Synthesis and Characterization of a Pendant Polymer Complex of [Ru(biq)$_2$(pvbpy)]$^{2+}$

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The preparation and characterization of a pendant polymer complex of [Ru(biq)$_2$(pvbpy)](ClO$_4$)$_2$ are described [biq = 2,2′-biquinoline; = pvbpy = poly(4-methyl-4′-vinyl-2,2′-bipyridine)]. The UV–visible absorption and luminescence properties of the complex are measured. Cyclic voltammetry is used to characterize the complex and to enable preparation of the reduced pendant polymer complex samples. The electron spin resonance data for the reduced one-, two-, three-, and four-electron-reduced species indicate that the reduced species are each $S = \frac{1}{2}$ ligand-localized materials. The first- and second-electron-reduction species give ESR signals with temperature-dependent line broadening. The third- and fourth-electron-reduced species show ESR signals without temperature-dependent line broadening but produce ESR signals with hyperfine structure.

Introduction

In a series of papers,[1–7] we have detailed the properties of the multielectron-reduced complexes of [RuL$_3$]$^{2+}$ and [RuL$_2$L′]$^{2+}$ (L and L′ are π diimine chelate ligands such as 2,2′-bipyridine) using electrolysis techniques to produce stable air-sensitive samples. The one-, two-, and three-electron-reduction products were examined using cyclic voltammetry,[1–4] optical absorption,[7–9] Raman spectroscopy,[7–9] and temperature-dependent ESR techniques.[1–6] From these data the spatially isolated orbital (single chelate ring localization)[4] model evolved in which the redox electrons are individually localized in the π ligand ring orbitals and, due to the orthogonality of the π^* chelate orbital, do not interact substantially with redox electrons in the other chelate rings. One consequence of this unique charge localization was that the one-, two-, and three-electron-reduced species (i.e. [Ru(bpy)$_2$(bpy⁻)]$^+$, [Ru(bpy⁻)$_2$(bpy)]^0, and [Ru(bpy⁻)$_3$]⁻) all gave characteristic structureless $S = \frac{1}{2}$ ESR spectra with no evidence for spin-coupled $S = 1$ or $S = \frac{3}{2}$ found. A second consequence of this single ring charge localization was the occurrence of a temperature-dependent ESR line broadening for the fluid solution sample which was interpreted as resulting from the hopping of the redox electron between diimine chelate rings. This line broadening was observed for the one- and two-electron-reduced tris complexes but could not be observed for the three-electron-reduced tris species. The magnitude of this thermal activation energy[1,2] for [Ru(bpy)$_2$(bpy⁻)]$^+$ was consistent with the occurrence of a ligand-based intervalence band transition[8] observed at 4500 cm⁻¹ and interpreted by the Creutz–Taube intervalence transfer theory developed for Ru(II) metal dimer complexes. Finally,

our observation[5] of ligand hyperfine structure for the three-electron-reduction product, [Ru(bpy⁻)$_3$]⁻, provided a verification of the "spatially isolated orbital" model since the absence of line broadening resulting from high electron hopping activation energies should enable observation of ESR hyperfine structure from the three identical reduced ligand units. Subsequently, the occurrence[6] of hfs (and absence of line broadening) for the mixed-ligand reduced [Ru(bpy)$_2$(bpz⁻)]$^+$ (bpz = 2,2′-bipyrazine) corroborated the complementary character of the ESR line broadening and the occurrence of hyperfine structure.

