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Oxidative Electropolymerization of Iron and Ruthenium Complexes Containing Aniline-Substituted 2,2'-Bipyridine Ligands

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New bipyridine ligands with pendant aniline groups [4-CH_2R-4'-CH_2R'-2,2'-bipyridine where R = NHC_6H_5 and R' = H (I; anilbpy) and R = R' = NHC_6H_5 (II; bis-anilbpy)] and the electrochemical properties of their iron and ruthenium complexes, [Fe(anilbpy)$_3$][PF_6]$_2$ (**1**), [Fe(bis-anilbpy)$_3$][PF_6]$_2$ (**2**), [Ru(anilbpy)$_3$][PF_6]$_2$ (**3**), [Ru(bis-anilbpy)$_3$][PF_6]$_2$ (**4**), [Ru(bpy)$_2$(anilbpy)][PF_6]$_2$ (**5**), and [Ru(bpy)$_2$(bis-anilbpy)][PF_6]$_2$ (**6**) [bpy = 4,4'-$(CH_3)_2$-2,2'-bipyridine], are described. All complexes, except **5**, form polymer films from an acetonitrile solution containing 0.1 M Bu_4NClO_4 on Pt and glassy carbon electrodes; **1–4** are also polymerized onto NESA glass electrodes by repetitively cycling the electrode potential between 0 and 1.1 V or 0 and 1.5 V vs SSCE. Two new redox couples arising from tail to tail and head to tail coupling of aniline groups on adjacent monomers are visible in the voltammograms during the film growth process carried out between 0 and 1.1 V. A broad, ill-defined redox couple for the tail to tail coupled aniline species is seen in polymer films grown at 1.5 V. The films exhibit voltammetric properties on all electrode materials expected for metal-centered oxidation and ligand-centered reductions when the coated electrodes are transferred to a CH_3CN solution containing only supporting electrolyte. The visible spectra of the polymers on conductive glass electrodes show MLCT bands in the same region as the monomers with λ_{max} ~540 nm for poly-**1** and poly-**2** and λ_{max} = 460 nm for poly-**3** and poly-**4**. A new absorption band appears at λ_{max} = 720 nm, assignable to a monocation of diphenylamine, for films on the conductive glass oxidized to 0.9 V, and its intensity decreases with application of increasing positive potentials, with a new band appearing at λ_{max} ~440 nm arising from the two-electron-oxidation products of diphenylamine and benzidine.

Introduction

The chemical and electrochemical properties of transition metal complex polymer modified electrodes (PMEs) continue to be of great interest,[1] with polypyridine ligand complexes, e.g. those of bipyridine (bpy), being the most extensively studied.[2] Many of the fundamental electrochemical properties of surface-immobilized species have been elucidated using bpy complexes, which still continue to be actively investigated, as they are stable in a variety of oxidation states, possess electrochromic behavior, and exhibit electrocatalytic activity.[3] The vinyl-substituted bipyridine ligand 4-methyl-4'-vinyl-2,2'-bipyridine (vbpy) is the commonly used ligand for preparing metal polypyridine PMEs by reductive electropolymerization techniques.[2] Recently, properties of Ru and Fe polymer films formed by oxidative electropolymerization of *N*-alkylpyrrole-[4] or thiophene-substituted[5] bpy ligands have been described. By working in the positive-potential regime, one is able to avoid the more rigorous experimental conditions needed for reductive polymerization.

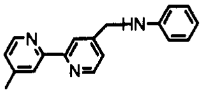
Chart I

	$[ML_nL'_{3-n}]^{2+}$			
cmpd	M	*n*	L	L'
1	Fe	3	I	
2	Fe	3	II	
3	Ru	3	I	
4	Ru	3	II	
5	Ru	1	I	bpy[a]
6	Ru	1	II	bpy

[a] bpy = 4,4'-$(CH_3)_2$-2,2'-bipyridine.

We have used aniline groups to oxidatively electropolymerize ferrocene monomers[6] and metal Schiff-base complexes[7] onto electrode surfaces, with oxidation of the aniline portion inducing successive head to tail or tail to tail coupling of monomer units.[8] This publication describes studies on the synthesis of polypyridine ligands with pendant aniline moieties and the oxidatively induced coupling chemistry of their Fe and Ru complexes, which provides the means for immobilizing the metal complexes onto electrode surfaces.

The two new ligands I (anilbpy) and II (bis-anilbpy) form complexes with ruthenium and iron, **1–6** shown in Chart I.



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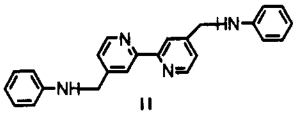

II

Polymer films of these complexes deposit onto Pt, glassy carbon, or conductive glass electrode surfaces upon oxidation of the pendant aniline groups. Electrochemical and spectroscopic measurements suggest that the polymer films form by both head to tail and tail to tail coupling of adjacent monomers.

Experimental Section

Physical Measurements. IR spectra of solids (KBr disks) and specular reflectance measurements on Pt electrodes were taken on a Perkin-Elmer 1800 FTIR spectrometer. UV–vis spectra were measured using a Hewlett-Packard HP8452A diode array spectrophotometer controlled with

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a Zenith computer. ^{1}H NMR spectra were recorded using either a Varian XL-200 or an IBM WP-100 spectrometer. CD_3CN and $CDCl_3$ (Cambridge Isotopes) were used as received. Elemental analyses were performed by Quantitative Technologies, Inc., Bound Brook, NJ.

Electrochemistry. Electrochemical measurements were made using an EG&G PAR Model 273 potentiostat/galvanostat controlled with the Zenith computer or a locally built potentiostat. Voltammograms were obtained in a three-compartment cell with either a Pt disk [$A \sim 0.15$ cm^2 (polished with 1-μm alumina (Buehler)] or a glassy carbon (GC) disk [$A \sim 0.07$ cm^2 (polished with 1-μm diamond paste (Buehler)] working electrode, a Pt wire counter electrode, and a SSCE (sodium chloride saturated calomel electrode) reference electrode. The supporting electrolyte was Bu_4NClO_4 (TBAP) (Baker analyzed), and CH_3CN (Burdick and Jackson) dried over molecular sieves was used as solvent. The conductive glass glass electrodes, NESA (glass substrates coated with fluorine-doped SnO_2), for spectroelectrochemical experiments were a generous gift from PPG Industries, Inc., Pittsburgh, PA. All experiments were performed under an N_2 atmosphere.

