

Contribution from Geo-Centers, Inc., Suitland, Maryland 20746,  
and Chemistry Division, U.S. Naval Research Laboratory, Washington, D.C. 20375

## Spectral, Electrochemical, and Conductivity Studies of Poly(pyridyl)ruthenium Complexes Containing Polymerizable Acetylenic and Olefinic Ligands<sup>†</sup>

JEFFREY M. CALVERT,<sup>\*†</sup> DALE L. PEEBLES,<sup>§</sup> and ROBERT J. NOWAK<sup>§</sup>

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The complexes *cis*-[Ru(bpy)<sub>2</sub>((py)<sub>2</sub>C<sub>2</sub>)<sub>2</sub>]<sup>2+</sup> ((py)<sub>2</sub>C<sub>2</sub> = 1,2-bis(4-pyridyl)acetylene) and *mer*-[Ru(trpy)((py)<sub>2</sub>C<sub>2</sub>)<sub>3</sub>]<sup>2+</sup> have been synthesized. Their optical and electrochemical redox properties are correlated and compared in two homologous series: [Ru(bpy)<sub>2</sub>(L)<sub>2</sub>]<sup>2+</sup> and [Ru(trpy)(L)<sub>3</sub>]<sup>2+</sup>, where L = 4-vinylpyridine (vpy), *trans*-1,2-bis(4-pyridyl)ethylene (BPE), and (py)<sub>2</sub>C<sub>2</sub>. The (py)<sub>2</sub>C<sub>2</sub> complexes are the first examples of transition-metal-complex monomers that undergo reductive electrochemical polymerization (EP) whose polymerizable functional group is not an olefin. The electrochemical behavior of the two series of complexes has been investigated in detail. An oxidative film formation reaction is reported, quantitative and mechanistic aspects of the EP reaction are discussed, and scanning electron microscopy, two-point conductivity ( $\sigma = 10^{-12} \Omega^{-1} \text{ cm}^{-1}$ ), and charge-transport measurements were made on the dry poly-[Ru(bpy)<sub>2</sub>((py)<sub>2</sub>C<sub>2</sub>)<sub>2</sub>]<sup>2+</sup> films.

### Introduction

Modification of electrode surfaces with insoluble, electroactive polymer coatings is currently an area of considerable interest due to the diversity of applications potentially afforded by such tailor-made interfaces.<sup>1-3</sup> Reductive electrochemical polymerization (EP) of transition-metal complexes containing bound ligands with polymerizable functional groups<sup>1,3</sup> has been found to be a relatively simple technique for producing stable, electroactive, and reasonably uniform films as homopolymers, copolymers, or spatially segregated bilayers. A recent study<sup>1</sup> extended to over 30 the number of polymerizable complexes and examined the mechanisms involved in the EP process. A common feature of the metallo-polymer films prepared to date by this method is that they are derived from monomer complexes that possess an olefinic site on at least one of the ligands of the molecule. An example is the prototype monomer *cis*-[Ru(bpy)<sub>2</sub>(vpy)<sub>2</sub>]<sup>2+</sup>, (bpy = 2,2'-bipyridine, vpy = 4-vinylpyridine).

In contrast to other electrochemically polymerized films that passivate the electrode<sup>4</sup> or are electronic conductors (e.g., poly(pyrrole)),<sup>5</sup> films formed from the (vpy)<sub>2</sub> complex and similar molecules are redox conductors.<sup>3a,b,m</sup> Reductive coupling of the vinyl monomers gives rise to polymers composed of noninteracting metal sites linked by a saturated hydrocarbon backbone. The conduction of electrons through these films depends on redox reactions of the metal complex sites. It involves both electronic motion within a narrow band at energy levels corresponding to the polymeric metal complex redox potentials and ionic motion (incorporation or expulsion of charge-compensating counterions from the electrolyte) to preserve charge neutrality within the film. Some doped polymers such as poly(pyrrole) and poly(acetylene),<sup>6</sup> have dry conductivities up to 3000  $\Omega^{-1} \text{ cm}^{-1}$ .<sup>6b</sup> In an attempt to create a metallo-polymer film with a conjugated backbone and possibly endow the film with the additional feature of electronic conductivity, the acetylenic ligand containing metal complex monomers *cis*-[Ru(bpy)<sub>2</sub>((py)<sub>2</sub>C<sub>2</sub>)<sub>2</sub>]<sup>2+</sup> ((py)<sub>2</sub>C<sub>2</sub> = bis(4-pyridyl)acetylene) and *mer*-[Ru(trpy)((py)<sub>2</sub>C<sub>2</sub>)<sub>3</sub>]<sup>2+</sup> (trpy = 2,2',2''-terpyridine) have been synthesized. With the knowledge that related organic monomers such as diphenylacetylene can be reductively polymerized in nonaqueous media,<sup>7</sup> the electrochemistry of the bis(pyridyl)acetylene complexes and their polymer analogues was investigated. Two-point conductivity measurements on the polymer-coated electrodes are reported.

The spectral and redox properties of the (py)<sub>2</sub>C<sub>2</sub> complexes are compared to complexes with similar polymerizable ligands in two homologous series: [Ru(bpy)<sub>2</sub>(L)<sub>2</sub>]<sup>2+</sup> and [Ru(trpy)(L)<sub>3</sub>]<sup>2+</sup>, where

L = vpy, (py)<sub>2</sub>C<sub>2</sub>, and BPE (BPE = *trans*-1,2-bis(4-pyridyl)ethylene).

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<sup>§</sup>Geo-Centers, Inc.

<sup>\*</sup>U.S. Naval Research Laboratory.

<sup>†</sup>NRL/NRC Postdoctoral Research Associate.

## Experimental Section

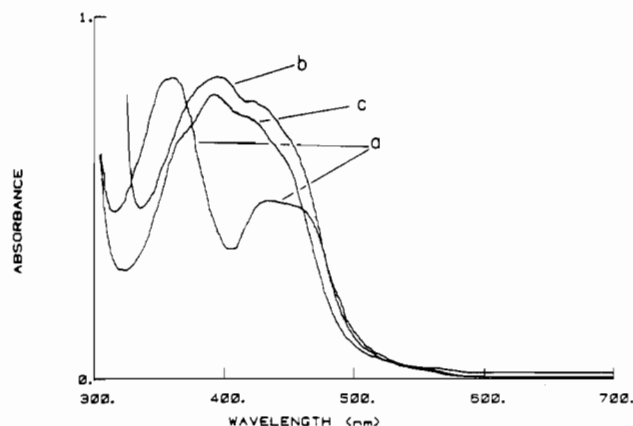
(a) **Materials.** Acetonitrile (Burdick & Jackson) for electrochemical measurements was stored over activated Davison 3A molecular sieves for at least 24 h before use. Tetraethylammonium perchlorate (TEAP) and tetra-*n*-butylammonium hexafluorophosphate (TBAH) were obtained from Southwestern Analytical Chemicals, dried in a vacuum oven for 12 h at 60 °C and stored in a desiccator. Bis(4-pyridyl)acetylene (King's Mountain Specialties, King's Mountain, NC) was found to match the literature melting point and infrared and NMR spectra.<sup>8</sup> [Ru(bpy)<sub>2</sub>(vpy)](PF<sub>6</sub>)<sub>2</sub>, [Ru(trpy)(vpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub>, and [Ru(trpy)(BPE)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> were prepared as described in the literature.<sup>1</sup> All other chemicals and solvents were reagent grade or better and were used as received. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

(b) **Preparation of *cis*-[Ru(bpy)<sub>2</sub>((py)<sub>2</sub>C<sub>2</sub>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>.** *cis*-Ru(bpy)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O (100 mg, 0.19 mmol)<sup>9</sup> was added to 20 mL of an N<sub>2</sub>-degassed 1:1 (v/v) ethanol/water solution of bis(4-pyridyl)acetylene (210 mg, 1.17 mmol). The mixture was protected from light<sup>10</sup> and heated under N<sub>2</sub> at gentle reflux for 5 h. After cooling to room temperature, 0.5 mL of saturated aqueous NH<sub>4</sub>PF<sub>6</sub> solution was added and the resulting orange precipitate was filtered, rinsed with water and diethyl ether, and then dried. The solid was purified by column chromatography on basic alumina (Fisher). A minor red-brown band, probably [Ru(bpy)<sub>2</sub>((py)<sub>2</sub>C<sub>2</sub>)Cl]<sup>+</sup>, was eluted with 1:1 acetonitrile/toluene before the major orange fraction (λ<sub>max</sub> = 393 nm) was collected by using a 2:1 CH<sub>3</sub>CN/toluene mixture. A second orange (likely due to thermal polymerization<sup>11</sup>) remained near the top of the column. Solvent was removed by rotary evaporation and the product isolated by reprecipitation from CH<sub>3</sub>CN into stirring ether. Yield: 70 mg (35%). Anal. Calcd for RuC<sub>44</sub>H<sub>32</sub>N<sub>8</sub>P<sub>2</sub>F<sub>12</sub>·2H<sub>2</sub>O: C, 48.02; H, 3.30; N, 10.19. Found: C, 47.87; H, 3.40; N, 10.18. (Note: the inclusion of one water of hydration per (py)<sub>2</sub>C<sub>2</sub> ligand in the ((py)<sub>2</sub>C<sub>2</sub>)<sub>2</sub> and (py<sub>2</sub>C<sub>2</sub>)<sub>3</sub> complexes has been observed for the structurally similar BPE complexes.<sup>12</sup>)

(c) **Preparation of *cis*-[Ru(bpy)<sub>2</sub>(BPE)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>.** This complex was prepared by using the same procedure as described above for the pyridylacetylene complex, with the substitution of the BPE ligand for (py)<sub>2</sub>C<sub>2</sub>. The properties of the complex produced by this method were identical with those observed previously<sup>1</sup> when a different synthetic route was employed.<sup>12</sup> Yield: 58%.

