansalen)][BF_4] film in solvent and supporting electrolyte containing no monomer. $\Gamma_{app} = 3.4 \times 10^{-9}$ mole/cm^2 based on the TMB$^{+/0}$ couple in this film. All voltammograms on Pt electrodes at 100 mV/s in 0.1 M [NEt_4][BF_4]/CH_3CN vs. SSCE reference electrode.

take this as strongly suggestive evidence that the electropolymerization reaction proceeds by the tail-to-tail coupling of the aromatic amine cation radical derived from oxidation of I. The rate of electropolymerization (as measured by the increase in the current-potential patterns) appears to be the same for the three metal complexes and in all instances becomes almost negligible after about twenty five to thirty cyclical scans. We believe that growth of the polymer film is eventually limited by a slowing of the rate of charge transport through the film and consequently of the current that initiates fresh monomer for polymer formation.

The electropolymerization current-potential patterns for the Ni and Mn complexes are similar and fairly straightforward. A rising oxi-

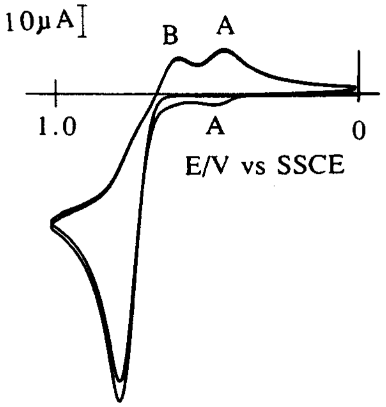


FIGURE 5 Cyclic voltammogram at a Pt electrode (100 mV/s) of a 1.0 mM solution of N,N-dimethylaniline in 0.1 M $[NEt_4][BF_4]/CH_3CN$ vs. SSCE reference electrode. Peaks labeled A are from the $TMB^{+/0}$ couple and the peak labeled B is the $TMB^{+/2+}$ couple. See text for details.

dation wave for monomer oxidation and an increasing envelope of $TMB^{+/0}$-like voltammetry in the accumulating polymer film. The pattern for the cobalt complex is more complicated because the TMB-like dimer waves interact with the Co(II/III) metal complex wave. The potential required to oxidize the DMA-like moiety in I is sufficiently positive to also oxidize the cobalt(II) centers to cobalt(III). The wave corresponding to the reverse reduction step, Co(III/II) (labeled in Figure 3b), rapidly diminishes after only a few scans, apparently a result of a slow electron transport rate (slow self exchange rate) for the Co(III/II) couple. Thus the polymer is being grown with the cobalt already in the film mainly in the Co(III) oxidation state. The Co(II/III) oxidation for fresh diffusing monomer

TABLE IV

Electrochemical data for polymer films[a,b,c]

Compound	$E_{polymerize}$	$E^0(TMB^{+/0})$	E^0(metal)	ΔE_p^d
TMB		0.450		
Ni(meansalen)	0.80	0.495	−1.69	50
Co(meansalen)	0.80	0.505	−1.28	60
			0.28	80
$[Mn(meansalen)][PF_6]$	0.90	0.565	−0.155	230

[a] $CH_3CN/[NEt_4][BF_4]$ solution.
[b] *vs* SSCE reference.
[c] Potentials in volts.
[d] ΔE_p in mV.