Materials. The following reagent grade chemicals were used as received: 4,4'-dimethyl-2,2'-bipyridine (bpy) and NH_4PF_6 (Aldrich); aniline and $NaH_2PO_2\cdot H_2O$ (Fluka); $RuCl_3\cdot xH_2O$ (Strem Chemical), $FeSO_4$, KI, and $NaHCO_3$ (Fisher Scientific). *N*-Bromosuccinimide (NBS) (Aldrich) and *p*-toluenesulfonyl chloride (Fluka) were purified prior to use.[9] *cis*-Ru(bpy)$_2$Cl$_2$ was prepared by a procedure described in the literature.[10]

Syntheses. 4-(Bromomethyl)-4'-methyl-2,2'-bipyridine (III). A mixture of 4,4'-dimethyl-2,2'-bipyridine (1.0 g, 5.43 mmol) and NBS (1.0 g, 5.62 mmol) in CCl_4 (50 mL), dried over molecular sieves, was refluxed for 30 min, and then benzoyl peroxide (30 mg) was added. The mixture was refluxed for another 3 h and cooled to room temperature, and the succinimide was filtered off. The filtrate was concentrated in vacuo, producing a yellow oil. The ^{1}H NMR spectrum of the oil in $CDCl_3$ showed it to be a mixture of mono- and dibrominated compounds and unreacted starting material. The mixture was used in the following step without further purification.

4-(Anilinomethyl)-4'-methyl-2,2'-bipyridine (anilbpy; I). A suspension of the above mixture (1.0 g), aniline (0.51 mL, 5.6 mmol), and $NaHCO_3$ (0.32 g, 6.25 mmol) in THF (25 mL) was refluxed for 2 h. The solution was cooled to room temperature and filtered. The brown filtrate was concentrated in vacuo and chromatographed on basic alumina with hexane/EtOAc (9:1) as eluent. The second fraction was collected and evaporated to give 4-(anilinomethyl)-4'-methyl-2,2'-bipyridine as a colorless solid (260 mg, 17% based on starting 4,4'-dimethyl-2,2'-bipyridine). Anal. Calcd (found) for $C_{18}H_{17}N_3$: C, 78.52 (77.48); H, 6.22 (6.05); N, 15.26 (14.90). ^{1}H NMR (δ (ppm), $CDCl_3$): 8.55 (d, 1 H, J = 4.8 Hz), 8.46 (d, 1 H, J = 5.1 Hz), 8.24 (s, 1 H), 8.38 (s, 1 H), 7.35 (d, 1 H, J = 5.1 Hz), 7.20 (d, 1 H, J = 5.1 Hz), 7.04–7.12 (m, 2 H), 6.57–6.64 (m, 3 H), 4.43 (s, 2 H), 2.41 (s, 3 H).

4,4'-Dimethyl-2,2'-bipyridine Di-*N*-oxide (IV). To a solution of 4,4'-dimethyl-2,2'-bipyridine (5.0 g, 10.9 mmol) in glacial acetic acid (21 mL) was added 14 mL of 30% hydrogen peroxide. The mixture was heated for 4 h at 110 °C. An additional 14-mL aliquot of H_2O_2 was added and heating continued at 110 °C for 4 h. After cooling, the reaction mixture was made alkaline with solid $NaHCO_3$ and extracted with $CHCl_3$. The extract was dried with Na_2SO_4 and then concentrated to give an off-white solid (4.9 g, 84%). ^{1}H NMR (δ (ppm), $CDCl_3$): 8.20 (d, 2 H, J = 6.8 Hz), 7.47 (s, 2 H), 7.13 (d, 2 H, J = 6.8 Hz), 2.35 (s, 6 H).

4,4'-Bis(chloromethyl)-2,2'-bipyridine (V). Freshly recrystallized *p*-toluenesulfonyl chloride (10.0 g, 52 mmol) in dioxane (25 mL), previously distilled from sodium/benzophenone, was added slowly to a refluxing solution of unpurified IV (1.5 g, 6.94 mmol) in the same solvent (15 mL). After a 40-h reaction period, 5% HCl (50 mL) was added, and the resultant mixture was extracted with toluene. Na_2CO_3 was added to increase the solution pH to 10. The aqueous phase was extracted with $CHCl_3$. The organic phase was washed with water, dried with Na_2SO_4, and concentrated to give a reddish-brown oil. Purification by chromatography on silica gel using $CHCl_3$ as eluent gave a fourth fraction, which was evaporated to give an off-white solid (0.46 g, 26%). ^{1}H NMR (δ (ppm), $CDCl_3$): 8.66 (d, 2 H, J = 6.2 Hz), 8.42 (s, 2 H), 7.37 (d, 2 H, J = 6.3 Hz), 4.61 (s, 4 H).

4,4'-Bis(anilinomethyl)-2,2'-bipyridine (bis-anilbpy; II). A mixture of V (200 mg, 0.8 mmol), KI (110 mg, 0.67 mmol), $NaHCO_3$ (150 mg, 1.8 mmol), and aniline (500 μL, 1 mmol) in acetone (20 mL) was refluxed for 3 h. The mixture was filtered and concentrated in vacuo, giving an orange solid. The solid was washed with hexane, EtOAc/hexane (1:5), and finally pure EtOAc, leaving a colorless solid (240 mg, 83%). Anal. Calcd (found) for $C_{24}N_4H_{22}$: C, 78.66 (76.76); H, 6.05 (5.90); N, 15.29 (14.73). ^{1}H NMR (δ (ppm), CD_3CN): 8.48 (d, 2 H, J = 4.9 Hz), 8.33 (s, 2 H), 7.28 (d, 2 H, J = 4.8 Hz), 6.96–7.11 (m, 4 H), 6.49–6.65 (m, 6 H), 4.37 (s, 4 H).

Tris[4-(anilinomethyl)-4'-methyl-2,2'-bipyridine]iron Hexafluorophosphate, [Fe(anilbpy)$_3$][PF$_6$]$_2$ (1). Ligand I (50 mg, 0.18 mmol), dissolved in hot distilled water (8 mL) and methanol (2 mL), was treated with $FeSO_4$ (22 mg, 0.08 mmol) and NH_4PF_6 (26 mg, 0.16 mmol) solution (2 mL, H_2O). The red solution was heated on a water bath under N_2 for 1 h and then left to cool to room temperature. The red crystalline product which separated was recovered by filtration, washed with distilled water, and dried in vacuo (49 mg, 70%). Anal. Calcd (found) for $FeC_{54}H_{51}N_9P_2F_{12}$: C, 55.35 (54.30); H, 4.39 (4.23); N, 10.76 (10.46). ^{1}H NMR (δ (ppm), CD_3CN): 8.46 (s, 1 H), 8.32 (s, 1 H), 7.04–7.30 (m, 6 H), 6.56–6.67 (m, 3 H), 4.51 (s, 2 H), 2.50 (s, 3 H).