(d) **Preparation of *mer*-[Ru(trpy)((py)<sub>2</sub>C<sub>2</sub>)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub>.** This complex was prepared similarly to other [Ru(trpy)(L)<sub>3</sub>]<sup>2+</sup> complexes reported in the literature.<sup>1</sup> Purification by column chromatography gave the desired product as an orange-brown solid in 35% yield. A minor red-brown component, likely [Ru(trpy)((py)<sub>2</sub>C<sub>2</sub>)<sub>2</sub>Cl]<sup>+</sup>, eluted prior to the main band and was isolated in 10% yield. Anal. Calcd for RuC<sub>51</sub>H<sub>35</sub>N<sub>9</sub>P<sub>2</sub>F<sub>12</sub>·3H<sub>2</sub>O: C, 50.2; H, 3.39; N, 10.35. Found: C, 48.4; H, 3.38; N, 10.45.

(e) **Electrodes, Instrumentation, and Electrochemical Procedures.** Before each experiment, Kel-F-shrouded platinum-disk electrodes (Bioanalytical Systems, West Lafayette, IN; 0.02 cm<sup>2</sup> area) were mechanically polished with diamond paste (Buehler) to a 1/4-μm finish and



**Figure 1.** UV-vis spectra of the [Ru(bpy)<sub>2</sub>(L)<sub>2</sub>]<sup>2+</sup> complexes in CH<sub>3</sub>CN solution: L = (a) vpy, (b) BPE, (c) (py)<sub>2</sub>C<sub>2</sub>. The concentration of complex used was ca. 10<sup>-4</sup> M.

then cleaned electrochemically<sup>13</sup> by anodizing and cycling in 1 M H<sub>2</sub>SO<sub>4</sub>. Electrochemical instrumentation included a PAR Model 174A polarographic analyzer and a PAR Model 175 universal programmer. Electrochemical experiments were performed in a fritted, three-compartment cell of conventional design. Measurements are referenced to a sodium chloride saturated calomel electrode (SSCE). A platinum wire served as the auxiliary electrode.

Electrolyte solutions were 0.1 M TEAP/CH<sub>3</sub>CN with the concentration of complex added being ca. 1 mM for the [Ru(trpy)(L)<sub>3</sub>]<sup>2+</sup> series and ca. 2 mM for the [Ru(bpy)<sub>2</sub>(L)<sub>2</sub>]<sup>2+</sup> complexes. In the case of [Ru(bpy)<sub>2</sub>(BPE)<sub>2</sub>]<sup>2+</sup>, the electrolyte solution for the film formation experiments was 0.1 M TBAH/CH<sub>3</sub>CN due to the low (<10<sup>-3</sup> M) solubility of the complex in perchlorate electrolyte. Solutions of the (L)<sub>2</sub> complexes were protected from light to avoid photosubstitution.<sup>10</sup> Film formation was accomplished by cycling the working electrode potential at 200 mV/s repeatedly from 0 to ca. 150 mV past E<sup>0'</sup> for the oxidative or reductive couple of interest. When the reverse component of the wave was not well-defined, the potential limit was set at about 100 mV past the peak potential, E<sub>p</sub>. After film formation, the electrode was rinsed with acetone and air-dried and its electrochemical response examined in fresh TEAP/CH<sub>3</sub>CN electrolyte. The coverage of electroactive material, Γ, was determined from the charge under the anodic M(III/II) wave under linear peak current vs. sweep rate conditions.

The intrinsic polymerizability of a complex, Γ/Γ<sub>0</sub>, is defined as the ratio of the measured coverage obtained with a particular monomer to the coverage obtained by polymerization at the first bpy reduction of the arbitrarily chosen standard complex, [Ru(bpy)<sub>2</sub>(vpy)<sub>2</sub>]<sup>2+</sup>. This ratio is then normalized for the concentrations of monomer complex and the numbers of potential cycles used to produce the films. This procedure was used for films formed by either oxidative or reductive cycling. The polymerization efficiency, Φ<sub>poly</sub>, was calculated from the measured coverage of electropolymerized complex (determined in clean electrolyte) divided by the amount of monomer complex undergoing redox per cycle (determined from the anodic charge under the Ru(III/II) wave for the monomer at a clean Pt electrode), multiplied by the number of cycles employed.<sup>14</sup> Although the electrochemical properties of the vpy and BPE complexes have been described in an earlier report,<sup>1</sup> experiments were repeated using independently synthesized materials. The results given here are summarized from the cumulative data of both the previous and present investigations.

*iR* compensation was used in chronoamperometry experiments to eliminate distortions in the *i*-*t* response due to the effects of uncompensated film resistance. *i*-*t* transients were recorded on a Hewlett-Packard storage oscilloscope.

Scanning electron micrographs of a poly-[Ru(bpy)<sub>2</sub>((py)<sub>2</sub>C<sub>2</sub>)<sub>2</sub>]<sup>2+</sup>-coated Pt foil were obtained by cementing the foil with conductive silver paint (SPI Supplies, West Chester, PA) to an aluminum specimen mount, which was then examined in an AMR 1000 microscope.

Two-point conductivity measurements were made on dry poly-[Ru(bpy)<sub>2</sub>(py<sub>2</sub>C<sub>2</sub>)<sub>2</sub>]<sup>2+</sup>-coated disk electrodes by using a Keithley Model 616 digital electrometer. Contact to the open film surface was made by immersing the electrode in a mercury pool. A copper wire completed the circuit. The films in Hg spontaneously generated an open-circuit voltage,

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- (11) (a) The formation of oligomeric or polymeric products during the preparation of the polymerizable-ligand-containing complexes has been noted before.<sup>1</sup> The relative amounts produced of these materials appear to correlate roughly with the reaction time and temperature, as well as the number of polymerizable groups in the molecule. The related observation that [Ru(bpy)<sub>2</sub>(vpy)<sub>2</sub>]<sup>2+</sup> can be polymerized by free-radical initiation (using AIBN in warm acetonitrile solution<sup>11b</sup>) suggests that the polymerization products may result from thermal generation of ligand-based free radicals in the metal complex monomers during synthesis. (b) Calvert, J. M., unpublished results.
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- (14) For a more detailed explanation of the origin and use of the parameters Γ/Γ<sub>0</sub> and Φ<sub>poly</sub>, see ref 1.

**Table I.** Spectral Properties of the Complexes in CH<sub>3</sub>CN Solution

	$\lambda_{\max}$ , nm
[Ru(bpy) <sub>2</sub> (vpy) <sub>2</sub> ] <sup>2+</sup>	465, 434, 358
[Ru(bpy) <sub>2</sub> (BPE) <sub>2</sub> ] <sup>2+</sup>	460 (sh), 427, 395 (sh)
[Ru(bpy) <sub>2</sub> ((py) <sub>2</sub> C <sub>2</sub> ) <sub>2</sub> ] <sup>2+</sup>	455 (sh), 425, 393 (sh), 375 (sh)
[Ru(trpy)(vpy) <sub>3</sub> ] <sup>2+</sup>	501, 372
[Ru(trpy)(BPE) <sub>3</sub> ] <sup>2+</sup>	501, 405
[Ru(trpy)((py) <sub>2</sub> C <sub>2</sub> ) <sub>3</sub> ] <sup>2+</sup>	490 (sh), 398

**Table II.** Reduction Potentials for the Free Ligands<sup>a</sup>

	$E_{p,c}$	$i_{p,a}/i_{p,c}$
vpy	-2.27	0
BPE	-1.86 <sup>b</sup>	0.60
(py) <sub>2</sub> C <sub>2</sub>	-1.92 <sup>b</sup>	0

<sup>a</sup>0.1 M TEAP/CH<sub>3</sub>CN electrolyte. <sup>b</sup>A second, quasi-reversible reduction process is observable for these ligands at potentials ca. 250 mV more negative, presumably due to conversion of the radical anion to the dianion.<sup>28</sup>

$V_{oc}$  of 0.3–0.7 V. Two approaches were employed to determine film resistance,  $R_f$ : (1) After measuring  $V_{oc}$ , the load resistance,  $R_l$ , through the electrometer was progressively lowered until the measured voltage was  $0.5V_{oc}$ . At this point,  $R_l = R_f$ . (2) The electrometer was used to pass progressively increasing currents through the film. At sufficiently large  $I$ ,  $V \gg V_{oc}$ , and  $R_f$  can be calculated from  $(V - V_{oc})/I$ .

