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Syntheses, electrochemistry and electrodeposition of ruthenium(II) complexes of 4,4′-bis(4-anilinovinyl)-2,2′-bipyridine

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Abstract—The synthesis of a new disubstituted bipyridine ligand, 4,4′-bis(4-anilinovinyl)-2,2′-bipyridine (L^2), and its homoleptic and heteroleptic ruthenium(II) complexes $[\mathrm{RuL}^2_3]^{2+}$ and $[\mathrm{RuL}^2(\mathrm{bpy})_2]^{2+}$ are described. Both complexes undergo electrochemical polymerization in acetonitrile. $[\mathrm{RuL}^2(\mathrm{bpy})_2]^{2+}$ produced a conducting but non-robust polymer film, while $[\mathrm{RuL}^2_3]^{2+}$ produced an insulating film. © 1997 Elsevier Science Ltd

Keywords: anilinovinyl-bipyridine; ruthenium(II); electropolymerization.

In this report we discuss the synthesis of the ligands 4,4′-bis(2-(4-anilino)-2-hydroxyethyl)-2,2′-bipyridine (L^1) and 4,4′-bis(4-anilinovinyl)-2,2′-bipyridine (L^2), the heteroleptic and homoleptic tris(diimine) ruthenium(II) complexes $[\mathrm{RuL}^2(\mathrm{bpy})_2]^{2+}$ and $[\mathrm{RuL}^2_3]^{2+}$, and the electropolymerization of these ruthenium(II) complexes bearing *p*-anilinovinyl groups. The impetus for these studies was threefold: (i) Photophysical properties of polypyridyl metal complexes have received much scrutiny and, in particular, the tris(2,2′-bipyridyl)ruthenium(II) dictation, $[\mathrm{Ru(bpy)_3}]^{2+}$, and closely related derivatives are intensely studied metal complexes because of their potential as photosensitisers for electron and/or energy-transfer processes [1]. (ii) There is also considerable interest in electroactive polymers incorporating ruthenium(II) polypyridyl systems and in the application of electrodes coated with these polymers to, for example, electronic devices, catalysis and electroanalysis [2]. Furthermore, tris(bipyridyl) ruthenium(II) complexes containing one or more olefin groups typically undergo cathodic electropolymerization [2,3], whereas analogous complexes with one or more anilino groups potentially can undergo anodic electropolymerization [4]. (iii) Complexes with two or more amine or anilino substituents can also be condensed with difunctional organic reagents to form macromolecules [5]. Consideration of points (i)–(iii) suggested that interesting electroactive polymers would be available from the targeted *p*-anilinovinylbipyridyl ruthenium(II) complexes by either electropolymerization or from reactions with appropriate difunctional organic reagents.

EXPERIMENTAL

Mass spectra were recorded on a VG Quattro mass spectrometer. ^{1}H and ^{13}C NMR spectra were obtained in the designated solvents on a Bruker AC-F 300 (300 MHz) spectrometer. Double quantum filtered (DQF) ^{1}H–^{1}H COSY spectra were acquired using a Bruker AC-F 300 NMR spectrometer with a standard (Bruker) multiphase sequence. IR spectra were recorded as Nujol mulls on a Perkin–Elmer 580B spectrometer. Electronic spectra were recorded using a CARY 5 spectrophotometer in the dual beam mode.

Electrochemical instrumentation and procedures

Acetonitrile and *N*,*N*-dimethylformamide (DMF) were highest-quality anhydrous grade sealed under argon (Aldrich) and were used as received. The supporting electrolyte in all measurements was tetra-*n*-butylammonium hexafluorophosphate ($\mathrm{Bu^n_4NPF_6}$, Aldrich), which was recrystallized twice from ethanol and then dried *in vacuo* at 70°C overnight.

Electrochemical measurements were recorded at ambient temperature using a Bioanalytical Systems

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(BAS) 100B Electrochemical Analyser interfaced to a 486 IBM compatible personal computer. Data was transferred to a Macintosh PowerPC for processing using the IgorPro 2.0™ software. Cyclic and differential pulse voltammetries were conducted in a standard three-electrode cell consisting of a platinum disc working electrode (0.8 mm diameter, BAS) press-fitted into a Kel F tube, platinum wire (0.05 mm diameter) auxiliary electrode and an Ag/AgCl reference electrode (BAS). The platinum working electrode was cleaned with 1 μm diamond polish (BAS) and polishing alumina (BAS), placed in water in an ultrasound bath for 5 min and then rinsed with water and acetone before use. All potentials are quoted relative to the ferrocenium/ferrocene (Fc^+/Fc) couple which was measured *in situ* as an internal reference [6].