Tris[4,4'-bis(anilinomethyl)-2,2'-bipyridine]iron Hexafluorophosphate, [Fe(bis-anilbpy)$_3$][PF$_6$]$_2$ (2). Ligand II (50 mg, 0.137 mmol), dissolved in a hot mixture of distilled water (4 mL) and ethanol (8 mL), was treated with excess $FeSO_4$ (25 mg, 0.09 mmol) and NH_4PF_6 (40 mg, 0.24 mmol). The resultant red solution was heated on a water bath for 1 h and then left to cool. The red crystalline solid which separated was recovered by filtration, washed with distilled water, reprecipitated from CH_2Cl_2 by addition of diethyl ether, and dried in vacuo at 40 °C for 16 h (45 mg, 69%). Anal. Calcd (found) for $FeC_{72}H_{66}N_{12}P_2F_{12}$: C, 59.84 (59.16); H, 4.60 (4.53); N, 11.63 (11.34). ^{1}H NMR (δ (ppm), CD_3CN): 8.43 (s, 2 H), 6.69–7.27 (m, 8 H), 6.47–6.71 (m, 6 H), 4.49 (s, 4 H).

Tris[4-(anilinomethyl)-4'-methyl-2,2'-bipyridine]ruthenium Hexafluorophosphate, [Ru(anilbpy)$_3$][PF$_6$]$_2$ (3). Ligand I (56 mg, 0.2 mmol), dissolved in a hot mixture of distilled water (2 mL) and ethanol (3 mL), was treated with "Dried" $RuCl_3$ (12 mg, 0.05 mmol) and $NaH_2PO_2\cdot H_2O$ (40 mg, 3.8 mmol). The deep brown mixture was heated on the water bath for 20 min and then left to cool to room temperature. Water (15 mL) was added to the cooled mixture, which was filtered, and a 10-fold molar excess of NH_4PF_6 was then added to the filtrate, causing precipitation of an orange-red powder. The product was chromatographed on basic alumina using toluene/acetonitrile (1:1) as eluent. The final product was obtained by precipitation from CH_2Cl_2 with slow addition of diethyl ether and dried in vacuo for 16 h at 40 °C (19 mg, 33%). Anal. Calcd (found) for $RuC_{54}H_{51}N_9P_2F_{12}$: C, 53.29 (52.25); H, 4.22 (4.07); N, 10.36 (9.99). ^{1}H NMR (δ (ppm), CD_3CN): 8.48 (s, 1 H), 8.31 (s, 1 H), 7.03–7.54 (m, 6 H), 6.57–6.78 (m, 3 H), 4.49 (s, 2 H), 2.49 (s, 3 H).

Tris[4,4'-bis(anilinomethyl)-2,2'-bipyridine]ruthenium Hexafluorophosphate, [Ru(bis-anilbpy)$_3$][PF$_6$]$_2$ (4). Ligand II (60 mg, 0.164 mmol), dissolved in a hot mixture of distilled water (2 mL) and ethanol (5 mL), was treated with "Dried" $RuCl_3$ (8.6 mg, 0.04 mmol) and $NaH_2PO_2\cdot H_2O$ (30 mg, 0.28 mmol). The deep brown mixture was heated on the water bath for 1 h and then left to cool to room temperature. A 10-fold molar excess of NH_4PF_6 was added to the orange mixture, and the resultant solution was refluxed for 10 min and then allowed to cool. The separated material was chromatographed on basic alumina using toluene/acetonitrile (1:1) as eluent, and the final product was obtained by precipitation from CH_2Cl_2 with slow addition of diethyl ether and dried in vacuo for 16 h at 40 °C (16 mg, 27%). Anal. Calcd (found) for $RuC_{72}H_{66}N_{12}P_2F_{12}$: C, 58.02 (57.04); H, 4.46 (4.38); N, 11.28 (10.87). ^{1}H NMR (δ (ppm), CD_3CN): 8.41 (s, 2 H), 7.25–7.50 (m, 4 H), 7.06–7.15 (m, 4 H), 6.51–6.80 (m, 6 H), 4.46 (s, 4 H).

[4-(Anilinomethyl)-4'-methyl-2,2'-bipyridine]bis(4,4'-dimethyl-2,2'-bipyridine)ruthenium Hexafluorophosphate, [Ru(bpy)$_2$(anilbpy)][PF$_6$]$_2$ (5). Ligand I (19 mg, 0.069 mmol), dissolved in 5 mL of ethanol, and *cis*-Ru(bpy)$_2$Cl$_2$ (26 mg, 0.046 mmol) were refluxed together for 2 h under a N_2 atmosphere. After the mixture was cooled to room temperature, the solvent was removed in vacuo and the resultant solid was slurried in water (6 mL). The slurry was then filtered to remove any excess ligand. A 5-fold molar excess of NH_4PF_6 (46 mg, 0.28 mmol) was added to the solution, causing precipitation of an orange powder which was chromatographed on basic alumina using toluene/acetonitrile (1:1) as eluent. The final product was obtained by precipitation from CH_2Cl_2 with slow addition of diethyl ether and dried in vacuo for 16 h at 40 °C (30 mg, 64%). Anal. Calcd (found) for $RuC_{42}H_{41}N_7P_2F_{12}$: C, 48.75 (47.85); H, 3.99 (3.88); N, 9.47 (9.18). ^{1}H NMR (δ (ppm), CD_3CN): 8.32 (s, 5 H), 8.57 (s, 1 H), 7.43–7.54 (m, 6 H), 7.06–7.22 (m, 8 H), 6.67–6.80 (m, 3 H), 4.52 (s, 2 H), 2.51 (s, 15 H).

[4,4'-Bis(anilinomethyl)-2,2'-bipyridine]bis(4,4'-dimethyl-2,2'-bipyridine)ruthenium Hexafluorophosphate, [Ru(bpy)$_2$(bis-anilbpy)][PF$_6$]$_2$ (6). *cis*-Ru(bpy)$_2$Cl$_2$ (28 mg, 0.05 mmol) and ligand II (29 mg, 0.08 mmol) dissolved in ethanol (5 mL) were heated under reflux for 2 h. The solvent was removed under reduced pressure, water (15 mL) was added, and the solution was filtered to remove any excess ligand. Addition of

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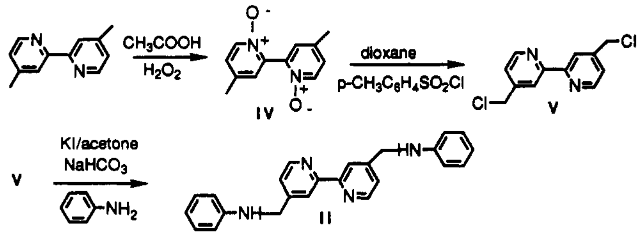
Scheme I



excess NH_4PF_6 to this solution caused precipitation of an orange-red powder. The product was chromatographed on basic alumina using toluene/acetonitrile (1:1) as eluent, the final product being obtained by precipitation from CH_2Cl_2 with slow addition of diethyl ether and dried in vacuo for 16 h at 40 °C (30 mg, 54%). Anal. Calcd (found) for $RuC_{48}H_{46}N_8P_2F_{12}$: C, 51.20 (50.23); H, 4.12 (3.98); N, 9.95 (9.67). ^1H NMR (δ (ppm), CD_3CN): 8.49 (s, 2 H), 8.30 (s, 4 H), 7.13–7.56 (m, 8 H), 7.02–7.10 (m, 8 H), 6.58–6.75 (m, 6 H), 4.49 (s, 4 H), 2.49 (s, 12 H).