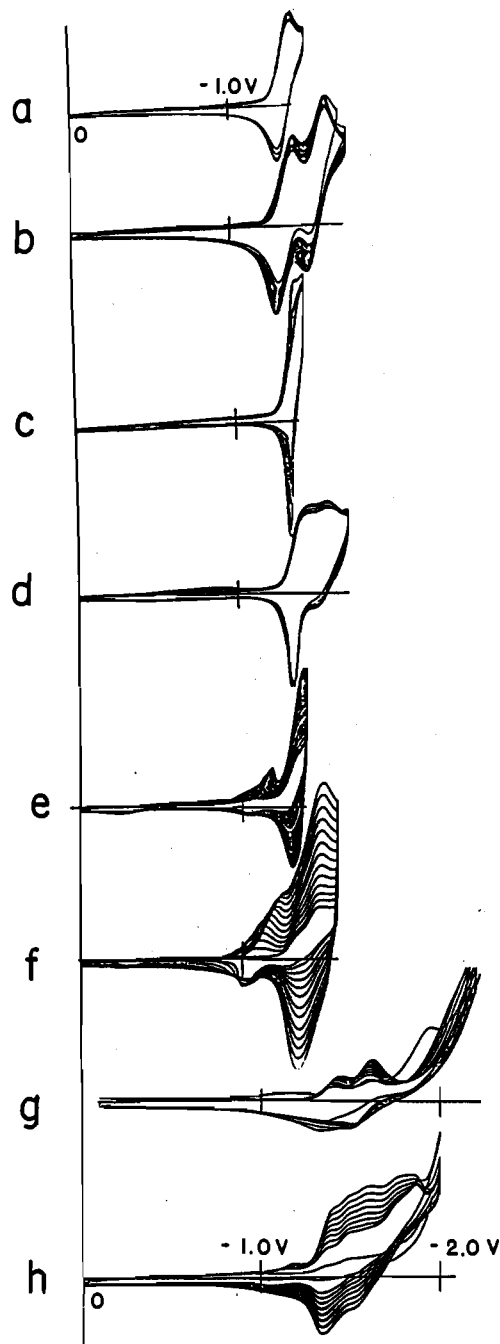
Conductivity measurements on a mixed-valence poly-[Ru(bpy)<sub>2</sub>((py)<sub>2</sub>C<sub>2</sub>)<sub>2</sub>]<sup>2+/+</sup> film were performed in a He-filled drybox (Vacuum Atmospheres Co.) by using the following procedure. The coated Pt disk was immersed in TEAP/CH<sub>3</sub>CN electrolyte and the applied potential was set to  $E^{\circ}$  for the first complex reduction, thereby producing a film with equal numbers of 2+ and 1+ Ru complex sites. When the current for the reduction reaction decayed to zero, the potentiostat was switched to open circuit and the coated electrode was removed from the electrolyte, rinsed briefly with CH<sub>3</sub>CN, and shaken dry. Conductivities were then obtained by using methods 1 and 2 described above.

UV-vis spectra were recorded on a Cary 14 spectrophotometer. Spectra and electrochemical data were digitized and plotted with an H-P 9872B plotter.

## Results and Discussion

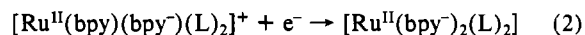
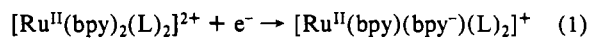
**(a) Disubstituted Complexes [Ru(bpy)<sub>2</sub>(L)<sub>2</sub>]<sup>2+</sup> (L = vpy, BPE, (py)<sub>2</sub>C<sub>2</sub>). Spectral Properties.** UV-vis spectra of the (L)<sub>2</sub> complexes in acetonitrile solution exhibit a manifold of transitions between 500 and 350 nm, as shown in Figure 1.  $\lambda_{\max}$  values are listed in Table I. In accordance with the spectral assignments of many other polypyridylruthenium(II) complexes in the literature,<sup>9,15</sup> these bands are assigned as MLCT  $\pi^*(bpy) \leftarrow Ru(d\pi)$  and  $\pi^*(L) \leftarrow Ru(d\pi)$  transitions. The most significant difference among the spectra is the blue shift of the highest energy transition of the (vpy)<sub>2</sub> complex ( $\lambda_{\max} = 358$  nm) relative to the maxima of the BPE and (py)<sub>2</sub>C<sub>2</sub> complexes, which occur at about 400 nm. This is consistent with the assignment of these bands as the metal to polymerizable ligand transition since greater delocalization of the excited electron in the BPE and (py)<sub>2</sub>C<sub>2</sub> ligands would be expected to lower the transition energy. Also, the presence of the electron-withdrawing pyridyl "substituent" on the bound pyridyl group of the BPE and (py)<sub>2</sub>C<sub>2</sub> ligands may contribute towards lowering the energy of the  $\pi^*(L)$  orbital. There is a smaller difference between the Ru  $\rightarrow$  L transitions in the BPE (395 nm) and (py)<sub>2</sub>C<sub>2</sub> (393 nm) complexes, which may be attributable to the greater  $\pi$ -donating ability of the acetylenic, as opposed to the olefinic, substituent. Thus, the UV-vis spectra show that the relative ordering of the three ligands in terms of their overall  $\pi$ -accepting ability is BPE  $\approx$  (py)<sub>2</sub>C<sub>2</sub>  $\gg$  vpy. The reduction potentials of the free ligands (shown in Table II), measured as  $E_{p,c}$  for the irreversible L(0/-) processes, corroborate the ordering determined from the spectra.

**(b) Electrochemistry.** Cyclic voltammograms (CVs) of the [Ru(bpy)<sub>2</sub>(L)<sub>2</sub>]<sup>2+</sup> complexes in acetonitrile solution are shown in Figure 2; formal potentials for the oxidative and reductive



**Figure 2.** Reductive cyclic voltammetry of the [Ru(bpy)<sub>2</sub>(L)<sub>2</sub>]<sup>2+</sup> complexes. Repeated cycling at the first bpy reduction: L = (a) vpy, (c) BPE, (e) (py)<sub>2</sub>C<sub>2</sub>. Repeated cycling at the second bpy reduction: L = (b) vpy, (d) BPE, (f) (py)<sub>2</sub>C<sub>2</sub>. Repeated cycling through the polymerizable ligand reductions: L = (g) vpy, (h) (py)<sub>2</sub>C<sub>2</sub>. Increasing currents are due to film growth on the electrode.

couples are summarized in Table III. The Ru(III/II) couples at  $E^{\circ}(ox,soln)$  are reversible ( $\Delta E_p = 60$ –70 mV) and occur between +1.25 and +1.33 V. Potentials for the first and second reductions (designated  $E^{\circ}(red,1,soln)$  and  $E^{\circ}(red,2,soln)$ ), corresponding to the sequential addition of electrons to each of the bipyridine ligand  $\pi^*$  orbitals (eq 1, 2), are also similar within each group, ranging from -1.30 to -1.36 V and from -1.47 to -1.58 V, respectively. Irreversible reductions localized at the



polymerizable ligands (represented by  $E^{\circ}(red,3,soln)$  and  $E^{\circ}(red,4,soln)$ ) can also be observed at more negative potentials. The process corresponding to eq 3 is well-defined for the vpy (Figure 2g) and (py)<sub>2</sub>C<sub>2</sub> monomers, whereas the fourth reduction can only

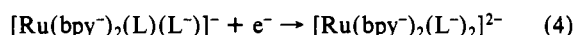
(15) (a) Kober, E. M.; Meyer, T. J. *Inorg. Chem.* **1982**, *21*, 3967. (b) Bryant, G. M.; Fergusson, J. G.; Powell, H. K. *J. Aust. J. Chem.* **1971**, *24*, 257.

**Table III.** Electrochemical Properties of the Complexes<sup>a,b</sup>

	[Ru(bpy) <sub>2</sub> (L) <sub>2</sub> ] <sup>2+</sup>			[Ru(trpy)(L) <sub>3</sub> ] <sup>2+</sup>		
	vpy	BPE <sup>c</sup>	(py) <sub>2</sub> C <sub>2</sub>	bpy	BPE	(py) <sub>2</sub> C <sub>2</sub>
<i>E</i> <sup>o'</sup> (ox,soln) <sup>d</sup>	+1.25	+1.29	+1.33	+1.23	+1.26	+1.32
<i>E</i> <sup>o'</sup> (ox,surf)	+1.22	+1.24	+1.32	+1.21	+1.24	+1.32
<i>E</i> <sup>o'</sup> (red,1,soln)	-1.36	-1.36	-1.30	-1.24	-1.22	-1.22
<i>E</i> <sup>o'</sup> (red,2,soln)	-1.54	-1.58	-1.47 <sup>e</sup>	-1.72 <sup>e</sup>	-1.50 <sup>e</sup>	-1.52 <sup>e</sup>
<i>E</i> <sup>o'</sup> (red,3,soln)	-1.94 <sup>e</sup>	-1.71 <sup>e</sup>	-1.73 <sup>e</sup>			
<i>E</i> <sup>o'</sup> (red,4,soln)			-1.85 <sup>e</sup>			
(Γ/Γ <sub>0</sub> ) <sub>1</sub>	1.0	0.4–16	72–173	5–12	6–14	34–46
(Φ <sub>poly</sub> ) <sub>1</sub> <sup>f</sup>	0.3	0.2–1.7	11–25	1.4–2.3	0.9–2.0	4–5
(Γ/Γ <sub>0</sub> ) <sub>2</sub>	3.7	1–4	310–640	200–310	160–460	250–370
(Φ <sub>poly</sub> ) <sub>2</sub>	1.1	0.3–0.5	48–99	58–60	45–65	28–42
(Γ/Γ <sub>0</sub> ) <sub>3</sub>	320–360	2.3	400–410			
(Φ <sub>poly</sub> ) <sub>3</sub>	38–43	3.3	63			
(Γ/Γ <sub>0</sub> ) <sub>4</sub>			430–600			
(Φ <sub>poly</sub> ) <sub>4</sub>			67–92			

<sup>a</sup>0.1 M TEAP/CH<sub>3</sub>CN electrolyte, except as noted. <sup>b</sup>Parameters are explained in the text. <sup>c</sup>0.1 M TBAH/CH<sub>3</sub>CN electrolyte. <sup>d</sup>All potentials are in volts vs. SSCE. <sup>e</sup>Irreversible reduction; value of *E*<sub>pc</sub>. <sup>f</sup>All polymerization efficiencies are reported in units of percent.

be seen clearly in the electrochemistry of the (py)<sub>2</sub>C<sub>2</sub> complex (Figure 2h).