Materials

All solvents were reagent-grade except where noted. Acetonitrile was distilled from calcium hydride; DMF was dried over calcium hydride and then distilled *in vacuo*; tetrahydrofuran (THF) was distilled from sodium/benzophenone. Flash chromatography was carried out using Merck silica gel 7730 $60GF_{254}$ as the support. 2,2′-Bipyridine, 4,4′-dimethyl-2,2′-bipyridine and ruthenium trichloride trihydrate were purchased from Aldrich and used as received. Ru $(bpy)_2Cl_2 \cdot 2H_2O$ was prepared according to a literature method [7].

Preparations

4,4′-Bis(2-(4-anilino)-2-hydroxyethyl)-2,2′-bipyridine (L^1). *n*-Butyl-lithium (35.0 cm^3, 2.5 M, 87.6 mmol) was added *via* syringe to a solution of di-*iso*-propylamine (12.5 cm^3, 87.6 mmol) in THF (80 cm^3) cooled to ~ -75°C in an acetone–solid carbon dioxide bath. The solution was stirred for 30 min and then 4,4′-dimethyl-2,2′-bipyridine (5.0 g, 27.2 mmol) in THF (250 cm^3) was slowly added *via* a dropping funnel and the reaction mixture allowed to slowly increase in temperature to 0°C (ice–water bath) and stirred for 1 h. Freshly prepared *p*-aminobenzaldehyde [8] (7.25 g, 60 mmol) in THF (250 cm^3) was added *via* a dropping funnel to the cooled mixture. The reaction mixture was stirred for 3 h and then slowly allowed to rise to room temperature and stirred for 16 h. The reaction was quenched by the addition of methanol (12 cm^3) and the solution added to water (300 cm^3). The mixture was extracted with chloroform (5×150 cm^3), the extract washed with brine, dried with magnesium sulfate and the solvent removed. The product precipitated after the addition of acetone (60 cm^3) and cooling the solution in ice–water. The solid was filtered and washed with diethyl ether. A second portion of product was obtained by chromatography (alumina, 2% methanol/dichloromethane eluent), removal of the solvent *in vacuo* and precipitation with acetone (total yield: 1.47 g, 13%). M.pt: decomposition 150°C. Found: C, 71.5; H, 6.4; N, 13.1. Calc. for $C_{26}H_{26}N_4O_2 \cdot 1/2H_2O$: C, 71.7; H, 6.2; N, 12.9%. ES-MS: $427(M+1)^+$. ^1H NMR $[(CD_3)_2CO]$: δ 8.45 (d, 2H, $J = 4.6$ Hz, H_6), 8.31 (s, 2H, H_3), 7.15 (dd, 2H, $J = 5.2$, 1.6, H_5), 7.06 (d, 4H, $J = 8.7$, Ph), 6.56 (d, 4H, $J = 8.7$, Ph), 4.81 (m, 2H, C$\underline{H}$OH), 4.46 (br s, 4H, NH_2), 4.09 (d, 2H, $J = 4.9$, OH), 3.01 (m, 4H, CH_2). ^1H NMR $[(CD_3)_2SO]$: δ 8.49 (d, 2H, $J = 4.9$ Hz, H_6), 8.24 (s, 2H, H_3), 7.20 (dd, 2H, $J = 5.1$, 2.8, H_5), 7.01 (d, 4H, $J = 8.5$, Ph), 6.49 (d, 4H, $J = 8.5$, Ph), 5.07 (d, 2H, $J = 4.6$, OH), 4.90 (s, 4H, NH_2), 4.66 (m, 2H, C$\underline{H}$OH), 2.93 (d, 4H, $J = 6.7$, CH_2). IR (Nujol mull): 3320w, 3205w, 1614m, 1600s, 1554w, 1515m, 1269m, 1205w, 1176m, 1110w, 1046m, 1004w, 995w, 934w, 880w, 860w, 830m cm^{-1}.