Electropolymerization. Continuous cycling of the working electrode potential to 1.1 or 1.5 V at 100 mV/s in a 0.1–1 mM solution of the monomers **1**–**4** and **6** dissolved in an N_2-saturated 0.1 M Bu_4NClO_4/CH_3CN solution resulted in formation of an adherent polymer film on the electrode surface. No polymer film deposited from monomer **5** under a variety of conditions. Copolymers of the Fe and Ru complexes were formed in a fashion analogous to that for their homopolymer counterparts. Thin polymer films were golden, while thick ones were purple or green.

Polymer films for visible spectroscopic studies were prepared on NESA glass by first depositing a thin layer of the film with five cyclic scans, scan rate 50 mV s^{-1}, followed by application of a constant potential at 1.1 or 1.5 V for 10–15 min. The potential was then slowly ramped back to 0 V (20 mV s^{-1}) and maintained at this value until background currents were noted. The electrode was then removed from solution and thoroughly washed with acetonitrile.

Polymer Film Characterization. The coated electrodes were transferred to a solution containing supporting electrolyte in acetonitrile and no monomer. The current–potential characteristics were then measured at various scan rates. Experiments in which the films were examined for ligand reductions were carried out in an N_2-filled glovebox (Vacuum Atmospheres). An Ag wire was used as a pseudoreference electrode in the glovebox experiments.

Apparent surface coverages, Γ_{app}, were determined from the area under the M(III/II) reduction wave using the relationship $\Gamma_{app} = Q/nFA$ [where Q is the charge under the metal reduction potential–current envelope, n is the number of electrons ($n = 1$, assuming that the polymer backbone makes little or no contribution to the current under the M(III/II) reduction wave), F is the Faraday constant, and A is the electrode area]. In the case of the copolymers, reliable Γ_{app} measurements are not possible owing to substantial overlap of the redox processes for the metals.

Visible Spectroelectrochemistry. Spectra of the polymers on NESA glass were obtained in 0.1 M TBAP/CH_3CN by stepping the potential in 0.05- or 0.1-V increments (starting and stopping at least 0.3 V from $i_{p,ox}$ for the polymer M(II/III) process), allowing the current to decay to background levels at the E_{app}, and then determining the visible spectrum.

Results and Discussion

Ligand Syntheses. The monosubstituted bipyridine ligand I was synthesized by reaction of the 4′-bromomethyl derivative, obtained by bromination of 4,4′-dimethyl-2,2′-bipyridine with NBS,[11] with aniline in the presence of $NaHCO_3$. The overall yield of I was about 20%, comparable to yields obtained in other free radical bromination reactions of the bpy ligand. In the initial bromination step, a mixture of mono- and disubstituted bromomethyl compounds as well as starting material was obtained. This mixture was reacted without purification with aniline because I was readily separated from the small quantity of II (<5%) and starting material by chromatography on basic alumina. The final ligand is a colorless product, somewhat less soluble than the starting material in similar solvents.

Table I. Electrochemical and UV–Vis Absorption Data for Metal Bipyridine Complexes

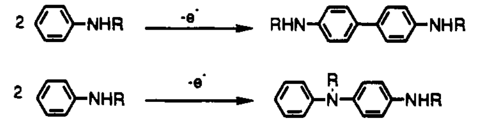
	$E°/V^a$		UV–Vis	
compd	$M^{3+/2+\,b}$	$L^{0/-}, L^{-/2-\,c}$	monomer λ_{max}, nm^d (ϵ, 10^{-3} M^{-1} cm^{-1})	polymer λ_{max}, nm^d
1	1.10		246 (62.0), 298 (61.8), 494 (sh), 530 (8.7)	540
2	1.27		246 (86.0), 300 (64.6), 496 (sh), 530 (8.9)	544
3	1.31	−1.20, −1.42	248 (55.7), 288 (70.7), 434 (sh), 460 (14.6)	460
4	1.52		246, 290 (68.7), 436 (sh), 462 (12.9)	460
5	1.15		248 (32.1), 288 (62.0), 434 (sh), 460 (11.8)	
6	1.26	−1.10, −1.30	246 (41.7), 288 (59.3), 434 (sh), 460 (11.1)	

[a] 0.1 M TBAP/CH_3CN. [b] E vs SSCE. [c] L refers to bipyridine ligand reductions; E vs Ag wire. [d] Spectra of polymer films taken on NESA glass in 0.1 M TBAP/CH_3CN for a freshly grown film at E_{app} = 0 V.

Synthesis of the disubstituted ligand II is shown in Scheme I. The N-oxide route[12] consistently produced II in 20–30% yield, in contrast to the bromination reaction with NBS, which we found to be unpredictable.[11] The intermediate V was not reactive toward aniline in the absence of KI, and a nearly stoichiometric amount of KI was used in the final reaction step in order to avoid formation of unidentified products which would lower the yield. Ligand II is a colorless material less soluble than I in common solvents.

Metal Complexes. Syntheses of the metal complexes shown in Chart I were carried out using procedures detailed in the literature.[13-15] Reaction times were lengthened owing to the low solublity of the ligands in alcohol and water. UV–vis spectral characteristics of the metal complexes are given in Table I. All metal complexes except **5** polymerize at potentials more negative than the metal oxidation, so it is not possible to report formal potentials for the M(II/III) couple in the monomers.

Electrochemical Studies. To facilitate presentation of the electrochemical results, the tail to tail and head to tail coupled products in the polymers shown in eqs 1 and 2, will be referred



(1)

(2)

R = bipyridine

to as benzidine and diphenylamine, respectively. Both compounds are electrochemically active, a property used to characterize their presence in the growing polymer film. As electrochemical standards, N,N,N',N'-tetramethylbenzidine, which has a one-electron couple at $E° = 0.65$ V,[7] and diphenylamine, which has a redox process at $E° = 0.4$ V,[16] both vs SSCE in CH_3CN, were used. The analogous couples in these PMEs are likely to appear at more positive potentials, probably 50–100 mV, owing to electrostatic effects.

Electropolymerization. $[Ru(bpy)_2(anilbpy)]^{2+}$ (cation of **5**) is the only complex that does not polymerize. Its cyclic voltam-

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mogram (CV) showed oxidation processes for the aniline moiety at 0.9 and at 1.3 V for the ruthenium center. Two reduction processes were observed at 1.2 and ~0.75 V upon scanning the potential back to 0 V. The former is reduction of the metal center, while the latter is assigned to reduction of a benzidine product. During the second potential cycle, a new oxidation process appeared at 0.8 V and was coupled to the reduction at 0.75 V supporting benzidine formation. The voltammogram remains unchanged upon continuous potential cycling, and there is no evidence for a polymer film on the electrode surface.