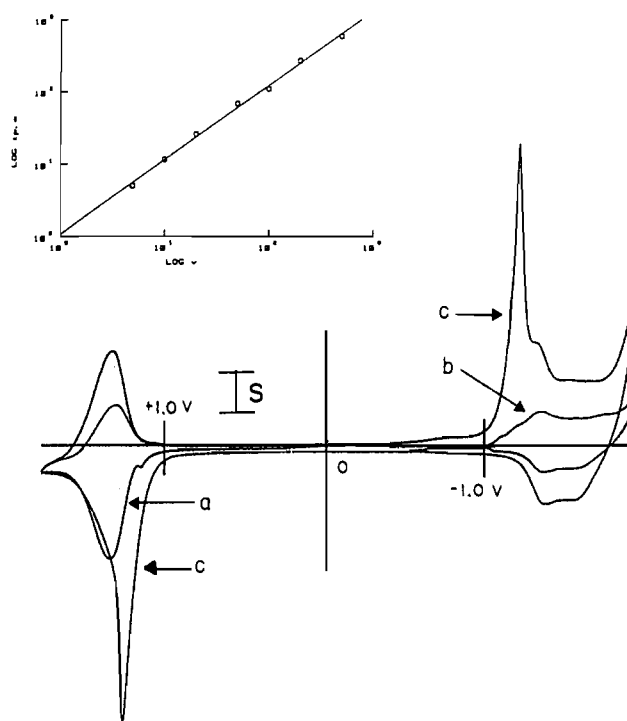


The highest energy peak at 375 nm in the spectrum of [Ru(bpy)<sub>2</sub>(py)<sub>2</sub>C<sub>2</sub>]<sup>2+</sup> is probably the optical transition corresponding to the fourth electrochemical reduction.

**Oxidative Film Formation.** Solutions of the polymerizable complexes were subjected to oxidative potential cycling. After numerous cycles (typically many tens to hundreds) through the Ru(III/II) couple, subtle hints of irreversibility appear in the CV. Examination of the electrodes used in these experiments in fresh electrolyte reveal the presence of up to a few monolayers of electroactive material at *E*<sup>o'</sup> values corresponding roughly to the particular monomer used. Efficiencies for oxidative film formation are low, the highest value being several tenths of 1% for the (BPE)<sub>2</sub> complex.<sup>16</sup> This feature will be discussed further in the section on the (L)<sub>3</sub> complexes.

**Reductive Film Formation.** Repeated cycling through the first bipyridine reduction results in the slow, but steadily increasing current at *E*<sup>o'</sup>(red,1) due to the reduction of both the monomer in solution and the metal complex sites in the incipient polymer film.<sup>1,3</sup> (Figure 2a,c,e). During EP of the (py)<sub>2</sub>C<sub>2</sub> complex a cathodic prewave (or quasi-reversible couple) develops, initially at -1.0 V, which increases in size and gradually shifts to more negative potentials with continued cycling. The origin of this phenomenon is unknown, but it occurs only with the acetylenic monomers. Similar CV behavior is observed when the potential sweep includes the second bpy reduction (Figure 2b,d,f). The more rapidly increasing current indicates faster film growth, especially for the (py)<sub>2</sub>C<sub>2</sub> complex, which again displays an apparent growing and shifting couple at potentials positive of the first bpy reduction wave. When the experiment is carried out by cycling through the polymerizable ligand reductions (Figure 2g,h), film growth is much faster than when cycling through either of the bpy couples (compare Figure 2g with Figure 2a,b).

Following EP, the coated electrodes were rinsed with acetone and transferred to a solution of fresh supporting electrolyte. In Figure 3, curve a is a representative example of a steady-state potential scan between 0 and +1.8 V of the surface-bound metallopolymers, which show the Ru(III/II) couples (and associated prewaves) at *E*<sup>o'</sup>(ox,surf) = +1.22 (vpy), +1.24 (BPE), and +1.32 ((py)<sub>2</sub>C<sub>2</sub>) V. The observed responses are nearly Nernstian in character for surface-immobilized species, as demonstrated by the 30-mV peak splitting and linear anodic peak current vs. sweep



**Figure 3.** Steady-state CVs of a poly-[Ru(bpy)<sub>2</sub>((py)<sub>2</sub>C<sub>2</sub>)<sub>2</sub>]<sup>2+</sup> film coated electrode. Potential limits used were as follows: curve a, 0 ↔ +1.80 V; curve b, 0 ↔ -1.95 V; curve c, +1.8 ↔ -1.95 V. Current sensitivity, *S*, was adjusted for clarity: curve a, 5 μA; curve b, 25 μA; curve c, 10 μA.

rate behavior. Curve b in Figure 3 shows the bpy reduction waves for the metal complex sites in the film as a result of repeated potential cycling from 0 to -1.95 V.

The response obtained from cycling the poly-[Ru(bpy)<sub>2</sub>((py)<sub>2</sub>C<sub>2</sub>)<sub>2</sub>]<sup>2+</sup>-coated electrode between +1.8 and -1.95 V in 0.1 M TEAP/CH<sub>3</sub>CN is shown in Figure 3, curve c. In addition to the expected metal oxidation and bpy reduction waves, the CV of this single-component film displays the enlarged, exponentially rising prewaves similar to those observed<sup>3c</sup> for a single-component poly-[Ru(vbpy)<sub>3</sub>]<sup>2+</sup> (vbpy = 4-methyl-4'-vinyl-2,2'-bipyridine) film.

The poly-(L)<sub>2</sub> complex films are quite stable with respect to oxidative cycling. The durability of the polymer derived from [Ru(bpy)<sub>2</sub>(vpy)<sub>2</sub>]<sup>2+</sup> has been previously noted.<sup>3a,b</sup> For the film formed by EP of the (py)<sub>2</sub>C<sub>2</sub> complex, a decrease in electroactivity of 20% was observed after 186 cycles through the Ru(III/II) wave at 100 mV/s, corresponding to the film having spent approximately 11 min in the Ru(III) state.

Oxidation of the polymeric metal complex sites occurs at slightly less positive potentials than that for each of the corresponding monomers in homogeneous solution (see Table III). This is a

(16) It has been previously reported<sup>3a,b</sup> that oxidation of [Ru(bpy)<sub>2</sub>(vpy)<sub>2</sub>]<sup>2+</sup> to the Ru(III) state does not result in metallopolymer formation. The necessity of prolonged cycling to produce a detectable coating is likely the cause for this inefficient process being overlooked.

**Table IV.** Comparison of the Optical and Electrochemical Reduction Potentials of the Bound Ligands in the  $[\text{Ru}(\text{bpy})_2(\text{L})_2]^{2+}$  and  $[\text{Ru}(\text{trpy})(\text{L})_3]^{2+}$  Complexes

	optical <sup>a</sup>			electrochemical <sup>b</sup>		
	bpy <sup>0/-</sup>	L <sup>0/-</sup>	$\Delta E$	bpy <sup>0/-</sup>	L <sup>0/-</sup>	$\Delta E^\circ$
vpy	2.67, 2.86	3.46	0.79, 0.60	-1.36, -1.54	-1.94	0.58, 0.40
BPE	2.69, 2.90	3.14	0.45, 0.24	-1.36, -1.58	-1.71	0.35, 0.13
(py) <sub>2</sub> C <sub>2</sub>	2.73, 2.92	3.16	0.42, 0.24	-1.30, -1.47	-1.73	0.43, 0.26

	optical <sup>a</sup>			electrochemical <sup>b</sup>		
	trpy <sup>0/-</sup>	L <sup>0/-</sup>	$\Delta E$	trpy <sup>0/-</sup>	L <sup>0/-</sup>	$\Delta E^\circ$
vpy	2.48	3.34	0.86	-1.24	-1.72	0.48
BPE	2.48	3.07	0.59	-1.22	-1.50	0.28
(py) <sub>2</sub> C <sub>2</sub>	2.50	3.12	0.62	-1.22	-1.52	0.30

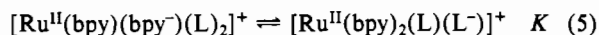
<sup>a</sup> Transition energies are in volts. <sup>b</sup> Reduction potentials are in volts vs. SSCE.

common feature of reductively polymerized films,<sup>1</sup> which may be attributable in part to the change of the pyridine substituent from an olefin to a more electron-rich saturated group.  $E^\circ$  for the poly- $[\text{Ru}(\text{bpy})_2(\text{py})_2\text{C}_2]^{2+}$  film is 80 mV positive of that for the BPE complex based film. This strongly suggests that the (py)<sub>2</sub>C<sub>2</sub> complex forms an unsaturated (conjugated?) backbone rather than undergoing a second reductive coupling step of the olefinic sites in the polymer, a sterically difficult process.

The polymerizability,  $(\Gamma/\Gamma_0)_1$ , and film formation efficiency,  $(\Phi_{\text{poly}})_1$ , of the vpy and BPE<sup>17</sup> complexes obtained by cycling through the first bpy reduction are much lower than the values obtained for the (py)<sub>2</sub>C<sub>2</sub> complex (see Table III). Film formation for the latter complex occurs up to 175 times faster than for the reference vpy monomer, with efficiencies of up to 25% (i.e. the charge under the surface wave corresponds to one-fourth of the charge passed during the polymerization reaction).

EP at the second bipyridine reduction has only a modest effect on the rate of film formation. Although the  $(\Gamma/\Gamma_0)_2$  values for the (py)<sub>2</sub>C<sub>2</sub> complex are numerically much larger than  $(\Gamma/\Gamma_0)_1$ , 310–640 vs. 72–173, the approximate factor of 4 increase is almost identical with that observed for the vpy complex. However, the high polymerizability of the bis(pyridyl)acetylene complex, at both the first and second reductions, is still unusual for a bis(polymerizable ligand) monomer as compared to the vpy and BPE complexes. The value of 640 for  $(\Gamma/\Gamma_0)_2$  is an order of magnitude larger than that for any other disubstituted monomer complex previously reported.<sup>1</sup>

For the (L)<sub>2</sub> complexes, EP effected at the bpy reductions is thought to occur via "indirect initiation"—an activated process wherein an electron located in a  $\pi^*$ (bpy) orbital is in intramolecular redox equilibrium with the  $\pi^*$  orbital of the polymerizable ligand located  $\Delta E^\circ$  higher in energy (eq 5, 6). Therefore, the



$$K = 10^{1.69n(\Delta E^\circ)} \quad (6)$$

polymerizability is related to the difference in energy of the bpy and L reduction potentials.<sup>1</sup> With the detection of the polymerizable ligand reduction potentials in CV,  $\Delta E$  can be obtained both from spectral and electrochemical experiments, as shown in Table IV. Correlations between the  $\Delta E$  values for a particular complex are in good qualitative agreement,<sup>18</sup> although the energy

differences measured optically are greater than electrochemical values.