4,4′-Bis(4-anilinovinyl)-2,2′-bipyridine (L^2). L^1 (1.30 g, 3.05 mmol) and pyridinium toluene-*p*-sulfonate (0.25 g, 1.0 mmol) were heated at reflux in dry toluene (150 cm^3) in Dean–Stark apparatus for 18 h. After this period the toluene was removed *in vacuo* and the residue dissolved in chloroform and washed with water, brine and then dried with magnesium sulfate. Removal of chloroform *in vacuo* gave a yellow powder (1.19 g, 84%). Found: C, 79.6; H, 5.7; N, 14.1. Calc. for $C_{26}H_{22}N_4O_2$: C, 80.0; H, 5.6; N, 14.4%. EI-MS: $390(M^+)$. ^1H NMR $[(CD_3)_2SO]$: δ 8.59 (d, 2H, $J = 5.1$ Hz, H_6), 8.44 (s, 2H, H_3), 7.53 (dd, 2H, $J = 6.9$, 1.5, H_5), 7.43 (d, 2H, $J = 16.4$, HC═), 7.40 (d, 4H, $J = 8.4$, Ph), 7.01 (d, 2H, $J = 16.4$, ═CH), 6.56 (d, 4H, $J = 8.4$, Ph), 5.52 (br s, 4H, NH_2). ^{13}C NMR $[(CD_3)_2SO]$: δ 156.10, 150.21, 149.17, 146.84, 134.41, 128.89, 123.99, 120.64, 120.57, 117.37, 114.06. IR (Nujol mull): 3435w, 3320w, 3210w, 1620w, 1600m, 1584s, 1535w, 1523w, 1305w, 1298w, 1282w, 1195w, 1176m, 1160w, 1109w, 986m, 972m, 965m, 955w, 938w, 903w, 833m, 820w cm^{-1}.

(4,4′-Bis(4-anilinovinyl)-2,2′-bipyridyl)bis(2,2′-bipyridyl) ruthenium(II)hexafluorophosphate, ($[RuL^2(bpy)_2]PF_6)_2$. L^2 (137 mg, 0.35 mmol) was dissolved in DMF (150 cm^3) at reflux. $Ru(bpy)_2Cl_2 \cdot 2H_2O$ (183 mg, 0.35 mmol) was added and the solution heated at reflux for 25 h. After cooling the solvent volume was reduced *in vacuo* to 50 cm^3 and excess NH_4PF_6 in water (10 cm^3) added. The resulting precipitate was filtered and washed well with water, diethyl ether and then dissolved in the minimum volume of acetonitrile and purified by flash chromatography [silica, 20:2:1 acetonitrile–water–saturated KNO_3 (aq) eluent]. The main bright red band was collected and recrystallized from aqueous methanol containing excess NH_4PF_6 to give a red microcrystalline solid (150 mg, 40%). Found: C, 49.5; H, 3.8; N, 9.8. Calc. for $C_{46}F_{12}H_{38}N_8P_2Ru \cdot H_2O$: C, 49.6; H, 3.6; N, 10.1%. ES-MS: 402 ($[RuL^2(bpy)_2]^{2+}$), 949 ($[RuL^2(bpy)_2](PF_6)^+$). ^1H NMR $[(CD_3)_2CO]$: δ 8.85 (d, 2H, $J = 1.8$ Hz, H_3), 8.77 (d, 4H, $J = 8.2$, H_{bpy}), 8.14 (m, 4H, H_{bpy}), 8.01 (d, 2H, $J = 5.6$, H_5), 7.74 (d, 2H, $J = 5.9$, H_6), 7.58 (d, 2H, $J = 15.9$, —HC═), 7.53 (m, 8H, $2H_{bpy}$), 7.36

(d, 4H, J = 8.7, Ph), 7.03 (d, 2H, J = 16.2, =CH—), 6.67 (d, 4H, J = 8.7, Ph), 2.32 (s, 4H, NH_2). ^{13}C NMR [$(CD_3)_2CO$]: δ 158.50, 158.43, 152.96, 152.09, 151.87, 149.23, 139.04, 138.74, 130.51, 129.05, 125.58, 125.35, 124.69, 121.35, 119.58, 115.42. IR (Nujol mull): 3400w, 1594s, 1516w, 1310w, 1269w, 1200w, 1176m, 1064w, 1020w, 972w, 838s, 790w cm^{-1}. UV–vis. (MeOH), λ_{max}/nm (10^{-3} ε/dm^3 mol^{-1} cm^{-1}): 465 (42.3), 396 (46.1), 291 (60.7), 246 (36.6).