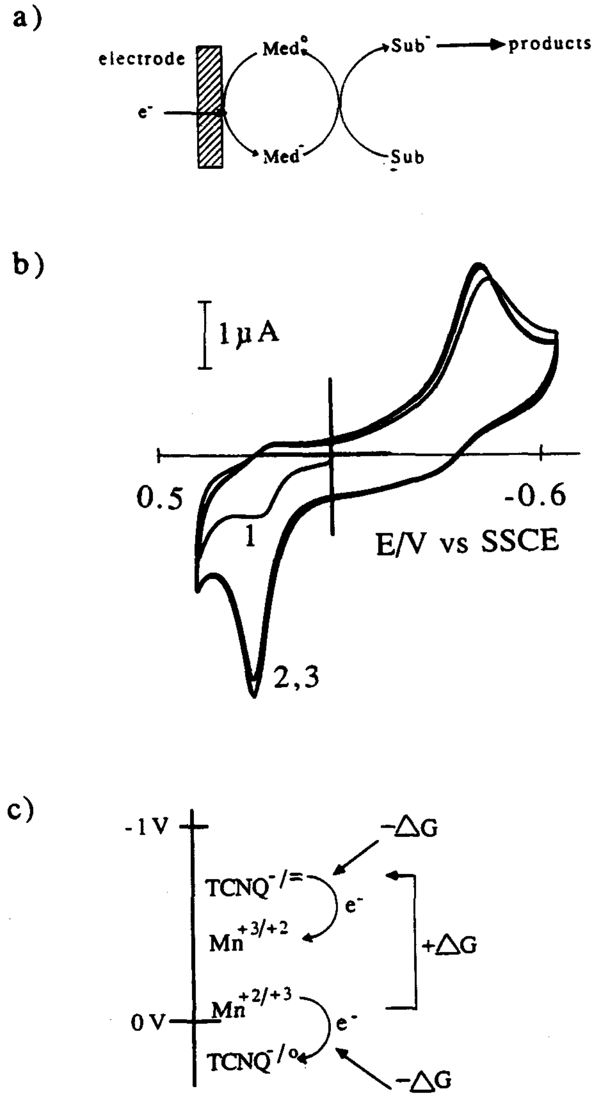


FIGURE 6 a) General scheme for a reductive electron transfer mediated reaction. (Sub = substrate and Med = mediator) b) Cyclic voltammogram (100 mV/s) of a poly-[Mn(meansalen)][BF_4] film contacted by a solution (0.1M [NEt_4][BF_4]/CH_3CN) containing a small quantity of [Li][TCNQ]. Scanning was initiated to positive voltages (labeled 1). See text for details. $\Gamma_{app} = 8 \times 10^{-10}$ mole/cm^2 for the mediated Mn(III/II) reduction. Value obtained by extrapolation to zero scan rate and subtracting the charge due to the TCNQ$^{-/2-}$ couple. c) Pseudo-energy level diagram to describe the electron transfer mediation reaction between [Li][TCNQ] and the manganese centers in poly-[Mn(meansalen)][BF_4].

gradually shifts during the electropolymerization to more positive potentials and eventually merges with the $TMB^{+/o}$ oxidation peak. This effect may arise from the increasing positive charge of the film as it is grown making oxidation of the monomer cobalt complex more difficult, but more likely slow delivery of electrons at the Co(II/III) potential (caused by the slow Co(II/III) self exchange)[13] causes reaction at that potential to become inefficient. However, electron transport by the $TMB^{+/o}$ and/or $TMB^{+/2+}$ reaction is relatively fast and thus the TMB oxidation mediates the oxidation of the cobalt(II) monomer in solution. However as the film thickness and positive charge of the film increase the mediation process becomes more difficult.

Film electrochemistry. When the polymer films are transferred to CH_3CN solutions that contain only supporting electrolyte and no monomer, all of the films exhibit electrochemical responses which are reminiscent of the corresponding monomer in solution: Figures 2c, 3c, d, and 4c, and Table IV.

poly-Ni(meansalen). The cyclic voltammogram of the nickel complex polymer is similar to the monomer complex (Figures 2a vs. 2c) in solution and consists of a wave for the Ni(II/I) couple at $E^{\circ} = -1.69$ V with a peak splitting of 50 mV (Table IV). This film is stable to repetitive potential cycling showing only a slow decrease in the current peaks. We believe that the slow current decrease is related to either loss of film solvation or exclusion of electrolyte as it cycles through the neutral oxidation state. Similar chemistry has been noted for other films that pass through an uncharged metal complex state at some point in the cyclic voltammogram. The film electrochemistry can be prolonged somewhat by using fairly dilute electrolyte solutions, 0.05 M $[NEt_4][BF_4]$.

poly-Co(meansalen). As previously noted the polymer film appears to reside mainly in the Co(III) state while being grown. When the potential applied to a fresh film is scanned to negative values, a large cathodic current burst appears at the foot of the wave associated with the Co(II/I) couple, Figure 3c. From prior work with Co tetraphenylporphyrin films[14] we associate this cathodic current burst with a mediated reduction of the Co(III) states (and perhaps other redox states as well) by Co(I) and to reduction of the Co(III) at potentials far more negative than its thermodynamic potential. All subsequent cyclical potential scans (Figure 3c) do not exhibit this current burst provided that one does not scan positive of approximately 0.4 V. The Co(II/I) couple has an E° of -1.28 V and a peak splitting of about 60 mV, (Table IV).

Figure 3d also shows the cyclic voltammogram of a film that had been initially reduced at negative potentials as in Figure 3c, but now the potential is scanned to a more positive voltage, 0.6 V. The first positive voltage scan shows a small wave at the potential of the Co(III/II) couple, $E^\circ = 0.28$ V and $\Delta E_P = 80$ mV, and a larger wave at the potential of the $TMB^{+/o}$ couple, $E^\circ = 0.50$ V and $\Delta E_P = 50$ mV. The peak height for the metal centered wave is smaller than that for the $TMB^{+/o}$ wave both because of the slow Co(III/II) electron self exchange rate and because there should be two electrons in the $TMB^{+/o}$ wave due to the disubstitution in I. Subsequent wide potentials scans in Figure 3d show current bursts at -1.15 V and 0.32 V that are due to incomplete re-reduction of TMB^+ and Co(III) states and incomplete re-oxidation of Co(I) states respectively, plus mediated reduction or oxidation of other, unknown charge trapped species in the film. The details of these current bursts, which have been observed in other films are not clear.

poly-[Mn(meansalen)][BF_4]. The voltammetry of the manganese polymer in pure supporting electrolyte is poorly defined (Figure 4c). The waves corresponding to the oxidation and reduction of the manganese center are small and are superimposed on a large background current. This behavior appears to be fairly common for polymer films containing manganese macrocycles.[15] We postulate a slow electron transport (self exchange) rate for the Mn(III/II) couple is responsible, much like the case for the diminished Co(III/II) waves. The E° for the polymer manganese(III/II) wave is also shifted positively (to -0.16 V) as compared to the monomer, and the peak splitting is large, 230 mV. It is not clear why the E° has changed; the solvent environment and associated anion positions around the metal center might be different from the complex in solution which could account for these changes. The polymer Mn(III/II) wave in the film is demonstrably sensitive to the nature of the solvent as addition of the coordinating solvent dimethylsufoxide, DMSO, to the solution produces a further shift in the positions of the metal centered wave.