From  $\Delta E^\circ$  considerations alone, both the BPE and (py)<sub>2</sub>C<sub>2</sub> monomers should show much greater  $(\Gamma/\Gamma_0)$  values than  $[\text{Ru}(\text{bpy})_2(\text{vpy})_2]^{2+}$ , yet in fact only the acetylenic complex does. For example, the ratio of  $K$  (which reflects the concentration of the polymerizable ligand radical anion and hence the rate of polymer formation) for the BPE complex relative to that for the vpy complex, from the electrochemical  $\Delta E^\circ$  values, is approximately  $10^4$ . The low polymerizability of the (BPE)<sub>2</sub> complex indicates that  $(\Gamma/\Gamma_0)$  must be a composite parameter, of which  $\Delta E^\circ$  is an important, although not necessarily determining, factor. Two considerations may contribute to this observation. First, as noted in the Experimental Section,  $[\text{Ru}(\text{bpy})_2(\text{BPE})_2]^{2+}$  is significantly less soluble in perchlorate electrolyte than either of the other disubstituted monomers. Therefore, if reductive EP of the ((py)<sub>2</sub>C<sub>2</sub>)<sub>2</sub> complex forms a network in which the individual units of the polymer resemble the BPE monomer, the lower solubility of these components will increase the rate of polymer film formation, which is in turn reflected in the high values of  $(\Gamma/\Gamma_0)$ . From the same reasoning, EP of the BPE monomer will produce a polymer with a saturated-backbone structure, which will consequently be more soluble and result in lower  $(\Gamma/\Gamma_0)$  values for the (BPE)<sub>2</sub> complex.

A second factor to consider is the reversibility of polymerizable ligand reduction. Table II gives the ratio of the anodic to cathodic peak currents,  $(i_{\text{pa}}/i_{\text{pc}})$ , for the free ligand L<sup>0/-</sup> couples in acetonitrile solution. These values show that no reverse wave is observed after reduction of vpy and (py)<sub>2</sub>C<sub>2</sub> at sweep rates of 200 mV/s. However, the BPE ligand reduction is partially reversible, indicating a somewhat more stable radical anion. This feature is likely to be carried over in the Ru-bound ligand and would have a direct bearing on the lower polymerizability of the complex. Thus, there are at least three factors that contribute to the relative magnitudes of the  $(\Gamma/\Gamma_0)$  values observed for the (L)<sub>2</sub> complexes:  $\Delta E^\circ$ , solubility of the reduced monomer units, and the reactivity of the polymerizable ligand radical anion.

A particularly interesting feature of the (py)<sub>2</sub>C<sub>2</sub> complex is the polymerization efficiency at the second reduction.  $(\Phi_{\text{poly}})_2$ , which has been found to be as high as 99% in several EP reactions, has been employed to support arguments concerning the mechanism of reductive EP.<sup>1</sup> Previously reported values of  $\Phi_{\text{poly}}$  for (L)<sub>2</sub> complexes ranged as high as 8–12%—already much higher than would be expected on the basis of  $\Delta E^\circ$  and  $K$  alone. Steps were included in the EP mechanism that involved recycling the electron initially used to reduce the monomer complex in various chain processes. The observed value of  $\Phi_{\text{poly}}$ , which is directly proportional to  $\Gamma$ , is necessarily a lower limit because  $\Gamma$  accounts only for the polymeric material which ultimately accretes onto the electrode and does not account for any soluble, oligomeric products. It could reasonably be expected that some polymerization reactions are more than 100% efficient. Efficiency values greater than 100% require invocation of a chain-growth process as at least part of the overall EP mechanism. However, for all the polymerizable monomers investigated to date, the maximum efficiencies do not exceed 100%, within experimental error. Therefore, while chain pathways must contribute to some extent, sequential hydro-

(17) Reductive electropolymerization was performed in 0.1 M TBAH/CH<sub>3</sub>CN (see Experimental Section). To determine the effect of PF<sub>6</sub><sup>-</sup> on film formation, the (vpy)<sub>2</sub> complex was also polymerized in this electrolyte.  $\Gamma/\Gamma_0$  was found to be 1.0 (to within 10%)—the same as in ClO<sub>4</sub> solution.

(18) Linear correlations between CT band energies and reduction potentials have been observed for other Ru(II) complexes: (a) Saji, T.; Aoyagui, S. *J. Electroanal. Chem. Interfacial Electrochem.* **1975**, *63*, 401. (b) Matsubara, T.; Ford, P. C. *Inorg. Chem.* **1976**, *15*, 1107. (c) Salmon, D. J. Ph.D. Dissertation, The University of North Carolina at Chapel Hill, 1976. (d) Rillema, D. P.; Allen, G. H.; Meyer, T. J.; Conrad, D. *Inorg. Chem.* **1983**, *22*, 1617.

(19) Calvert, J. M. Ph.D. Dissertation, The University of North Carolina at Chapel Hill, 1982; Chapter 4.

(20) (a) Daum, P.; Murray, R. W. *J. Phys. Chem.* **1981**, *85*, 389. (b) Ellis, D.; Eckhoff, M.; Neff, V. D. *J. Phys. Chem.* **1981**, *85*, 1225.

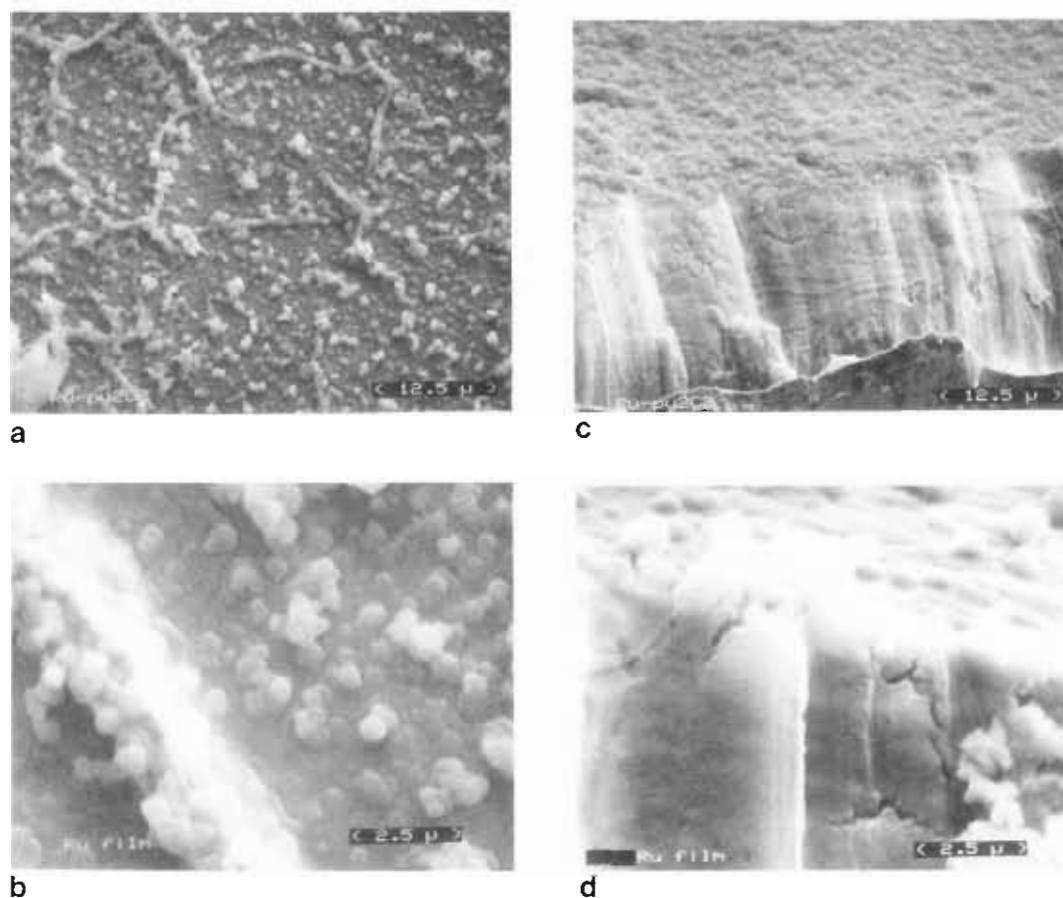


Figure 4. SEMs of a poly-[Ru(bpy)<sub>2</sub>((py)<sub>2</sub>C<sub>2</sub>)<sub>2</sub>]<sup>2+</sup> film on a Pt foil: (a, b) top view; (c, d) edge view. Electrochemical coverage =  $4.5 \times 10^{-8}$  mol/cm.

dimerization of the reactive polymerizable ligand radical anions is most likely the dominant (and limiting) route to metallopolymer formation.

The observation of the polymerizable ligand based reductions in the (L)<sub>2</sub> monomers,  $E^{\circ'}$ (red,3,soln) and  $E^{\circ'}$ (red,4,soln), also supports the mechanism described above. Complexes that are found to be difficult to polymerize at the bpy reductions become good monomers under conditions of direct initiation. However, although  $\Phi_{\text{poly}}$  values are much higher, they still never exceed unity. Another ramification of the direct-initiation results is that  $(\Gamma/\Gamma_0)_3$  appears to be relatively insensitive to the nature of the polymerizable ligand. While this is beneficial in terms of providing an effective means of producing good coatings of any (L)<sub>2</sub> monomer, it also greatly reduces the potential for increasing complex polymerizabilities by virtue of improved synthetic design.