In an effort to produce this "charge localization" phenomenon in a more useful package (as a photocatalyst or molecular electronics system), three pendant polymer [Ru(bpy)$_3$]$^{2+}$ materials were examined by the redox and ESR methods.[10] The two polymer complexes in which the pendant [Ru(bpy)$_2$]$^{2+}$ unit is attached directly to vinyl-bpy produce a unique result: hfs structure for the two-electron-reduction product [Ru(bpy⁻)$_2$(pvbpy)]^0 as well as the three-electron-reduction product. The fact that the cyclic voltammetry pattern for the [Ru(bpy)$_2$(pvbpy)]$^{2+}$ complex species gave a pattern nearly equivalent to that of the monomeric [Ru(bpy)$_3$]$^{2+}$ led us to speculate that the π orbital energy of pvbpy ligand in the pendant complex was nearly equivalent to that of the bpy ligand in the [Ru(bpy)$_3$]$^{2+}$ complex. The one-electron-reduction product for the two pvbpy complexes and the one- and two-electron-reduced species for a third pendant polymer complex with a copolymer of styrene and pvbpy all exhibited typical temperature-dependent line broadening as do the monomers. This behavior and hfs for the two-electron-reduced species suggested that the hydrophobic structure of pvbpy might produce an environmental perturbation affecting the kinetics of the intramolecular hopping.

Most recently, we reported the electrochemistry and ESR of a rigid-rod poly(bpy)[11] pendant Ru(bpy) complex in which the one-electron-reduction product produces an ESR line shape suggesting that the occurrence of a poly(bpy) backbone where this electron resides may produce a conducting backbone.

The addition of a second electron to a single ring orbital to produce the four-, five-, and six-electron-reduced species as [Ru(L²⁻)$_2$L⁻]$^{3-}$ has been limited by the solvent window required to produce these highly reduced species. However, preliminary results[12] for four- and five-electron-reduced species indicated

⊛ Abstract published in *Advance ACS Abstracts*, April 1, 1994.
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behavior comparable to that of the first three electron-reduced species with broad $S = {}^1/_2$ signals but no temperature-dependent line broadening for $n = 4$ or $n = 5$ reduced species. The $n = 6$ (six-electron-reduction) product is diamagnetic, as expected from the simple spatially isolated single-ring model.

Thus, the motivation for this study was the desire to further clarify the effect of the polymer environment upon the magnetic properties of these reduced species. In addition, the use of 2,2′-biquinoline ligands in the pendant complex should enable production not only of one-, two-, and three-electron-reduction products but also of a four-electron-reduction species for this pendant polymer complex.

Experimental Section

Safety Note. Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution.

Materials. 4-Methyl-4′-vinyl-2,2′-bipyridine (vbpy) was prepared according to the procedure described by Abruna et al.[13] [Ru(biq)$_2$]Cl$_2$ was prepared by the method reported by Sullivan et al.[14] Poly(4-methyl-4′-vinyl-2,2′-bipyridine) (pvbpy) was prepared by the literature method.[15] AgClO4 (Aldrich), acetone (Aldrich, HPLC), and benzene (Aldrich, HPLC) were used as received. AIBN [2,2′-azobis(isobutyronitrile)] was recrystallized three times from ether and dried under vacuum. TBAH (tetrabutylammonium hexafluorophosphate) was recrystallized three times from methanol. NMP (1-methyl-2-pyrrolidone) (EM, HPLC for electrochemistry) was used as received. DMSO (dimethyl sulfoxide) (Aldrich, HPLC) was purified as reported by Kolthoff et al.[16]

Synthesis of Poly(4-methyl-4′-vinyl-2,2′-bipyridine) (pvbpy). A 10-mL portion of a dry benzene (freshly distilled) solution of 4-methyl-4′-vinyl-2,2′-bipyridine (1.96 g, 10 mmol) and AIBN (initiator, 4.1 mg) was thoroughly degassed on a vacuum line and then heated for 24 h at 60 °C. Poly(4-methyl-4′-vinyl-2,2′-bipyridine) was precipitated with hexane, purified by two dissolution–precipitation steps, and dried under reduced pressure.

Synthesis of [Ru(biq)$_2$(pvbpy)](ClO4)$_2$. This complex was prepared by using [Ru(biq)$_2$(CH$_3$COCH$_3$)$_2$](ClO4)$_2$ as an intermediate.