Complexes like **5** with only a single pyrrole- or vinyl-substituted bipyridine ligand per metal complex often do not polymerize to a significant extent,[17] although careful choice of the ligands on the metal center and polymerization conditions can produce reasonably thick polymer films for the vinyl-substituted complexes.[18] For the complexes prepared here, dimerization of adjacent metal complexes will most likely be the primary mode of polymerization, and no attack of the oxidized aniline on a bpy ligand of an adjacent metal complex is anticipated or observed for **5**. This behavior is in contrast to that reported for the electropolymerization of (5-amino-1,10-phenanthroline)metal complexes.[19]

All the remaining metal complexes in Chart I formed polymer films which adhere to GC, Pt, and NESA glass electrode surfaces when a potential of at least 1.1 V was applied to the working electrode. It is particularly noteworthy that $[Ru(bpy)_2(bis\text{-}anilbpy)]^{2+}$ is electrodeposited and forms a polymer film that withstands repetitive potential cycling. This result demonstrates that one disubstituted bpy ligand like II on a metal center is sufficient to form an electrochemically and chemically stable polymer film. Complexes with interesting and desirable electrochemical and chemical properties having only one bpy ligand now are accessible for modified-electrode studies.

The electropolymerization of **4** on a GC electrode (Figure 1a) is representative of the gross features for all complexes polymerized at E_{polym} = 1.1 V. The first positive potential scan showed no oxidation processes between 0 V and the aniline oxidation. Two reduction peaks were observed at 0.8 and 0.65 V upon scanning the potential back to 0 V. Following the unique first oxidative scan, steady growth in two new oxidation processes at 0.85 and 0.7 V and the reduction waves noted above were observed. The more positive redox couple arises from benzidine formation, while the other process is most likely the result of diphenylamine structures. The prominence of the benzidine wave was not unexpected owing to the steric demands of the bipyridine ligand, but the occurrence of head to tail coupling during electropolymerization is an interesting observation. Support for a diphenylamine structure in the backbone is provided by the visible spectroelectrochemical experiments described below. The curvature seen in a plot of $i_{p,red}$ for the benzidine portion (✱ on Figure 1a) vs the number of cyclic potential scans used to prepare the polymer (inset, Figure 1a) indicates that film growth is more rapid at early times than in the latter stages of the experiment (this plot is shown for 24 polymerization scans, while 12 scans are shown in the figure for purposes of clarity). Similar growth behavior is seen for the electropolymerization of **2**. The same plots for the less highly substituted compounds, **1** and **3**, are more linear for the same number of cyclic potential scans than those for **2** and **4**.

Electropolymerization of compound **2** at E_{polym} = 1.5 V (Figure 1b) occurred with metal-centered oxidation and reduction processes at 1.25 and 1.18 V, respectively, growing continuously during potential cycling, consistent with polymer film deposition. Redox couples for the aromatic amine coupled products were less well defined in this instance. The broad wave at approximately 0.8 V is attributed to the benzidine group. Plots of $i_{p,red}$ for the metal-centered redox process vs the number of cyclic scans used to prepare the polymers (inset, Figure 1b) are curved like those observed for polymerizations at 1.1 V. Analogous plots for **1** and **3** are also curved, but the effect is generally not as large as in the more highly substituted compounds.

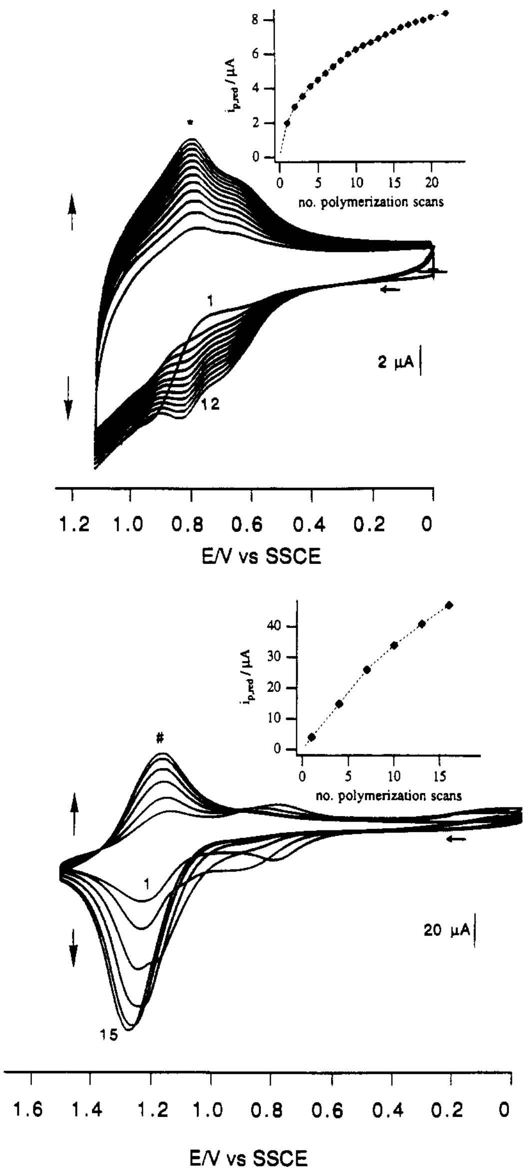

Figure 1. (a) Top: Repetitive cyclic voltammograms at 100 mV s^{-1} of 0.20 mM $[Ru(bis\text{-}anilbpy)_3]^{2+}$ in 0.1 M Bu_4NClO_4/CH_3CN at a glassy carbon electrode. The inset is a plot of $i_{p,red}$ for the wave marked with a ✱ for an analogous polymerization performed for 24 cyclic potential scans vs the number of cyclic potential scans. (b) Bottom: Repetitive cyclic voltammogram at 100 mV s^{-1} of 0.26 mM $[Fe(bis\text{-}anilbpy)_3]^{2+}$ in 0.1 M Bu_4NClO_4/CH_3CN at a glassy carbon electrode. Polymerization scans 2, 4, 6, 10, 13, and 15 are shown. The inset is a plot of $i_{p,red}$ for the wave marked with a # vs the number of cyclic potential scans.

Ion-transport limitations are probably the dominant factor for the decrease in polymerization rate with increasing number of scans.[20] At the higher polymerization potential for any of the monomers, more aniline groups are likely to be oxidized, resulting in a greater degree of cross-linking than at E_{polym} = 1.1 V. A similar situation applies to those compounds with a higher concentration of aniline groups available for dimerization. At this time, we cannot determine the number of aniline groups per monomer involved in the polymerization. A second factor decreasing polymerization efficiency with prolonged scanning relates

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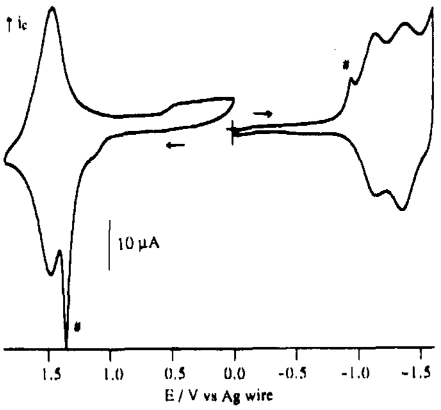

Figure 2. Cyclic voltammogram for poly-[Ru(bpy)$_2$(bis-anilbpy)]$^{2+}$ on a glassy carbon electrode at 50 mV s^{-1} in 0.1 M Bu_4NClO_4/CH_3CN. Peaks marked with # are prepeaks (see text). Voltage excursions limits are 0 to +1.85 V and 0 to −1.55 V. $\Gamma_{app} = 6.6 \times 10^{-9}$ mol cm^{-2} for the Ru(III/II) process.