The rate of charge transport through the poly-[Ru(bpy)<sub>2</sub>((py)<sub>2</sub>C<sub>2</sub>)<sub>2</sub>]<sup>2+</sup> film was measured as the diffusion coefficient,  $D_{\text{ct}}$ , by chronoamperometry.<sup>38</sup> The applied potential step was sufficient to cause oxidation of the sites in the film from Ru(II) to Ru(III). Initial potentials ranged from +0.6 to +1.0 V; final potentials were +1.6 to +1.9 V.  $D_{\text{ct}}$  was found to be independent of the final potential beyond approximately +1.6 V. The anodic current for the Ru(II) → Ru(III) reaction was plotted vs.  $t^{-1/2}$ , and  $D_{\text{ct}}$  was calculated from the linear short-time slope by using the Cottrell equation. The concentration of the Ru sites was estimated to be  $1.3 \times 10^{-3}$  mol/cm<sup>3</sup> from the molecular weight of the monomeric Ru complex unit (972) and by using 1.3 g/cm<sup>3</sup> for the density of the metallopolymer, by analogy to the value of 1.35 g/cm<sup>3</sup> measured for the density of samples of poly-[Ru(vbpy)<sub>3</sub>]<sup>2+</sup>.<sup>3b</sup>  $D_{\text{ct}}$  ranged between  $2.4 \times 10^{-9}$  and  $4.0 \times 10^{-9}$  cm<sup>2</sup>/s, in agreement with values for numerous other electrochemically polymerized films of vinyl monomers.<sup>3b,8</sup> It is distinctly different, though, from  $D_{\text{ct}}$  measured for the oxidation of neutral poly(acetylene), which is slower by approximately 2–3 orders of magnitude.<sup>21</sup>

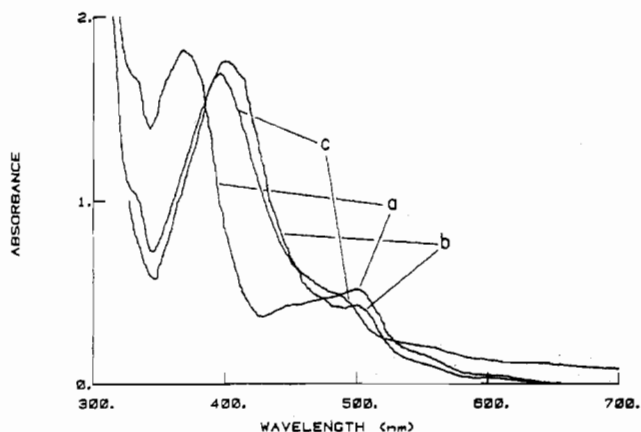
(c) **Microscopy.** The morphology of the metallopolymer films was investigated by scanning electron microscopy. Figure 4 shows SEMs of poly-[Ru(bpy)<sub>2</sub>((py)<sub>2</sub>C<sub>2</sub>)<sub>2</sub>]<sup>2+</sup> coated onto a Pt foil electrode. The internal structure of the film appears dense and homogeneous, as shown by the cross section views. The dimensions of surface features, which take the form of amorphous balls and ridges of polymer, are small compared to the thickness of the film. Pores or pinholes in the top surface of the film are not observable at this magnification (4000×), although cracks are present at the outer edges. There is no evidence for a fibrillar structure typical of poly(acetylene) films,<sup>22</sup> a feature that is observable at this magnification.

(d) **Conductivity Studies.** Two-point conductivity measurements were performed on the dry-film-coated electrodes as described in the Experimental Section. Film resistances,  $R_f$ , were found by using both methods to be in the range  $10^9$ – $10^{10}$  Ω. For an electrode area,  $A$ , of  $1.8 \times 10^{-2}$  cm<sup>2</sup> and a film thickness,  $d$ , of  $\sim 1$  μm, the conductivity of the film,  $\sigma$ , can be calculated from the relationship  $\sigma = d/AR_f$  to be approximately  $10^{-12}$  Ω<sup>-1</sup> cm<sup>-1</sup>. This compares favorably with an estimated value of  $\sim 10^{-11}$  Ω<sup>-1</sup> cm<sup>-1</sup> for a poly-[Ru(vbpy)<sub>3</sub>]<sup>2+</sup> film.<sup>23</sup> The poor conductivity of the polymer films formed from the bis(pyridyl)acetylene complex is somewhat disappointing given the presumably conjugated backbone of the metallopolymer chain or network. The reason for this may have two origins. First, reduction of the acetylenic complex to form a conjugated polymer may have been followed by further reduction of some of the remaining olefinic sites to produce a partially saturated system. Second, a number of (CH)<sub>x</sub> derivatives such as poly(phenylacetylene) have been prepared, and the doped versions of the substituted materials are found to be

(21) Calvert, J. M.; Nowak, R. J., manuscript in preparation.

(22) Shirakawa, H.; Ikeda, S. *Synth. Met.* 1979, 1, 175.

(23) A value of  $R_{\text{film}} = 5 \times 10^7$  Ω was reported by Murray<sup>3c</sup> for the effective resistance of a poly-[Ru(vbpy)<sub>3</sub>]<sup>2+</sup> film, determined in a bilayer trapping experiment. The conductivity was calculated by using  $10^{-4}$  cm as the film thickness and 0.1 cm<sup>2</sup> as the electrode area.



**Figure 5.** UV-vis spectra of the  $[\text{Ru}(\text{trpy})(\text{L})_3]^{2+}$  complexes in  $\text{CH}_3\text{CN}$  solution: L = (a) vpy, (b) BPE, (c)  $(\text{py})_2\text{C}_2$ . The concentration of complex used was ca.  $10^{-4}$  M.

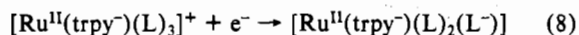
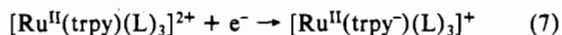
less conductive than the analogously doped parent polymer.<sup>24</sup> In the present case, substitution of the conjugated chain (if one is actually present) in addition to the fact that the metallopolymer almost certainly has a network, rather than a linear structure, may be the cause of the low conductivity.

By comparison, neutral poly(acetylene) is not a much better conductor.  $\sigma$  for *trans*-( $\text{CH}$ )<sub>x</sub> is  $10^{-5} \Omega^{-1} \text{cm}^{-1}$ ; *cis*-( $\text{CH}$ )<sub>x</sub> is  $10^{-9} \Omega^{-1} \text{cm}^{-1}$ .<sup>6</sup> Conductive ( $\text{CH}$ )<sub>x</sub> is only obtained upon partial oxidation or reduction of the ( $\text{CH}$ )<sub>x</sub>  $\pi$  network. Similarly, many linear-chain conductors or other quasi-one-dimensional materials such as the partially oxidized tetracyanoplatinates, TTF/TCNQ, and various phthalocyanine polymers owe their conductivity to their partially oxidized, or mixed-valence, characters.<sup>25</sup> With this fact in mind, the conductivity of the reduced mixed-valence poly- $[\text{Ru}(\text{bpy})_2(\text{py})_2\text{C}_2]^{2+}$  film was investigated.

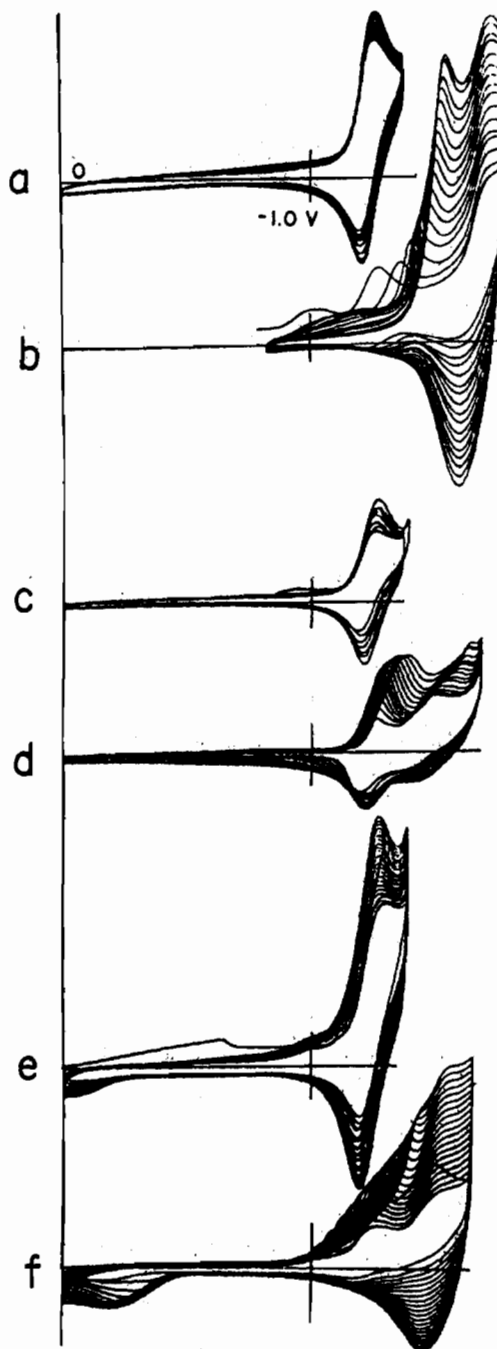
The mixed-valence polymer was prepared by fixing the electrode potential at  $-1.23$  V, which is  $E^{\circ}(\text{red},1)$  for the surface-bound complex. Visual inspection of the partially reduced film showed a distinct darkening from the initial gold color. The conductivity of the mixed-valence film was determined as described in the Experimental Section. The films were then oxidized to the 2+ form (restoring the gold color), and the conductivity was re-measured. In most cases,  $\sigma$  for the mixed-valence and subsequently oxidized films remained at  $10^{-12} \Omega^{-1} \text{cm}^{-1}$ .