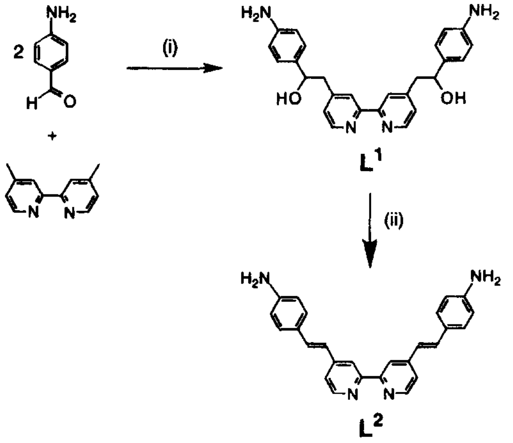
Tris(4,4′-bis(4-anilinovinyl)-2,2′-bipyridyl)ruthenium(II)hexafluorophosphate, $[RuL^2_3](PF_6)_2$. L^2 (260 mg, 0.67 mmol) and $RuCl_3 \cdot 3H_2O$ (58 mg, 0.22 mmol) were heated at reflux in DMF (80 cm^3) under nitrogen for 40 h. The solution was cooled and filtered through celite. The solvent volume was reduced *in vacuo* to 10 cm^3 and excess NH_4PF_6 in water (10 cm^3) was added and the solution cooled in ice. The precipitate was separated by filtration, washed with water and then dissolved in the minimum volume of acetonitrile and purified by flash chromatography [silica, 20 : 2 : 1 acetonitrile–water–saturated KNO_3 (aq) eluent]. The main bright red band was collected and recrystallized from aqueous methanol containing excess ammonium hexafluorophosphate (122 mg, 35%). Found: C, 58.5; H, 4.5; N, 10.2. Calc. for $C_{78}F_{12}H_{66}N_{12}P_2Ru \cdot 2H_2O$: C, 58.6; H, 4.4; N, 10.5%. ES-MS: 636 ($[RuL^2_3]^{2+}$). ^{1}H NMR [$(CD_3)_2SO$]: δ 8.96 (s, 2H, H_3), 7.69 (m, 4H, —HC= and H_5), 7.56 (d, 2H, J = 6.2 Hz, H_6), 7.44 (d, 4H, J = 8.5, Ph), 7.05 (d, 2H, J = 16.1, =CH—), 6.66 (d, 4H, J = 8.2, Ph), 5.73 (s, NH_2). ^{13}C NMR [$(CD_3)_2SO$]: δ 156.90, 150.62, 150.24, 146.95, 137.20, 129.41, 124.02, 123.77, 119.81, 118.68, 114.42. IR (Nujol mull): 3380w, 1594s, 1516w, 1300w, 1200w, 1176m, 1140w, 1020w, 963w, 840m, 734w, 719w, 660w cm^{-1}. UV–vis. (MeOH), λ_{max}/nm (10^{-3} ε dm^3 mol^{-1} cm^{-1}): 484 (37.8), 403 (61.7), 311 (36.2), 251 (29.8).

RESULTS AND DISCUSSION

Syntheses and properties of the complexes

The preparations of the bipyridyl ligands L^1 and L^2 are summarized in Scheme 1. Monolithiation of 4,4′-dimethyl-2,2′-bipyridine using lithium diisopropylamide, followed by addition of freshly prepared p-aminobenzaldehyde [8] afforded L^1. Dehydration of L^1 was achieved by heating it in toluene at reflux with pyridinium toluene-p-sulfonate [9] to afford L^2 in high yield. The homoleptic and heteroleptic ruthenium(II) complexes $[RuL^2_3]^{2+}$ and $[RuL^2(bpy)_2]^{2+}$ were prepared by heating L^2 in DMF at reflux with either $RuCl_3$ or $Ru(bpy)_2Cl_2$, respectively. The complexes were purified by flash chromatography on silica and precipitated as hexafluorophosphate salts by metathesis with NH_4PF_6.