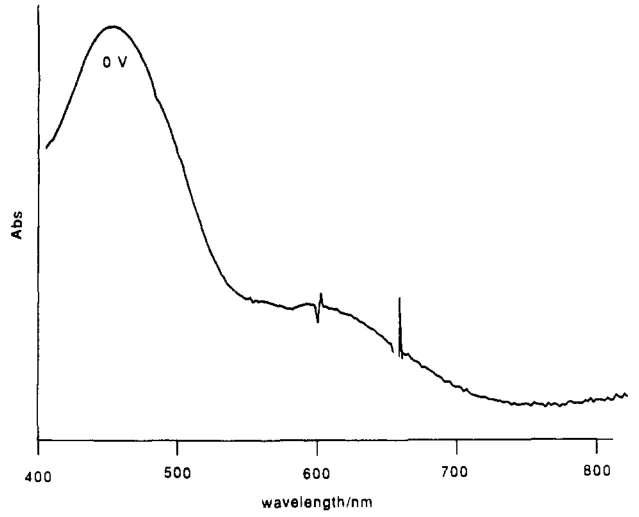

Figure 3. Visible spectrum of poly-[Ru(bis-anilbpy)$_3$]$^{2+}$ on NESA glass at E_{app} = 0 V in 0.1 M Bu_4NClO_4/CH_3CN. The polymer was prepared at E_{polym} = 1.1 V.

to electrostatic repulsion between the cationic metal complex and the polycationic polymer film.[18] As the charge on the polymer increases, the natural tendency will be to repel the oxidized monomers and oligomers. Despite this possible limitation to film growth, surface coverages as high as 10^{-7} mol cm^{-2} have been recorded.

Polymer Film Characterization. All of the polymers show electroactivity when the coated electrode is transferred to an acetonitrile solution containing only supporting electrolyte. The voltammograms are similar to those reported by others for Fe or Ru complex PMEs prepared by oxidative or reductive electropolymerizations.[2] Table I contains the redox potentials for the M(II/III) couples in the polymers as well as any ligand reductions. The CV for poly-[Ru(bpy)$_2$(bis-anilbpy)]$^{2+}$ (cation of poly-**6**) is shown in Figure 2, and prior to recording the voltammogram the film was cycled at least five times between 0 and 1.8 V. During this initial cycling period, a broad, ill-defined redox process was observed around 0.8 V which rapidly decreased with each potential cycle. As illustrated by the small background current evident in Figure 2, five cyclic scans were usually sufficient to extinguish all redox processes other than those attributable to the metal center and the prepeaks marked with a #. The prepeaks near both the metal oxidation and the first ligand reduction in Figure 2 are analogous to those seen for metal complex bpy polymers prepared from both the pyrrole- and vinyl-substituted ligand.[2,4] They are substantially larger if the voltage range includes both the metal oxidation and ligand reductions in the same scan. These observations are consistent with those of others[2] and theory regarding the origin of the prepeaks.[21] The conditioning period was utilized for all of the polymer films prepared in this study. Spectroelectrochemical results, described below, demonstrate that irreversible oxidation of the polymer backbone occurred during the initial cycling period.

Peak splittings in these films were on the order of 10 mV at 10 mV s^{-1}, increasing to 50–100 mV at 200 mV s^{-1}. Polymer films prepared from the more highly substituted compounds and those deposited at E_{polym} = 1.5 V exhibited the larger peak splittings. The increased peak splitting is consistent with charge-transport limitations within the polymer. In all cases, the M(II/III) couple is stable to prolonged potential cycling, despite the loss in electroactivity for the polymer backbone. Ruthenium films also show good stability to potential cycling through the first two ligand reductions. Iron films are less stable to reductive cycling.

Under all polymerization conditions studied and using either ligand, there is a distinctly lower apparent surface coverage, Γ_{app}, when the iron complex is replaced by the corresponding ruthenium complex. For example, polymerization of a 0.5 mM solution of **1** (12 cyclic scans) and a 0.58 mM solution of **3** (15 cyclic scans) at E_{polym} = 1.1 V produced films with $\Gamma_{app} = 1.1 \times 10^{-8}$ and 0.47×10^{-8} mol cm^{-2}, respectively. The close proximity of the Fe(II/III) couple to the aniline oxidation for films grown at 1.1 V likely functions to aid in the oxidation of the monomer near the electrode surface. For Ru polymers grown at 1.1 V, the charge propagation is primarily through the coupled aniline products, as this potential it is not sufficient to oxidize a significant quantity of metal sites. This leads to the conclusion that the aniline backbone in the growing polymer is electroactive and that it is not necessary to rely on redox hopping by the metal centers to prepare polymer films of these aniline-substituted bpy ligands. Support for the contention regarding the electroactive polymer backbone is provided by the spectroscopic measurements described below.

Copolymers containing an Fe–Ru complex are rich in the iron component, even when the electrolysis solution is composed, for example, of a 1:6 ratio of Fe:Ru. This behavior mirrors the results obtained with the homopolymers, where Γ_{app} is greater for Fe polymer than for analogously prepared Ru films. An exact measure of the relative compositions in the copolymer films is not possible, since the redox waves for the metal centers partially overlap.