To 50 mL of acetone which was deaerated with N$_2$ for 15 min, using a syringe needle, were added 0.192 g of [Ru(biq)$_2$]Cl$_2$ (0.27 mmol) and 0.113 g of AgClO$_4$ (0.54 mmol). The mixture was stirred with a magnetic stirrer for 3 h under N$_2$ and filtered. The filtrate was dried under reduced pressure.

To 80 mL of a 1-propanol solution of [Ru(biq)$_2$(CH$_3$COCH$_3$)$_2$](ClO$_4$)$_2$ (0.27 mmol) which was deaerated with N$_2$ for 15 min, using a syringe needle, was added 0.025 g of poly(vinylbipyridine) (0.13-mmol vbpy unit). The mixture was stirred with a magnetic stirrer for 14 h under N$_2$ and filtered. The violet product was washed thoroughly with acetone (removing the unreacted [Ru(biq)$_2$]$^{2+}$) and THF (removing the unreacted polymer). The product is soluble in DMSO, DMF, and NMP.

Measurements. The UV–visible absorption spectrum was measured on a modified Cary 14 spectrophotometer with a computer-controlled operating and data acquisition system. The emission measurements were performed using an LS-100 luminescence system (PTI). The electrochemistry measurements were done with a BAS-100B electrochemical system. A three-compartment cell was used with a Pt wire working electrode, a