The partial elemental analysis, ^{1}H NMR and mass spectral data for the ligands L^1 and L^2 and the ruthenium(II) complexes $[RuL^2(bpy)_2]^{2+}$ and $[RuL^2_3]^{2+}$, are consistent with the proposed structures.



Scheme 1.

Electron ionization mass spectra of L^1 and L^2 both showed ions at 390 m/z corresponding to M^+ for L^2 (L^1 was assumed to have dehydrated during the ionization). The electrospray mass spectrum of L^1 shows a molecular ion at 427 m/z corresponding to $(M+1)^+$. Electrospray mass spectra of the complexes showed peaks for the ions $[RuL^2(bpy)_2]^{2+}$ and $[RuL^2(bpy)_2](PF_6)^+$ at 402 and 949 m/z, respectively, and $[RuL^2_3]^{2+}$ at 636 m/z. NMR assignments were made by comparison with ^{1}H NMR spectra reported for other 4,4′-substituted bipyridyl ligands and homoleptic and heteroleptic ruthenium(II) bipyridyl complexes [3–5] and where necessary confirmed by ^{1}H–^{1}H DQF COSY experiments.

The IR spectra of the ligands and the complexes all exhibited characteristic absorptions for the —NH_2 groups at ~3350 cm^{-1} [10] and L^2 and its complexes showed a weak band at ~1600 cm^{-1}, which is assigned to the vinyl absorption [10]. Both ruthenium(II) complexes also showed a strong absorption in their IR spectra at 840 cm^{-1} for the hexafluorophosphate counterion [11]. The electronic spectra of the ruthenium complexes are shown in Fig. 1. The visible regions are dominated by intense broad absorption bands which tail into the UV region. An intense band observed at ~400 nm in the spectra of both complexes is ascribed to a ligand-centred anilino transition similar to that observed for 4″-(4-anilino)-2,2′:6′,2″-terpyridine and its complexes [5b]. As expected, this band was more intense in the spectrum of the homoleptic ruthenium(II) complex containing six anilino groups than the heteroleptic ruthenium(II) complex that contains two anilino groups. The highest wavelength band (~470 nm) is assigned to spin-allowed $d(Ru) \rightarrow \pi^*(L^2)$ metal-to-ligand-charge-transfer (m.l.c.t.) transitions by comparison with the voluminous literature on closely related complexes with $[Ru(bpy)_3]^{2+}$ cores [1–4,12]. The shift to higher wavelengths of the m.l.c.t. absorption of the ruthenium(II) complexes of L^2 relative to $[Ru(bpy)_3]^{2+}$ (λ_{max} = 452 nm [1h]) is indicative of the

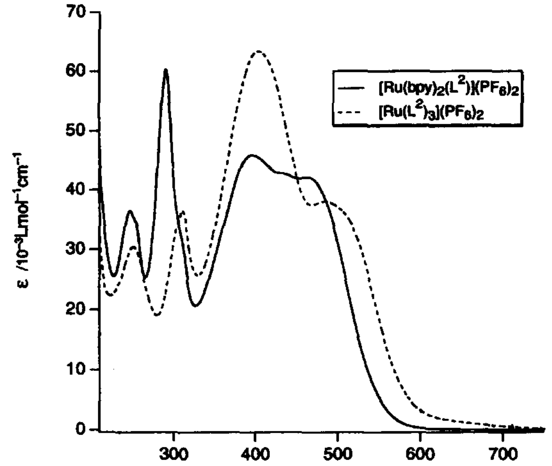


Fig. 1. Electronic spectra of the ruthenium(II) complexes of L^2 recorded in methanol.

electron-withdrawing nature of the olefinic groups lowering the energy of the m.l.c.t. states [1,12]. To higher energy a number of intense $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ bands are observed.