**(e) Trisubstituted Complexes  $[\text{Ru}(\text{trpy})(\text{L})_3]^{2+}$ . Spectral and Redox Properties.** The UV-vis spectra of the ( $\text{L}$ )<sub>3</sub> homologues are shown in Figure 5; peak maxima are listed in Table I. By analogy to other Ru(II)-terpyridine complexes<sup>19,26</sup> and to the closely related Ru-bpy systems, the lowest energy bands at ca. 500 nm are assigned as  $\pi^*(\text{trpy}) \leftarrow \text{Ru}(d\pi)$ . The well-resolved bands at higher energies (between 372 and 405 nm) are the metal to polymerizable ligand charge transfers. As above for the ( $\text{L}$ )<sub>2</sub> complexes, the ordering of the Ru  $\rightarrow$  L transition energies remains: vpy  $\gg$   $(\text{py})_2\text{C}_2 \approx$  BPE.

Reduction potentials were obtained from CV experiments. The Ru(III/II) potentials lie between  $+1.23$  and  $+1.32$  V. The first reductions, localized at the trpy ligand (eq 7), are easily observable,



ranging from  $-1.52$  to  $-1.72$  V in the sequence listed above, and correlate well with optical measurements. The cathodic peak

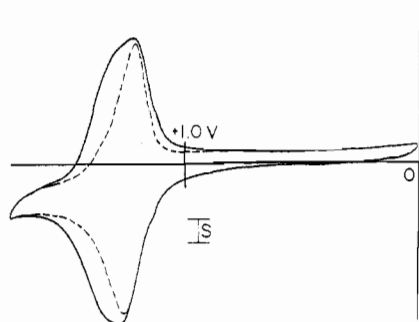


**Figure 6.** Reductive cyclic voltammetry of the  $[\text{Ru}(\text{trpy})(\text{L})_3]^{2+}$  complexes. Repeated cycling through the trpy reductions: L = (a) vpy, (c) BPE, (e)  $(\text{py})_2\text{C}_2$ . Repeated cycling through the polymerizable ligand reductions: L = (b) vpy, (d) BPE, (f)  $(\text{py})_2\text{C}_2$ . Increasing currents are due to film growth on the electrode.

potentials,  $E_{\text{pc}}$ , for the individual complexes occur ca. 200 mV more positive than for the analogous bipyridine monomers, reflecting the absence of a second polypyridine ligand reduction prior to the  $\text{L}(0/1^-)$  process.

**Reductive Film Formation.** EP of the complexes was carried out by either constraining the negative potential limit to encompass only the  $\text{trpy}^{0/-}$  couple or by including the  $\text{L}^{0/-}$  process in the sweep as well. These correspond, respectively, to the indirect and direct initiation cases discussed in the section on ( $\text{L}$ )<sub>2</sub> complexes. CVs of the film-formation reaction are shown in Figure 6. When potential cycling is confined to the trpy reduction only (Figure 6a,c,e), the CV displays the normal slow, steadily increasing growth observed for complexes such as  $[\text{Ru}(\text{bpy})_2(\text{vpy})_2]^{2+}$  and  $[\text{Ru}(\text{vbpy})_3]^{2+}$ . Values for  $(\Gamma/\Gamma_0)_1$  are moderate, ranging from 5 to 50, the acetylenic monomer again being the easiest to polymerize. Extending the negative sweep limit beyond the po-

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**Figure 7.** Cyclic voltammetry of a poly-[Ru(trpy)(BPE)<sub>3</sub>]<sup>2+</sup>-coated electrode produced by indirect initiation (dashed line,  $S = 1.0 \mu\text{A}$ ) and direct initiation (solid line,  $S = 2.5 \mu\text{A}$ ).

**Table V.** Oxidative Film Formation Characteristics of the [Ru(trpy)(L)<sub>3</sub>]<sup>2+</sup> Complexes<sup>a</sup>

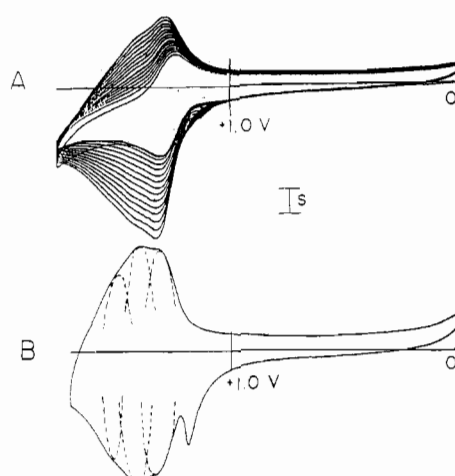
	vpy	BPE	(py) <sub>2</sub> C <sub>2</sub>
$E^{\circ}$ (soln)	+1.23	+1.26	+1.32
$E^{\circ}$ (surf)	+1.24	+1.48, +1.38, +1.30	+1.48, +1.38
$(\Gamma/\Gamma_0)$	1.1	100–130	5–16
$\Phi_{\text{poly}}$	0.2	15–18	0.6–1.8

<sup>a</sup>0.1 M TEAP/CH<sub>3</sub>CN electrolyte.

lymerizable ligand reduction (Figure 6b,d,f) gives rise to the rapidly growing, shifting wave pattern seen, for example, during EP of the ((py)<sub>2</sub>C<sub>2</sub>)<sub>2</sub> complex. As was the case for the (L)<sub>2</sub> complexes, polymerizability at the ligand-based reductions is high ( $(\Gamma/\Gamma_0) = 160\text{--}460$ ) but is relatively insensitive to which polymerizable ligand is involved. This is an indication that steric hindrance from coupling of pyridyl-substituted monomers plays a less important role than other factors in the overall polymerizability of a complex. The continual shifting of the waves to more negative potentials during the direct initiation experiments can most likely be accounted for by  $iR$  losses, due to slower charge transport through the fast-growing, increasingly thicker, and more highly cross-linked incipient film.<sup>27</sup>

CVs of the films derived from direct initiation of the trpy monomers exhibit the unusual feature of two apparently overlapping peaks in the potential region corresponding to the Ru(III/II) couple. This effect is most pronounced for the CV of the (BPE)<sub>3</sub> complex, shown in Figure 7. The major component of the two occurs at ca. +1.24 V, the minor component at about +1.29 V. Only the former couple is observed in films formed by EP at the trpy reduction. The similarity of  $E^{\circ}$  for the minor component to that for the solution monomer suggests that the minor couple may arise from incompletely polymerized Ru complex sites that are incorporated into the polymer network under conditions of rapid film growth. The presence of multiple couples in a film produced by EP of a single monomer also raises questions about interpretation of the behavior of other similar, ostensibly single-component films in electrocatalysis or charge-trapping applications.

**Oxidative Film Formation.** The [Ru(trpy)(L)<sub>3</sub>]<sup>2+</sup> complexes were also subjected to oxidative potential cycling. The oxidative electrochemical characteristics of the (L)<sub>3</sub> monomers and polymers are summarized in Table V. As shown in Figure 8a for the BPE complex, repeated sweeps between 0 and +1.7 V result in rapid growth and distortion of the Ru(III/II) couple, reminiscent of the reductively initiated film formation reaction described above. The CV of the resulting coated electrode in fresh electrolyte (Figure 8b) is composed of at least three resolvable couples, two of which do not correspond to the potentials observed for either the monomer in solution or the reductively polymerized films of the same complex.



**Figure 8.** (a) Oxidative EP of [Ru(trpy)(BPE)<sub>3</sub>]<sup>2+</sup>,  $S = 2.5 \mu\text{A}$ . (b) CV of the resultant film-coated electrode,  $S = 1.0 \mu\text{A}$ . Electrochemical coverage =  $5.2 \times 10^{-9} \text{ mol/cm}^2$ . The three proposed components of the surface wave were resolved by eye.

The film-forming ability of the (L)<sub>3</sub> complexes is actually quite respectable, although not as high as when reductive initiation is employed. The anodic oxidation of various organics such as amines,<sup>28a,b</sup> phenols,<sup>28c</sup> crown ethers,<sup>29</sup> and pyrrole<sup>5</sup> or functionalized transition-metal complexes<sup>2n</sup> such as [Ru(5-NH<sub>2</sub>-phen)<sub>3</sub>]<sup>2+</sup> (5-NH<sub>2</sub>-phen = 5-amino-1,10-phenanthroline) to yield polymers via established coupling paths is well-known. However, films from oxidation of olefinic and acetylenic monomers were unexpected. While it is possible that precipitation of the complex as Ru(III) and slow dissolution of the Ru(II) form may account for the behavior of these complexes, the stability of the coated electrodes in fresh electrolyte solution argues against this explanation. An alternative hypothesis is that an initial metal-centered oxidation could promote an intramolecular ligand oxidation, introducing hydroxyl groups (from trace water in the solvent), which could then couple to form polymers. The resulting oxidized carbon sites in the ligand would also explain the shift to more positive potentials of the metal complex sites in the film. A direct ligand oxidation pathway to give rise to a cationic chain polymerization pathway is not plausible because (1) the observed  $E^{\circ}$  for the monomer is at the correct potential for the Ru(III/II) couple and (2) no oxidative process is observed for the free ligands up to +2.0 V.

## Summary

In this paper, the properties of two homologous series of complexes, [Ru(bpy)<sub>2</sub>(L)<sub>2</sub>]<sup>2+</sup> and [Ru(trpy)(L)<sub>3</sub>]<sup>2+</sup> (L = polymerizable ligand), were investigated. The following conclusions can be summarized from the data:

(1) The electrochemistry of the bpy complexes is characterized by sequential reduction of each of the bpy and then the polymerizable, ligands. For the trpy complexes, reduction of the trpy and then the L groups is observed. Cycling through any of these reductions results in polymerization and film formation. The fastest rates of film formation result from direct initiation at the polymerizable ligand. A functional group (alkyne) other than an olefin was shown to undergo reductive EP. With the trpy complexes in particular, oxidative film formation was observed. The mechanism is not understood.