Electron transfer mediation is often used as a method to derive electrochemistry from a species which otherwise displays poor electrochemical response.[16] The general idea is shown in Figure 6a; a heterogeneous electron transfer between the electrode and the mediator, Med, is followed by a homogeneous electron transfer between the mediator and the substrate, Sub. We have utilized this strategy to enhance the electrochemical response from the manganese Schiff-base film. In this instance the substrate is the Mn(III/II) couple in the metal complex polymer, and the electron transfer mediator is tetracyanoquinodimethane, TCNQ.

Figure 6b shows the cyclic voltammogram of a manganese polymer film contacted by a solution containing a small amount of the salt [Li][TCNQ]. The initial potential scan, initiated in the positive direction (labeled scan 1), shows only an oxidation ($TCNQ^{-/0}$) and a subsequent reduction ($TCNQ^{0/-}$) from the $TCNQ^-$ which is near the electrode surface. The observed E^0 for the $TCNQ^{-/0}$ couple is the same in this experiment as it is at a bare Pt electrode, E^0 = 190mV. The current for the $TCNQ^{-/0}$ wave in Fig. 6b is approximately eighty percent of that at a bare Pt electrode, which means the film is fairly permeable to this species and perhaps sequesters the $TCNQ^-$ anion by ion-exchanging with the internally charge-compensating $[BF_4]^-$ counterions.

Upon continuing the potential scan past the $TCNQ^{0/-}$ wave to more negative potentials a large cathodic current is observed with a peak potential at −0.43 V. This corresponds to the $TCNQ^{-/2-}$ mediated reduction of Mn(III) sites in the polymer film to Mn(II) sites. The anodic peak observed (−0.33 V) upon reversing the potential scan is much smaller since it is associated with the oxidation of $TCNQ^{2-}$ to $TCNQ^-$. Figure 6c further explains the voltammetric behavior. According to this pseudo energy level diagram, oxidation of Mn(II) by $TCNQ^-$ at −0.33 V is a thermodynamically uphill process by approximately 300 mV, but oxidation by $TCNQ^0$ is a thermodynamically downhill process. Thus the reoxidation of Mn(II) to Mn(III) occurs at 0.22 V.

Using the electrochemical mediation reaction it is now possible to access approximately twenty five percent of the manganese in the film based on a comparison to the amount of charge under the $TMB^{+/0}$ wave in this same film. This result is very interesting because we have demonstrated that a polymer film which has poor electrochemistry under normal conditions can be induced to demonstrate reasonable electrochemistry provided a suitable mediating reagent is employed. There exist only a limited number of examples of utilizing the mediation method for enhancing currents in redox polymer films[17] but in principle it is a general approach.

Another interesting result of the mediation reaction in Figure 6 is that the TCNQ voltammetry shows diffusional behavior, i.e. plots of the peak currents at −0.16 V versus (scan rate)$^{1/2}$ are linear.[18] Furthermore, the amount of manganese that is electrochemically accessed by the TCNQ displays a coverage versus (scan rate)$^{1/2}$ behavior which is linear. It is not clear why the coverage shows this dependence on scan rate, but it does suggest, as noted above, that less than 100% of the Mn sites become mediated, since in that case the coverage should be independent of the scan rate. At infinitely slow scan rates it may be possible to sense all of the manganese present in the polymer film. We also note that the peak potential for the mediated reduction of Mn(III) to Mn(II) is sensitive to the scan rate. At a scan rate of 200 mV/s the peak potential appeas at -0.45 V while at 5 mV/s the peak potential is at -0.395 V. This suggests a fairly slow mediation reaction is occurring. The situation for the mediated oxidation is more complicated and not well understood at this time.

CONCLUSION

We have found from these studies a new approach to the formation of polymer films on electrode surfaces. The coupling of DMA like moieties to form an electroactive dimer, TMB, allows for a detailed understanding of the nature of the polymer backbone. This is a significant advantage over the more common vinyl substituted ligand electropolymerization reactions where composition of the polymer backbone in terms of chain lengths is generally uncertain.

The use of electrochemical mediators to "turn-on" polymer film electrochemistry is a promising approach to studying what are normally electro-inactive or poor electro-responsive films. This method could eventually lead to the derivation of interesting electrochemical reactions from these films.

Acknowledgments

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