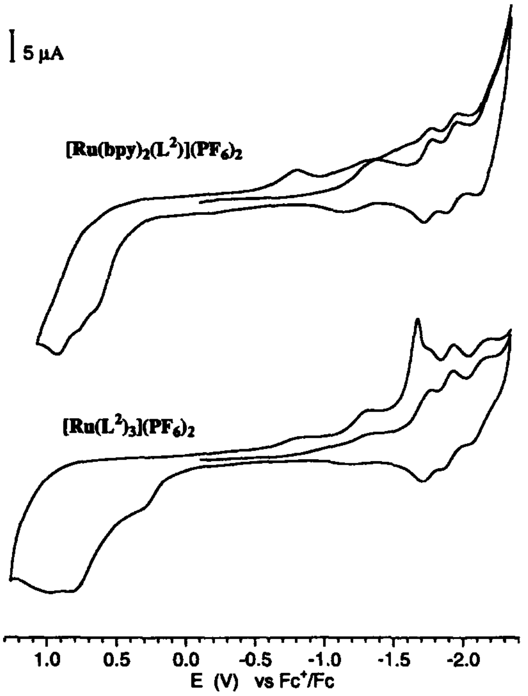


Fig. 2. Cyclic voltammograms of the ruthenium(II) complexes of L^2 ($\sim 0.70 \times 10^{-3}$ M) recorded in DMF containing 0.1 M $Bu^n_4NPF_6$; Pt disk working electrode; $T = 295$ K, scan rate = 100 mV s^{-1}.

Electrochemistry

Cyclic and differential pulse voltammograms of $[RuL^2(bpy)_2]^{2+}$ and $[RuL^2_3]^{2+}$ were recorded in acetonitrile and DMF solutions and data are summarized in Table 1. Representative cyclic voltammograms for $[RuL^2(bpy)_2]^{2+}$ and $[RuL^2_3]^{2+}$ recorded in DMF are shown in Fig. 2. In the first cycle, both complexes exhibited three quasi-reversible couples (the third reduction couple in the cyclic voltammogram of $[RuL^2(bpy)_2]^{2+}$ is partly obscured by the cathodic discharge), which are assigned to sequential reductions of the three bipyridine ligands of the $[Ru(bpy\text{-})_3]^{2+}$ core [13]. $[RuL^2(bpy)_2]^{2+}$ also showed an irreversible reduction at −1.2 V, positive of the bipyridyl-centred reductions. In the second and subsequent cycles (i.e. after the potential was cycled over the oxidation processes) an irreversible reduction peak was observed at −0.8 V, which may be associated with the reduction of an oxidation product formed on the positive cycle. To positive potentials, the cyclic voltammograms of both complexes showed a broad irreversible oxidation with shoulders to lower potential. This process is ascribed to the overlap of the expected reversible Ru^{III}/Ru^{III} couple and the irreversible anilino oxidation. The cyclic voltammetric response of both ruthenium(II) complexes in DMF were essentially consistent after the second scan.

The first scans to both positive and negative potential for $[RuL^2(bpy)_2]^{2+}$ and $[RuL^2_3]^{2+}$ in acetonitrile are shown in Figs 3(a) and 4(a), respectively. The expected reversible Ru^{II}/Ru^{III} couples are observed as broad oxidation processes for both complexes, similar to the behaviour observed in DMF. Beer *et al.* in

Table 1. Cyclic voltammetric data for the complexes; potentials are V *vs* Fc^+/Fc

	Acetonitrile[a]			DMF[a]		
Complex	E^b	E^c	E^d	E^b	E^c	E^d
$[RuL^2(bpy)_2]^{2+}$	0.86	0.63	−1.72, −1.93, −2.16	0.82	0.57	−1.74, −1.93, −2.22
$[RuL^2_3]^{2+}$	0.98	0.48	−1.69, −1.82, −2.06	0.94	0.33	−1.75, −1.90, −2.10
$[Ru(bpy)_3]^{2+e}$	0.90		−1.71, −1.90, −2.15	0.86		−1.63, −1.82, −2.06

[a] 0.1 M $Bu^n_4NPF_6$.

[b] Ru^{II}/Ru^{III}.

[c] E_a(anilino).

[d] First, second and third bipyridyl-centred reductions of the $[Ru(bpy)_3]^{2+}$ core.

[e] Data from [13].