Visible Spectroelectrochemistry. The polymers that deposited onto NESA glass electrodes produced orange or red films, starting from the Ru or Fe monomers, respectively. Colors for the copolymers depended on on the relative monomer concentrations. A spectrum of poly-[Ru(bis-anilbpy)$_3$]$^{2+}$ recorded immediately after its growth at 1.1 V is shown in Figure 3. The absorption at 460 nm is the MLCT band (Table I), but the broad absorption at ~620 nm has no counterpart in the spectrum of the monomer and its intensity was unchanged by positive or negative potential cycling of the polymer film. This 620-nm band was seen in all Ru polymers, but for Fe polymers, the MLCT band partially obscured the absorption; however, it was observable as a weak feature when the MLCT band for the iron complex was bleached upon oxidation of the metal center. UV–vis spectra of some polyaniline model compounds are reported to have weak absorptions in the 600-nm region arising from quinoid groups in the backbone; thus we assume a similar origin for the 620-nm band in these PMEs.[22]

The visible spectrum of poly-[Fe(anilbpy)$_3$]$^{2+}$ prepared at 1.1 V is particularly informative with regard to the makeup of the polymer backbone. In the resting state of a freshly prepared film, E_{app} = 0 V, the MLCT band at λ_{max} = 540 nm is the only feature seen in the spectrum (Table I) and Figure 4a. Oxidation of the film by a series of potential steps to 0.85 V resulted in generation

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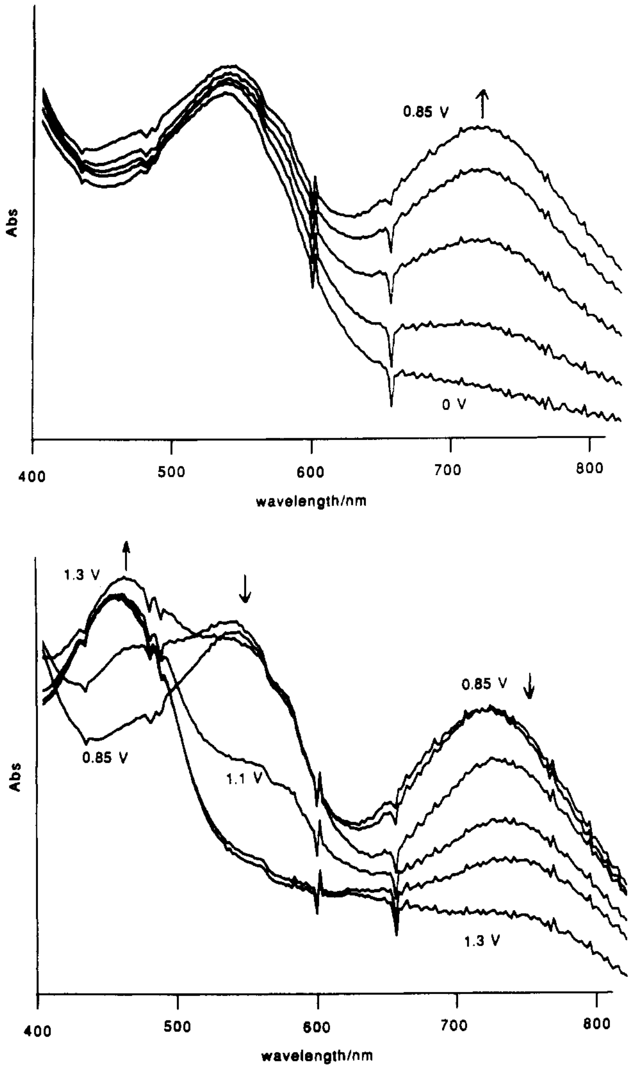
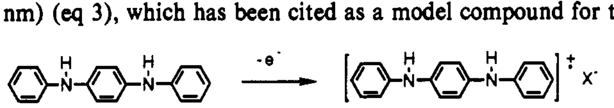


Figure 4. (a) Top: Visible spectra of poly-[Fe(bis-anilbpy)$_3$]$^{2+}$ on NESA glass at the potentials indicated on the figure in 0.1 M Bu_4NClO_4/CH_3CN. E_{app} = 0, 0.7, 0.75, 0.8, 0.85 V vs SSCE. The polymer was prepared at E_{polym} = 1.1 V. (b) Bottom: Visible spectra of poly-[Fe(bis-anilbpy)$_3$]$^{2+}$ on NESA glass in 0.1 M Bu_4NClO_4/CH_3CN. E_{app} = 0.85, 0.9, 1.1, 1.2, 1.3 V vs SSCE. The polymer was prepared at E_{polym} = 1.1 V.

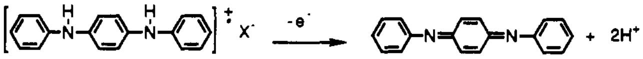
of a broad absorption at λ_{max} = 720 nm. This absorption appears in a region similar to that of the radical cation VII (λ_{max} = ~700 nm) (eq 3), which has been cited as a model compound for the



(3)

head to tail coupled polymer in polyaniline.[16] The 720-nm absorption band was bleached when the film was reduced at 0 V, and it was regenerated by application of potentials similar to those shown in the figure. With each successive potential cycle, the intensity of the low-energy band decreased. The absorption was irreversibly destroyed upon making E_{app} more positive than 0.9 V.

When the potential was increased to more positive values, the absorption at 720 nm decreased and a new feature appeared at 460 nm (Figure 4b). The 460-nm band maintained a constant intensity between E_{app} = 1.1 and 1.3 V, but a further increase in potential caused it to lose intensity. The diimine VIII (eq 4)[16] and the two-electron-oxidized form of benzidine, IX[23] (eq 5), have absorptions at roughly 440 nm. Thus the 460-nm band in the polymer is most likely a composite of these two species.



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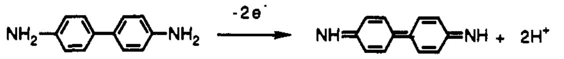

(5)

The band at 460 nm was only observed the first time the film was oxidized. This behavior is consistent with the cyclic voltammetric results, where electroactivity for the benzidine and the diphenylamine are lost during the first few potential cycles. The electrochemical irreversibility is likely related to the loss of protons during oxidation and possibly to overoxidation of the backbone. Despite the irreversible changes in the polymer backbone, the MLCT band at 540 nm could be reversibly bleached and regenerated multiple times with little change in intensity.

All polymer films prepared at E_{polym} = 1.1 V showed the absorption band at 720 nm upon oxidation to 0.9 V, but it was not usually as obvious as the one shown in Figure 4a. The decrease in the 720-nm band and the increase in the absorption at 460 nm as the potential was stepped to 1.3 V were also observed for these polymer films. For Ru films, the 460-nm feature overlapped the MLCT band, giving the appearance that the MLCT band increased in intensity during the oxidation to 1.3 V. However, application of further positive potentials where the metal center is oxidized resulted in the expected decrease in intensity for the MLCT band.

Polymer films grown at 1.5 V showed no absorption in the 700-nm region during oxidation. An intense absorption band at 460 nm was observed when the applied potential was >1.0 V. The intensity was much greater (2–3 times) than that shown in Figure 4a. Lack of an absorption at 720 nm can be accounted for by irreversible oxidation of the monocation VII to VIII (eq 4) with proton loss during growth of the polymer film and/or the fact that fewer diphenylamine structures form when the films are deposited at 1.5 V. Both explanations are consistent with the CV shown in Figure 1b, where the diphenylamine waves are negligible. It has been reported that use of high current densities during oxidation of *N*-alkylanilines in acetonitrile greatly favor benzidine formation over that of the head to tail product.[24] It seems most likely that the absorption band at 460 nm in films grown to 1.5 V arises from oxidation of a benzidine-like polymer backbone.