Pt mesh counter electrode, and a Ag$^+$/Ag reference electrode. A Pt mesh electrode was used for bulk electrolysis. Electrochemistry measurements were performed with NMP as solvent and TBAH as supporting electrolyte under a N$_2$ atmosphere in a glovebox equipped with O$_2$ and water scrubbing columns. The ESR measurements (X-band) were performed on a Bruker ESR 300 ESR spectrometer equipped with a Bruker VT-411 variable-temperature unit.

Results

The loading factor of [Ru(biq)$_2$](ClO$_4$)$_2$ in [Ru(biq)$_2$(pvbpy)]-(ClO4)$_2$ was calculated by assuming that this polymer complex has the same absorption extinction coefficient as the corresponding

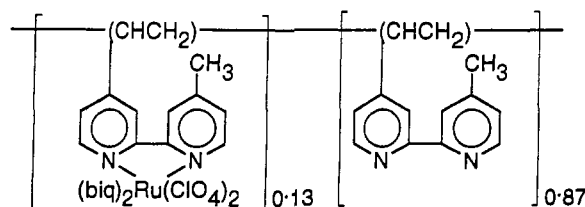(13) Abruna, H. D.; Breihss, A. I.; Collum, D. B. *Inorg. Chem.* **1985**, *24*, 987.
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Figure 1. Structure and loading factor of [Ru(biq)$_2$(pvbpy)](ClO$_4$)$_2$.
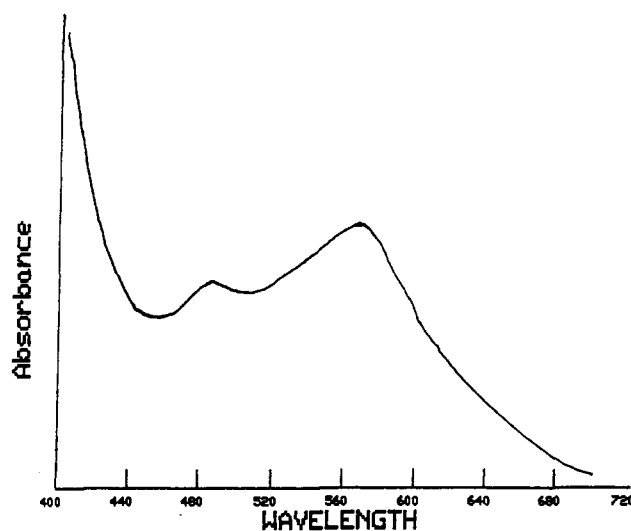
Figure 2. Absorption spectrum of [Ru(biq)$_2$(pvbpy)](ClO$_4$)$_2$ in DMF.
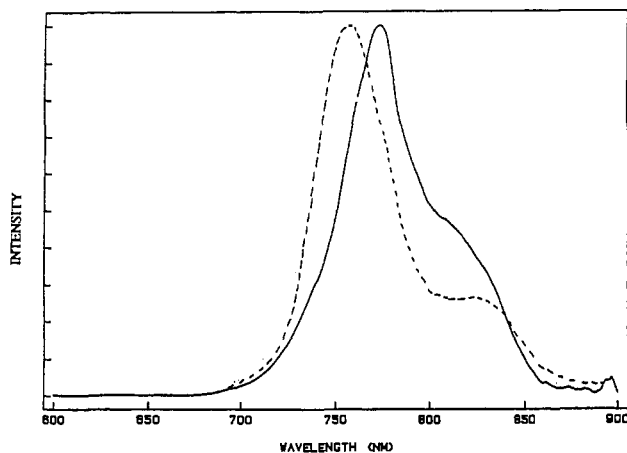
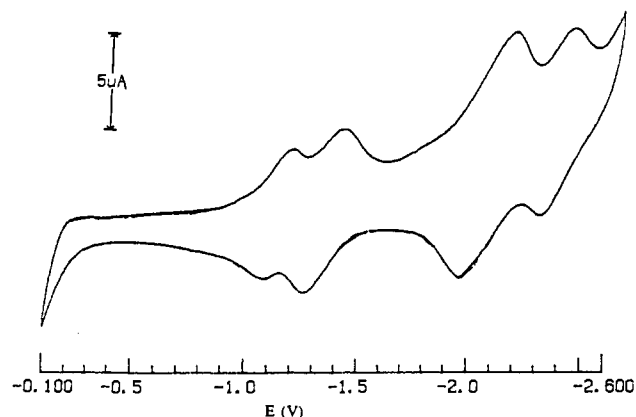**Figure 3.** Luminescence spectra of [Ru(biq)$_2$(pvbpy)](Cl)$_4$)$_2$ in DMF: (- - -) 77 K; (—) 293 K.