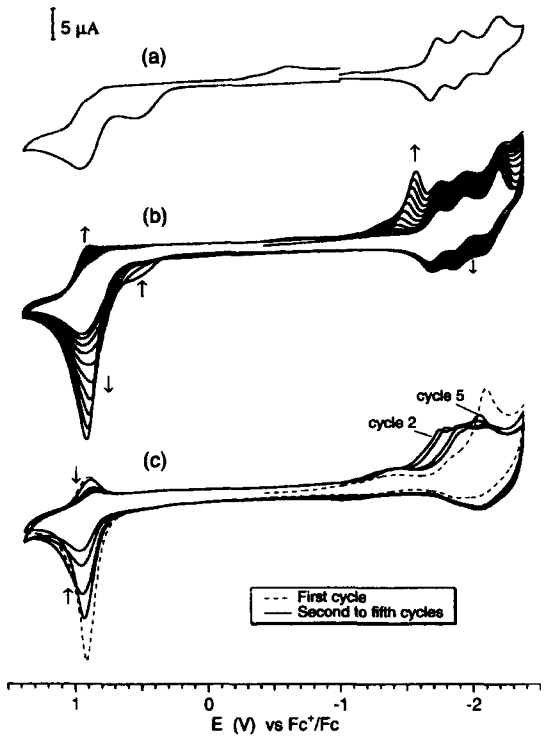


Fig. 3. Cyclic voltammograms of $[Ru(bpy)_2(L^2)]^{2+}$ (1.0×10^{-3} M) recorded in acetonitrile containing 0.1 M $Bu^n_4NPF_6$; Pt disk working electrode; $T = 295$ K, scan rate = 100 mV s^{-1}. (a) First cycle. (b) Ten sequential cycles. (c) Five sequential voltammograms for a poly-$[Ru(bpy)_2(L^2)]^{2+}$ modified electrode from (b) in fresh acetonitrile containing 0.1 M $Bu^n_4NPF_6$. The arrows indicate increasing or decreasing current as appropriate.

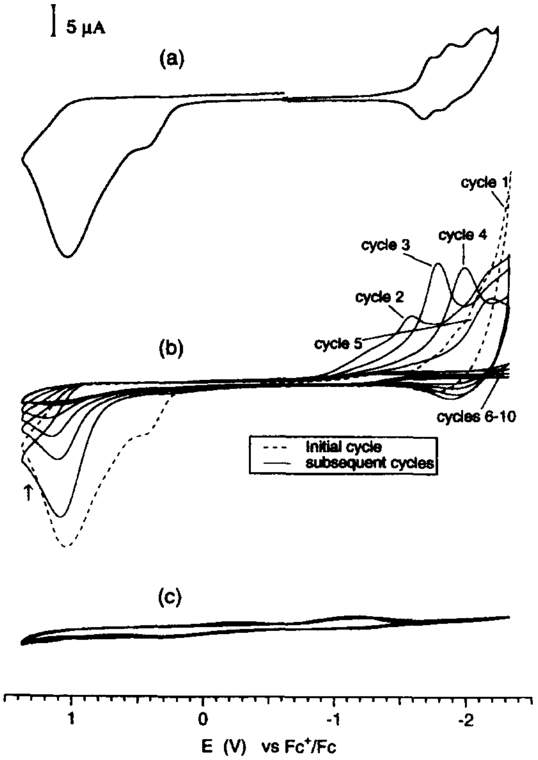


Fig. 4. Cyclic voltammograms of $[Ru(L^2)_3]^{2+}$ (0.8×10^{-3} M) recorded in acetonitrile containing 0.1 M $Bu^n_4NPF_6$; Pt disk working electrode; $T = 295$ K, scan rate = 100 mV s^{-1}. (a) First positive and negative scans. (b) Ten sequential cycles. (c) Five sequential cycles for the poly-($[Ru(L^2)_3]^{2+}$) modified electrode from (b) in fresh acetonitrile containing 0.1 M $Bu^n_4NPF_6$. The arrow in (b) indicates decreasing current.

their study of ferrocenylvinyl bipyridyl complexes [3c] reported an Ru^{II}/Ru^{III} couple with a peak-to-peak separation of 120 mV for the complex $[Ru(bpy)_2(L)]^{2+}$ (L = 4-ferrocenylvinyl-4′-methyl-2,2′-bipyridine), in acetonitrile, but observed a broad irreversible process for the complex $[Ru(bpy)_2(L)]^{2+}$ [L = 4,4′-bis(ferrocenylvinyl)-2,2′-bipyridine], behaviour similar to that of the complexes of L^2. Preceding the Ru^{III}/Ru^{III} couple in the first scan of $[RuL^2(bpy)_2]^{2+}$ and $[RuL^2_3]^{2+}$ in both acetonitrile and DMF is an irreversible process which can be assigned to irreversible oxidation of the vinylanilino group (for comparison, aniline exhibits a similar oxidation process in acetonitrile at ~ +0.66 V [5,14]). Hence, the irreversibility of the Ru^{II}/Ru^{III} couple is likely associated with the irreversible oxidation of the anilino group at similar potentials.