The visible spectra of copolymers clearly showed MLCT bands arising from both metal complexes. As for the homopolymers, appearance of the feature at 720 nm depends on E_{polym}. Growth of an absorption at 460 nm during the first cycle was also seen in the copolymers. When the potential was stepped to 1.2 V, the iron MLCT band decreased and application of still further positive potentials resulted in loss of the ruthenium MLCT band. There is no clear evidence in the visible spectra of the copolymers that some Fe or Ru sites are electrochemically isolated, but the concentration could be low. As for the homopolymers, the absorption bands for the metal centers can be bleached and regenerated multiple times with no evidence for decomposition.

FTIR Specular Reflectance. The FTIR specular reflectance spectrum of a freshly grown [Fe(bis-anilbpy)$_3$]$^{2+}$ polymer, E_{polym} = 1.5 V, on a Pt electrode is illustrated in Figure 5b. The spectrum is similar to that of the monomer (Figure 5a), except for the loss of intensity at 3500 cm^{-1} for the NH stretch in the polymer which can be accounted for by head to tail coupling in the polymer backbone. A spectrum of poly-**2** taken after one potential cycle between 0 and 1.5 V in supporting electrolyte only is shown in Figure 5c. The decrease in the intensity of the NH stretching vibration is consistent with backbone oxidation and loss of protons (eqs 4 and 5). A new feature in the spectrum of the polymer is the absorption band at 1710 cm^{-1} that persisted when the electrode was maintained at 0 V for a few minutes but was

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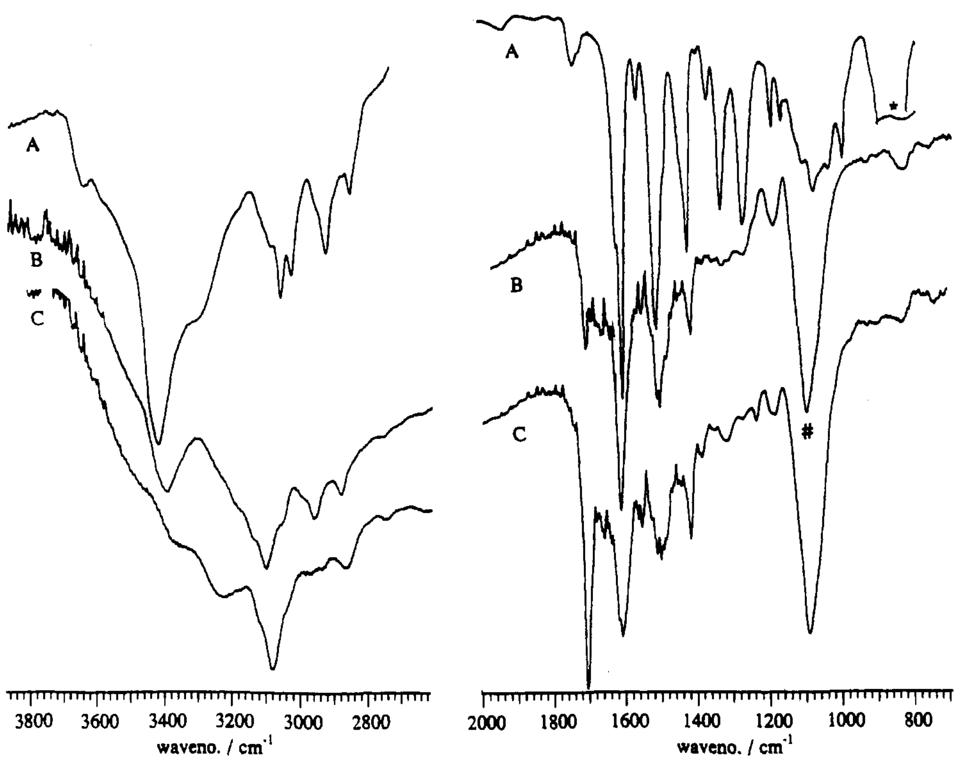

Figure 5. (A) FTIR spectrum of the monomer $[Fe(bis\text{-}anilbpy)_3]^{2+}$ as a KBr disk. The band marked with a * is due to the $[PF_6]^-$ counterion. (B) Specular reflectance FTIR spectrum of poly-$[Fe(bis\text{-}anilbpy)_3]^{2+}$ on a Pt electrode taken after it was grown at $E_{polym} = 1.5$ V and then reduced at 0 V vs SSCE. The band marked with a # is due to the $[ClO_4]^-$ counterion. (C) Specular reflectance FTIR spectrum of poly-$[Fe(bis\text{-}anilbpy)_3]^{2+}$ on the same Pt electrode as in part B taken after it was exhaustively electrolyzed at $E_{appl} = 1.5$ V vs SSCE in 0.1 M Bu_4NClO_4/CH_3CN. The band marked with a # is due to the $[ClO_4]^-$ counterion.

bleached to the same intensity level as in Figure 5b when a potential of −1.5 V (vs Ag wire) was applied to the working electrode. This 1710-cm^{-1} band was regenerated by reoxidizing the polymer to 1.5 V (vs SSCE) and thus is probably not related to oxidation of the benzidine or diphenylamine portions of the polymer, as absorption characteristics for the benzidine dication in the visible spectrum could be seen only on the first oxidative cycle. It is possible that the band at 1710 cm^{-1} is related to the prepeaks seen in Figure 2, but there is not sufficient information to make a structural assignment.

It can also be seen in Figure 5c that the quantity of perchlorate ions in the film is greater than that in the fresh film (Figure 5b). The intensity of this absorption remained larger than that in the spectrum of the freshly grown film, even after cycling the electrode to −1.5 V. These persistent, "extra" perchlorate ions must act as charge-compensating ions for oxidized sites in the polymer, possibly from the polymer backbone, that are electrochemically inactive, but there are no new features in the spectrum that allow a structural assignment.

Conclusions

The utility of the aniline group for preparing PMEs is most vividly demonstrated by polymerization of $[Ru(bpy)_2(bis\text{-}anilbpy)]^{2+}$. There has been no general method for preparing thick, stable polymer films of metal complexes with only one functionalized bipyridine ring. The straightforward synthesis of II, Scheme I, makes it desirable for use with a wide variety of metal complexes. Furthermore, as noted by one of the reviewers, these ligands should be useful for preparing polymer films for metals that are labilized during reductive electropolymerization, as with the vbpy-type ligands.

The mode of polymerization for the monomers provided some interesting results. Tail to tail coupled structures were anticipated to be the primary, if not the exclusive, polymerization route. However, cyclic voltammetry and visible spectra of the polymers show that head to tail coupled products also comprise the polymer backbone. Regardless of how polymerization occurs, the approach of using the oxidative coupling reactions of the aniline group for preparing PME surfaces appears general. Ferrocene,[6] metal Schiff-base complexes,[7] metalloporphyrins,[25] and now polypyridine complexes all form polymer films through aniline-coupling reactions.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. We are grateful to Prof. K. T. Potts for insightful discussions regarding the ligand syntheses.

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