Table 1. Absorption and Luminescence Data

complex	absorption (nm)		emission (nm)	
			293 K	77 K
[Ru(biq)$_2$(pvbpy)]$^{2+}$	565	486	733	755
[Ru(biq)$_2$(bpy)]$^{2+}$	547	481	733	742

monomer [Ru(biq)$_2$(bpy)]$^{2+}$, since the absorption in the UV–visible region of this polymer complex can be assigned to the MLCT (metal–ligand charge-transfer) transition which is little affected by the backbone part of the molecule. Therefore, the extinction coefficients for MLCT bands of both polymer and monomer complexes are likely similar. Since the molar weight of the vbpy unit is known, the molar ratio of [Ru(biq)$_2$](ClO4)$_2$ to the pvbpy unit can be calculated, The loading factor of the [Ru(biq)$_2$](ClO4)$_2$ unit is 13 mol %. The composition of the polymer complex is shown in Figure 1. The absorption and luminescence spectra of the polymer complex are presented in Figures 2 and 3. The data are listed in Table 1. The cyclic

Figure 4. Room-temperature cyclic voltammogram of [Ru(biq)₂(pvbpy)]-(ClO₄)₂ in 0.1 M TBAH/NMP solution (E vs Ag⁺/Ag reference).

Gauss
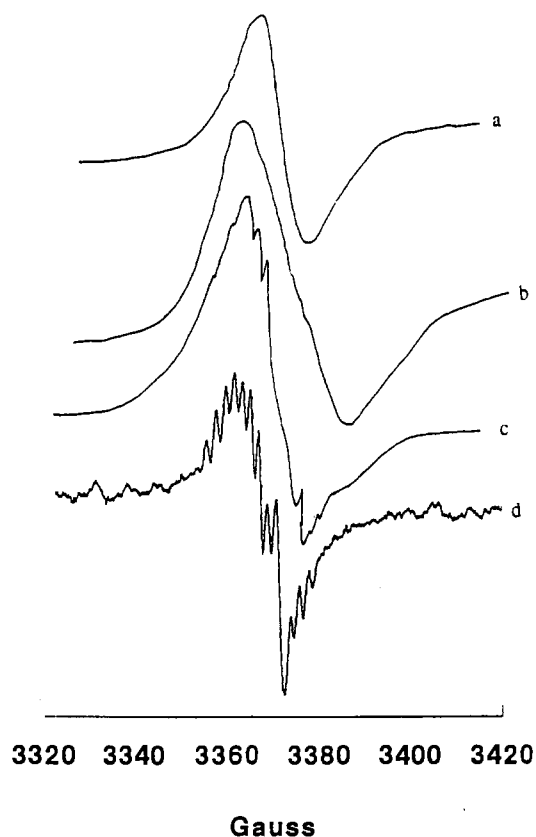
Figure 5. Room-temperature ESR of the first four reduction products of [Ru(biq)₂(pvbpy)](ClO₄)₂: (a) one electron; (b) two electron; (c) three electron; (d) four electron.

Table 2. $E_{1/2}$ Values vs SCE (V)

complex	2+/1+	1+/0	0/1–
[Ru(biq)₂(pvbpy)]²⁺	–0.740	–0.980	–1.66
[Ru(biq)₂(bpy)]²⁺	–0.820	–1.05	–1.61

voltammogram of the polymer complex is given in Figure 4, and the data are listed in Table 2. The ESR spectra for the one-, two-, three-, and four-electron-reduction products are shown in Figure 5. One- and two-electron-reduction product ESR signals exhibit temperature-dependent line broadening in the temperature range 270–330 K. The activation energies are obtained from log(ESR line width) vs 1/T plots. For the one-electron-reduction product, the activation energy is 495 cm⁻¹, and the two-electron-reduction product has an activation energy of 520 cm⁻¹. The three- and four-electron-reduction product ESR signals show no temperature-dependent line broadening but do exhibit hyperfine structure. In each case a g value of 2.003 is measured.

Discussion

The complex exhibits a broad absorption band in the visible region which can be identified as the MLCT [dπ(t₂) → π*(ligand)] transition. The absorption with maximum at 565 nm belongs to the electronic transition from the metal t₂(dπ) orbital to the ligand biq π* orbital. This is the same assignment as that reported by Meyer et al.[17] for the analogous monomeric complex. In their work on mixed-ligand Ru(II) complexes (Ru(bpy)ₓ(bpz)₃₋ₓ), the results indicated that the lowest energy transition can be assigned to the ligand containing the lowest π* level. According to Klassen,[18] biq has a smaller energy gap between the π and π* levels than that in bpy ligand. This is shown in Figure 6 a–d. Therefore, the 565-nm absorption band in [Ru(pvbpy)(biq)₂]²⁺ can be assigned to the transition between the metal t₂ and the ligand biq π* orbitals, i.e. dπ–π* MLCT.

The MLCT bands of [Ru(pvbpy)(biq)₂]²⁺ are very similar to those of the corresponding monomer [Ru(bpy)(biq)₂]²⁺ except for the red shifts of the band maxima. The red shifts could result from (a) a decrease in π* level in the polymer, (b) an increase in the energy of the t₂ metal orbital in the polymer, or (c) the combined effects of both (a) and (b). According to Meyer,[17] it is necessary to consider both σ- and π-bonding effects in order to account for bonding of mixed-heterocyclic-ligand Ru(II) complexes. The weaker σ donor capacity of the biq ligand gives rise to a larger effective nuclear charge on the ruthenium. This larger effective nuclear charge would have the effect of lowering the energy of the biq ligand π* level through charge interaction.