(2) The relative ordering of the MLCT transition energies for the complexes was found to track the electrochemical reduction potentials.

(3)  $\Gamma/\Gamma_0$ , the "intrinsic polymerizability", was shown to be a composite parameter, dependent upon  $\Delta E$ , the reactivity of the

(27) (a) Preliminary studies of the relative rates of charge transport through films prepared from monomers containing two vs. three polymerizable groups indicate that  $D_{\text{ox}}$  may be as much as several orders of magnitude slower in the trisubstituted complexes.<sup>27b</sup> (b) Calvert, J. M.; Facci, J. S., unpublished results.

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ligand-based radical anion, and the solubility of the polymerized metal complex units.

(4) The polymerization efficiency,  $\Phi_{\text{poly}}$ , approaches but never exceeds unity. This argues for hydrodimerization, and against a chain-growth mechanism, as the dominant pathway for monomer coupling.

(5) Charge-transport rates, film morphology, and dry-film conductivity measurements show the  $((\text{py})_2\text{C}_2)$ -based films to be similar to other metallopolymer films prepared by EP but not to poly(acetylene).

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**Registry No.** TEAP, 2567-83-1; TBAH, 3109-63-5; vpy, 100-43-6; BPE, 13362-78-2; *cis*- $[\text{Ru}(\text{bpy})_2((\text{py})_2\text{C}_2)](\text{PF}_6)_2$ , 97351-73-0; *cis*- $[\text{Ru}(\text{bpy})_2(\text{BPE})_2](\text{PF}_6)_2$ , 97414-91-0; *mer*- $[\text{Ru}(\text{trpy})((\text{py})_2\text{C}_2)_3](\text{PF}_6)_2$ , 97351-75-2;  $[\text{Ru}(\text{bpy})_2(\text{vpy})_2]^{2+}$ , 82769-08-2;  $[\text{Ru}(\text{bpy})_2(\text{BPE})_2]^{2+}$ , 97414-00-1;  $[\text{Ru}(\text{bpy})_2((\text{py})_2\text{C}_2)]^{2+}$ , 97351-72-9;  $[\text{Ru}(\text{trpy})(\text{vpy})_3]^{2+}$ , 83419-19-6;  $[\text{Ru}(\text{trpy})(\text{BPE})_3]^{2+}$ , 83082-73-9;  $[\text{Ru}(\text{trpy})((\text{py})_2\text{C}_2)_3]^{2+}$ , 97351-74-1;  $[\text{Ru}(\text{bpy})_2(\text{vpy})_2]^{3+}$ , 85661-74-1;  $[\text{Ru}(\text{bpy})_2(\text{BPE})_2]^{3+}$ , 97414-01-2;  $[\text{Ru}(\text{bpy})_2((\text{py})_2\text{C}_2)]^{3+}$ , 97351-76-3;  $[\text{Ru}(\text{trpy})(\text{vpy})_3]^{3+}$ , 85661-90-1;  $[\text{Ru}(\text{trpy})(\text{BPE})_3]^{3+}$ , 97414-02-3;  $[\text{Ru}(\text{trpy})((\text{py})_2\text{C}_2)_3]^{3+}$ , 97351-77-4;  $[\text{Ru}(\text{bpy})_2(\text{vpy})_2]^+$ , 97351-78-5;  $[\text{Ru}(\text{bpy})_2(\text{BPE})_2]^+$ , 97351-79-6;  $[\text{Ru}(\text{bpy})_2((\text{py})_2\text{C}_2)]^+$ , 97351-80-9;  $[\text{Ru}(\text{trpy})(\text{vpy})_3]^+$ , 97351-81-0;  $[\text{Ru}(\text{trpy})(\text{BPE})_3]^+$ , 97351-82-1;  $[\text{Ru}(\text{trpy})((\text{py})_2\text{C}_2)_3]^+$ , 97351-83-2;  $[\text{Ru}(\text{bpy})_2(\text{vpy})_2]$ , 97351-84-3;  $[\text{Ru}(\text{bpy})_2(\text{BPE})_2]$ , 97351-85-4;  $[\text{Ru}(\text{bpy})_2((\text{py})_2\text{C}_2)]$ , 97351-86-5;  $[\text{Ru}(\text{trpy})(\text{vpy})_3]$ , 97351-87-6;  $[\text{Ru}(\text{trpy})(\text{BPE})_3]$ , 97351-88-7;  $[\text{Ru}(\text{trpy})((\text{py})_2\text{C}_2)_3]$ , 97351-89-8;  $[\text{Ru}(\text{bpy})_2(\text{vpy})_2]^-$ , 97351-90-1;  $[\text{Ru}(\text{bpy})_2(\text{BPE})_2]^-$ , 97351-91-2;  $[\text{Ru}(\text{bpy})_2((\text{py})_2\text{C}_2)]^-$ , 97351-92-3;  $[\text{Ru}(\text{bpy})_2((\text{py})_2\text{C}_2)]^{2-}$ , 97351-93-4; *cis*- $\text{Ru}(\text{bpy})_2\text{Cl}_2$ , 19542-80-4;  $(\text{py})_2\text{C}_2$ , 73564-69-9; Pt, 7440-06-4.

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

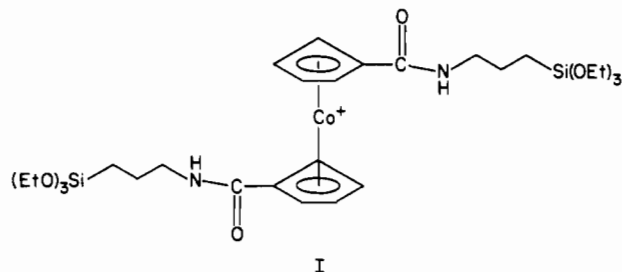
## Electrochemical Characterization of Surface-Bound Redox Polymers Derived from 1,1'-Bis[[(3-(triethoxysilyl)propyl)amino]carbonyl]cobaltocenium: Charge Transport, Anion Binding, and Use in Photoelectrochemical Hydrogen Generation

RICHARD A. SIMON, THOMAS E. MALLOUK, KAREN A. DAUBÉ, and MARK S. WRIGHTON\*

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This paper describes the behavior of electrode-bound redox material derived from the hydrolysis of the  $-\text{Si}(\text{OEt})_3$  groups of 1,1'-bis[[(3-(triethoxysilyl)propyl)amino]carbonyl]cobaltocenium (I). Surfaces of the conventional electrodes  $\text{SnO}_2$  and Pt derivatized with I have a reversible electrochemical response in  $\text{H}_2\text{O}$ /electrolyte; the  $E^\circ$  is pH independent at  $-0.62$  V vs. SCE. The photoelectrochemical behavior of p-type Si photocathodes derivatized with I reveals that the photoreduction of the cobaltocenium derivative can be effected at an electrode potential  $\sim 500$  mV more positive than on metallic electrodes, consistent with the known behavior of p-type Si photocathodes. When polymer from I is deposited on p-type Si and subsequently coated with a small amount of Rh or Pd ( $\sim 10^{-7}$  mol/cm<sup>2</sup>), the photoelectrochemical generation of  $\text{H}_2$  is possible with 632.8-nm ( $\sim 15$  mW/cm<sup>2</sup>) radiation and efficiencies in the vicinity of 2%. The polymer derived from I is more optically transparent and more durable at negative potentials than redox polymers derived from viologen monomers. Potential-step measurements and steady-state-current measurements for mediated redox processes show that the charge-transport rate for the polymer derived from I is about the same as for polymers from viologen monomers. As for other positively charged redox polymers, the material from I will electrostatically bind large transition-metal complex anions such as  $\text{IrCl}_6^{2-}$ ,  $\text{Fe}(\text{CN})_6^{3-}$ , and  $\text{Mo}(\text{CN})_6^{3-}$ . A quantitative study of the relative binding of  $\text{Cl}^-$  and  $\text{Fe}(\text{CN})_6^{3-}$  has been done;  $\Delta H^\circ = +12 \pm 0.5$  kcal/mol, and  $\Delta S^\circ = +52 \pm 2$  cal/(mol K). Thus, entropy drives the displacement of  $\text{Cl}^-$  by  $\text{Fe}(\text{CN})_6^{3-}$ . The redox potential of the  $\text{Fe}(\text{CN})_6^{3-}$  system is approximately 50 mV more negative in the polymer compared to the solution potential.

In this paper we describe the behavior of electrode surfaces functionalized with a derivatizing reagent based on the cobaltocenium cation, 1,1'-bis[[(3-(triethoxysilyl)propyl)amino]carbonyl]cobaltocenium (I). The electrode-bound polymer from



I is to be given the symbol  $[(\text{CoCpR}_2^{+/0})_n]_{\text{surf}}$ . Our interest in a cobaltocenium-based polymer is due to the known durability and reversible redox properties of the cobaltocenium/cobaltocene couple.<sup>1-3</sup> To form a covalently anchored polymer based on I, the known chemistry of the  $-\text{Si}(\text{OEt})_3$  functionality is exploited via its reaction with  $\text{H}_2\text{O}$  and surface  $-\text{OH}$  groups.<sup>4</sup> Despite a

considerable literature<sup>5</sup> on electrode-confined ferrocene reagents, there is only one report of the use of the cobaltocene system: the surface-confined cobaltocenium redox polymer poly(ethylene-imidocarbonylcobaltocenium) has been reported.<sup>6</sup>

The  $[(\text{CoCpR}_2^{+/0})_n]_{\text{surf}}$  system offers an attractive alternative to surface-confined viologen-based polymers<sup>7-9</sup> in photoelectro-

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