$[RuL^2(bpy)_2]^{2+}$ could be electropolymerized. Repetitive cycling of the potential of a Pt disc working electrode between −1.90 and +1.80 V in an acetonitrile solution containing $[RuL^2(bpy)_2]^{2+}$ resulted in the deposition of a polymeric film on the electrode surface, Fig. 3(b). Polymerization did not occur unless the applied potential was cycled to include the oxidation processes, as reported in the aforementioned study of Beer *et al.* [3c] on the deposition of complexes with ferrocenylvinyl bipyridyl ligands. A steady increase in peak currents is observed with increasing scans attributable to deposition of the complex on the electrode surface. Note that the Ru^{III}/Ru^{II} couple is still poorly reversible and that the preceding irreversible oxidation attributed to the oxidation of the vinylaniline moiety was only observed in the first cycle. A cathodic peak at −1.5 V began to form after the first cycle and its peak current increased at a rate faster than the other reduction processes. After 10 sequential cycles, a smooth, adherent red–gold film was observed on the platinum surface of the electrode after it was removed from the solution. Figure 3(c) shows the electrochemical response of a rinsed poly-($[RuL^2(bpy)_2]^{2+}$) modified electrode in a fresh acetonitrile solution containing 0.1 M $Bu^n_4NPF_6$. The cathodic region of the first cycle is significantly different from the subsequent cycles. The cathodic peak found at −1.5 V in the cyclic voltammogram showing polymer formation is noticeably absent in the cyclic voltammogram of the modified electrode. Most notable in the cyclic voltammetric response of the polymer-modified electrode is the current decay for all peaks over successive scans indicating that the polymer degrades very quickly. Unfortunately, the poly-([RuL^2(bpy)$_2$]$^{2+}$) modified electrode is poorly stable and, therefore, of limited utility. Similar behaviour was observed by Beer *et al.* in their studies of ruthenium complexes with vinylferrocene or vinyl crown ether substituted bipyridyl ligands [3c,d].

Leidner *et al.* have demonstrated the importance of radical–radical coupling of the olefinic groups in the electropolymerization of ruthenium(II) complexes containing vinyl-substituted bipyridines [3b]. [RuL$^2_3$]$^{2+}$ would be expected to show a greater rate of electropolymerization than [RuL^2(bpy)$_2$]$^{2+}$ because of the presence of six olefinic groups [2,3]. Although [RuL$^2_3$]$^{2+}$ was only slightly soluble in acetonitrile, electropolymerization did occur and resulted in the deposition of a thin, dark adherent film onto the electrode surface. Polymerization occurred for [RuL$^2_3$]$^{2+}$ when the potential was cycled above +0.0 V. As shown in Fig. 4(b), the film deposited onto the electrode became essentially non-conducting after five cycles and exhibited none of the expected characteristic electrochemical processes of tris(diimine) ruthenium(II) complexes. The electrochemical response of the [RuL$^2_3$]$^{2+}$ modified electrode in a fresh acetonitrile solution is shown in Fig. 4(c). The absence of redox processes in the voltammogram suggested either that the polymer layer was insulating or the complex decomposed during the electropolymerization. When ferrocene was added to the solution and the potential cycled, the ferrocenium/ferrocene couple was not observed, revealing the electrode coating to be insulating.

CONCLUSION

We have shown that ruthenium(II) complexes of the new anilino-pendant bipyridine ligand 4,4′-bis(4-anilinovinyl)-2,2′-bipyridine (L^2) are subject to electrodeposition by potential cycling through the oxidation processes in acetonitrile solution. Unfortunately, the heteroleptic ruthenium(II) complex [RuL^2(bpy)$_2$]$^{2+}$ results in the deposition of a non-robust, electroactive polymer film and the homoleptic ruthenium(II) complex [RuL$^2_3$]$^{2+}$ deposits as a non-conducting film. Finally, we note that the ligand L^2 and its complexes also seem suitable for incorporation into macromolecular systems through reactions of the pendant anilino moieties [5], but examples of these reactions have not been explored.

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