A polymer prepared from a monomer, CH₂=CHR, will have one stereochemical configuration of the following three: isotactic, syndiotactic, or atactic, as shown in Figure 7. In our case, R is a 4-methylbipyridine ring which will combine with [Ru(biq)₂]²⁺ to form the polymer complex. Considering the short C–C bond distance in the backbone and the large size of the 4-methylbipyridine and biquinoline rings, steric hindrance is inevitable. This steric hindrance results in a decrease in the ligand field strength as a result of the increased metal–ligand bond distance. Therefore, the energy of the metal t₂ orbital is higher in the polymer than in the corresponding monomer. This weaker σ-bonding would result in increasing the formal charge of Ru, which results in lowering the biq ligand π* orbital energy level by charge interaction. This same net effect occurs with the biq ligand π* orbital energy level in the complex [Ru(biq)₂(pvbpy)]²⁺ relative to that in the free biq ligand. We can add this result to Figure 6, as parts e and f. Thus, the conclusion must be made that the red shift in the absorption band of the polymer comes from both metal t₂ orbital energy rising and the ligand π* level lowering as a result of steric hindrance caused by the backbone polymer. The red shift in the MLCT absorption band appears to result mainly from a lowering of the ligand biq π* energy level. This latter conclusion is further proved by the fact that the first- and second-reduction potentials of [Ru(biq)₂(pvbpy)]²⁺ are shifted positive relative to those of the corresponding nomomer complex of [Ru(biq)₂(bpy)]²⁺. According to the "spatially isolated orbital" model, the first- and second-reduction electrons will be placed in the two biq ligand π* orbitals, one electron in each biq ligand ring. Therefore, the positive shifts of the first two reduction potentials of the pvbpy complex indicate that the biq ligand π* orbitals in [Ru(biq)₂(pvbpy)]²⁺ have the lowest energy level.

The emission spectrum structure of [Ru(pvbpy)(biq)₂]²⁺ is very similar to that of the monomer [Ru(bpy)(biq)₂]²⁺ with a red shift measured. The 13-nm red shift at room temperature (luminescence) parallels the 18-nm red shift for the lowest charge transition in the absorption band.

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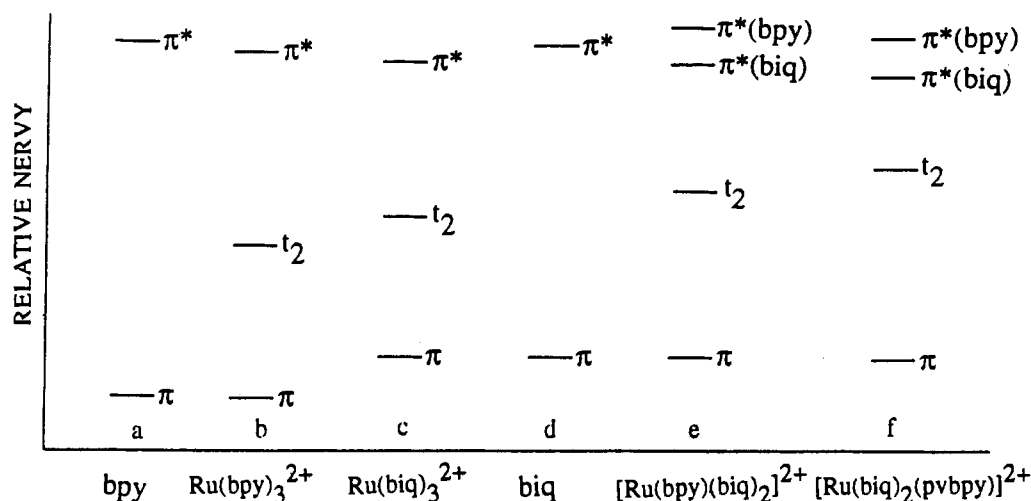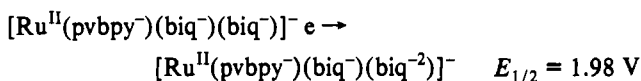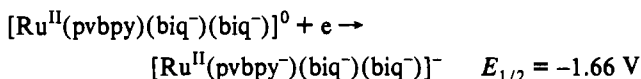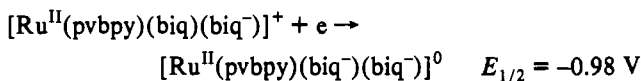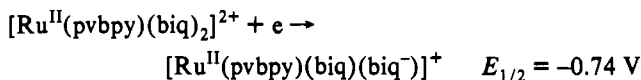(18) Klassen, D. M. *Inorg. Chem.* **1976**, *15*, 3166.

Figure 6. Relative orbital energy of ligand and Ru(II) complexes.

The redox data for the polymer are consistent with a description of the reduction of [Ru(pvbpy)(biq)₂]²⁺ as ligand centered. This conclusion is consistent with the results reported by us[19] where the electron is considered to be localized in the π^* levels of a single diimine ligand rather than delocalized over the whole molecule. The reductions are stepwise ligand reductions and involve minimum metal character. On the basis of this argument, the reduction potentials can be assigned as follows:

$$[Ru^{II}(pvbpy)(biq)_2]^{2+} + e \rightarrow$$

$$[Ru^{II}(pvbpy)(biq)(biq^-)]^+ \quad E_{1/2} = -0.74 \text{ V}$$

$$[Ru^{II}(pvbpy)(biq)(biq^-)]^+ + e \rightarrow$$

$$[Ru^{II}(pvbpy)(biq^-)(biq^-)]^0 \quad E_{1/2} = -0.98 \text{ V}$$

$$[Ru^{II}(pvbpy)(biq^-)(biq^-)]^0 + e \rightarrow$$

$$[Ru^{II}(pvbpy^-)(biq^-)(biq^-)]^- \quad E_{1/2} = -1.66 \text{ V}$$

$$[Ru^{II}(pvbpy^-)(biq^-)(biq^-)]^- e \rightarrow$$

$$[Ru^{II}(pvbpy^-)(biq^-)(biq^{-2})]^- \quad E_{1/2} = 1.98 \text{ V}$$

The excited-state redox potential $E_{1/2}{}^{2+*/+}$ of Ru(II) complexes can be estimated from the equation: $E_{1/2}{}^{2+*/+} = E_{1/2}{}^{2+/+} + E_{em}$, where $E_{1/2}{}^{2+/+}$ is the ground-state reduction potential and E_{em} is the emission energy. The calculation leads to the following results: for [Ru(pvbpy)(biq)₂]²⁺, $E_{1/2}{}^{2+*/+} = 0.90$ V; for [Ru(bpy)(biq)₂]²⁺, $E_{1/2}{}^{2+*/+} = 0.85$ V.

The ESR results for one-, two-, three-, and four-electron-reduction products of [Ru(biq)₂(pvbpy)]²⁺ show that, in each case, an $S = {}^1/_2$ signal and a g value about 2.003 are observed, corresponding to the single chelate ring localized orbital model used for the monomeric [RuL₃]²⁺ complexes. The first- and second-reduction electrons enter into separate biq ligand rings which are spatially isolated (localized) orbitals. The ESR signals for each case exhibit temperature-dependent line broadening. This temperature-dependent line broadening is due to the movement (hopping) of π^* reduction electrons between the chelate rings. The third-reduction electron enters the backbone bpy ring. At this point, the three spatially isolated orbitals are occupied, respectively, by a single electron. The energy barrier for reduction electron movement (hopping) between π chelate rings is larger than that in one- and two-electron-reduction products. Therefore, the three-electron-reduction product ESR signal shows no temperature-dependent line broadening but produces hyperfine
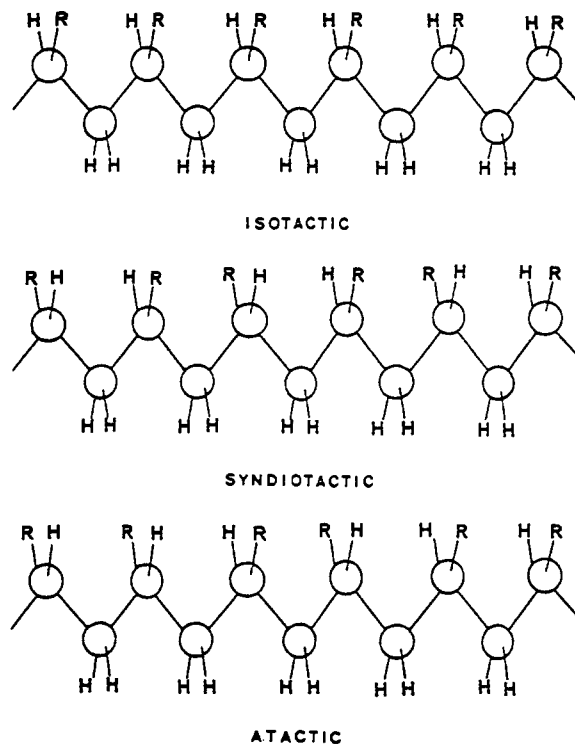
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Figure 7. Stereochemical configurations of a polymer prepared from a monomer of CH₂=CHR.

structure. The cyclic voltammetry and ESR of the pendant polymer complex reported here produce a cyclic voltammogram pattern (spacing and number of waves) comparable to that of the solution monomer species. [Ru(biq)₂bpy]²⁺ but distinct from the ESR that is measured for the three pendant bpy Ru(II) complexes first reported[10] in which a unique hyperfine structure is observed and rationalized as resulting from a small polymer environment effect.

The four-electron-reduction product has two electrons in one biq chelate ring, one electron in the other biq chelate ring, and one electron in the backbone bpy ring. As expected from the spatially isolated orbital model, the four-electron-reduction product will have two paired electrons in one biq ring and one unpaired electron in each of the other two chelate rings. With this electron configuration, it could be assumed that the ESR of the four-electron-reduction product would be like that of the two-electron-reduction product because both have two unpaired electrons. Alternatively, the ESR of the four-electron-reduction product might be similar to that of the one-electron-reduction product since both configurations have an electron that is capable

of hopping to the other two ligand rings. If either assumption were true, the ESR line of the four-electron-reduction product would be temperature dependent, as are those of the one- and the two-electron-reduction products. Our results indicate that the ESR signal of the four-electron-reduction product shows no temperature-dependent line broadening but produces hyperfine structure. This indicates that the fourth-reduction electron is localized in a single ligand ring with a large energy barrier for intervalence electron transfer (hopping) between chelate ligand rings, which prevents hopping.

The fourth-reduction electron enters a π^* orbital which is already occupied by an electron and, therefore, is paired. Consequently, the hopping rate is diminished for the fourth-reduction electron, since additional energy will be required to break up the electron pair. Therefore, the four-electron-reduction product produces an ESR signal with well-resolved hyperfine structure. This result is consistent with the result[20] in our laboratory for the four-electron-reduction product of $[Ru(biq)_3]^{2+}$. It is not surprising that these two four-electron-reduction products of $[Ru(pvbpy)(biq)_2]^{2+}$ and $[Ru(biq)_3]^{2+}$ have very similar hyperfine patterns since, in both reduction products, the fourth-reduction electron enters into a biq π^* chelate orbital already occupied by one reduction electron.

Conclusion

We report here the first example of pendant polymer Ru(II) complex in which as many as four reduction electrons have been introduced into the material. The ESR results for one-, two-, three-, and four-electron-reduction products provide further verification of the "spatially isolated orbital" model and "charge localization" phenomenon. The fourth electron added to the complex is localized in a single ligand ring with an energy barrier to intervalence electron transfer much larger than was found for the first two electron reduction products. The temperature-dependent ESR line broadening observed for one- and two-electron-reduction products is the result of localized electrons hopping between ligand rings. The hyperfine structure ESR of three- and four-electron-reduction products is the result of a higher energy barrier to intervalence electron transfer between ligand rings. The results reported here and those reported earlier[12] for the oligomeric poly(bpy) Ru(II) material suggest that combination of the biq ligand with the poly(bpy) Ru(II) fragment could produce a material with a unique ability to store charge. We are currently investigating these possibilities.

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