

for the estimation of these molecular physical properties. Furthermore, it has been shown that even the effect of isotopes of such a heavy element as tellurium can be studied with high-field (5.8 T) NMR spectrometers.

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Metallopolymer Photochemistry. Photophysical, Photochemical, and Photoelectrochemical Properties of (bpy)₂Ru^{II}< Sites Bound to Poly(4-vinylpyridine)

Jeffrey M. Calvert, Jonathan V. Caspar, Robert A. Binstead, T. David Westmoreland, and Thomas J. Meyer*

Contribution from the Department of Chemistry, The University of North Carolina, Chapel Hill, North Carolina 27514. Received March 26, 1982

Abstract: The photochemical and photophysical properties of the polymer-bound chromophore Ru(bpy)₂(PVP)₂²⁺ (PVP is poly(4-vinylpyridine)) have been investigated in homogeneous solution. Results have been obtained with polymers both dilute and concentrated in chromophore. Lifetime and quantum yield data are interpreted in terms of models of excited-state behavior previously proposed for analogous monomeric poly(pyridyl) complexes of Ru(II). Excited-state sites within the metallopolymers undergo oxidative and reductive electron-transfer quenching. The quenching reactions were investigated by Stern-Volmer quenching and conventional microsecond flash photolysis. Sensitization of n-TiO₂ to visible light has been observed on a semiconductor coated with a film of the metallopolymer.

Introduction

We have described the synthesis and characterization of a variety of poly(pyridyl) complexes of ruthenium(II) bound to poly(4-vinylpyridine) (PVP), including the title compound Ru(bpy)₂(PVP)₂²⁺ (bpy is 2,2'-bipyridine).^{1,2} Synthetic procedures were developed that allowed for variation in the extent of the loading of the metal complex onto the PVP backbone. The earlier work also showed that systematic modifications could be made in the coordination environment of the polymer-bound metal complex site. Our investigations of these materials led to the conclusion that, for the most part, the inherent chemical and physical properties of the monomers were maintained in the polymeric materials either in solution or as films on electrodes. Some notable exceptions did appear. One example relevant to the present work was the observation of an apparent onset of electronic communication between sites based on measurements involving both ground and excited states of Ru(trpy)(bpy)(PVP)₂²⁺ (trpy is 2,2'-2''-terpyridine) as the loading of the metal complex in the polymer exceeded a critical value.¹ In terms of chemical properties, when differences occurred between monomeric and polymeric sites, they were attributed to two major factors: (1) the ability to control the spatial separation of the sites in the polymers by diluting them along the polymer backbone and (2) the effect of the local polymeric environment on the reactivity properties of the sites.

One of our principal interests in metallopolymers containing poly(pyridyl)ruthenium(II) groups is in their photochemical properties. The metal to ligand charge-transfer (MLCT) excited states of Ru(bpy)₂²⁺ have an extensive redox photochemistry. The

photoredox properties have provided a basis for energy conversion processes based on molecular excited states.³ The basic photochemical and photophysical properties of the MLCT excited states of Ru(II) poly(pyridyl) complexes⁴⁻⁶ have been shown to exist for Os(II) as well.⁷

Compared to monomers, metallopolymeric analogues appear to offer at least three advantages: (1) the presence of multiple chromophoric sites in a fixed chemical matrix, (2) the ability to prepare materials containing both catalytic and chromophoric sites, and (3) the ability to create an interface by physical adsorption on electrodes or on particles in solution. A preliminary report has appeared that describes the preparation of polymer-bound Ru(bpy)₂²⁺ units by means of a polystyrene backbone to which 2,2'-bipyridine had been attached.⁸ The Ru sites in the polymer

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were found to emit and were shown to be quenched by methylviologen. In this manuscript we report the first example of a detailed study of the photochemical and photophysical properties of a polymer-based Ru-bpy chromophore in homogeneous solution. We also describe how the film-forming ability of the metallopolymers can be utilized to sensitize photoelectron transfer at TiO₂ to visible light.

Experimental Section

Materials. Water was deionized and then distilled from alkaline KMnO₄. For photochemical experiments, conductivity water (16 M Ω) was used. Acetonitrile and propylene carbonate (Burdick and Jackson) were used as received. Acetonitrile for flash photolysis experiments was distilled in an all-glass apparatus from fresh P₂O₅ and then redistilled from CaH₂. The preparation of tetraethylammonium perchlorate (TEAP) has been described.⁹ *N,N,N',N'*-tetramethylphenylenediamine (TMPD) and *N,N,N',N'*-tetramethylbenzidine (TMBD) were sublimed at reduced pressure and stored in the dark. Phenothiazine (PTZ) was recrystallized from toluene. [Ru(NH₃)₆]Cl₃ (Matthey-Bishop) was purified as described in the literature.¹⁰ Preparations for the chloride and hexafluorophosphate salts of Ru(bpy)₃²⁺ have been reported previously.¹¹ The synthesis and characterization of the metallopolymers has been described elsewhere.² Two loadings of the metal complex sites onto the polymer were used: a "dilute" sample in which two of every twenty pyridyl units of PVP are bound by ruthenium (designated Ru(bpy)₂(PVP)_{2/20}²⁺) and a "concentrated" sample in which two of five pyridyl groups are bound (designated Ru(bpy)₂(PVP)_{2/5}²⁺). The metallopolymers were maintained as the trifluoroacetate (TFA) salts in a methanol-water mixture. The solutions must be protected from light to prevent photodecomposition. All other materials were of reagent quality and were used as received.

Instrumentation and Procedures. Absorption spectra were recorded on a Varian Model 634 spectrophotometer. Emission spectra were taken at room temperature with a Hitachi MPF-2A spectrofluorimeter and at 77 K in a 4:1 ethanol-methanol glass with an SLM 8000 photon counting spectrofluorimeter. The instrumentation required for and basic procedures followed in determining quantum yields and lifetimes⁵ and in performing luminescence quenching^{12,13} and conventional flash photolysis^{13,14} are well documented in the literature. For flash photolysis experiments polymeric solutions 7 × 10⁻⁶ M in Ru-bpy sites were used; in the luminescence quenching and lifetime experiments the solutions were ~10⁻⁴ M. The higher than usual concentrations were necessary because the polymeric chromophores are weak emitters. Also in the quenching experiments, sufficient quencher was added to obtain ~10, ~20, ~30, and ~100% quenching in order to define the Stern-Volmer slope when I⁰/I was plotted vs. [Q]. Because of the relatively short lifetimes of the polymer excited states, relatively high quencher concentrations, 10⁻²-0.3 M, were used.

Photoelectrochemical Experiments. A disk (0.25 cm²) of single-crystal n-type TiO₂ (NL Industries, South Amboy, NJ) was sealed in a glass tube with epoxy. Electrical contact was made to the back of the TiO₂ electrode by means of a copper wire and gallium-indium eutectic (Alfa). A methanol-water solution of Ru(bpy)₂(PVP)_{2/5}²⁺ (~1 mM in Ru²⁺) was applied to the electrode and allowed to evaporate, producing a fairly thick (~10⁻⁷ mol/cm²), orange coating on the surface. The extent of coverage was determined by evaporating a known volume of a standard solution onto the electrode surface. The electrode was immersed in an acetonitrile solution with 0.1 M [N(C₂H₅)₄](ClO₄) as electrolyte, which was held in a cell fitted with an optical quartz window. After the electrode is coated with the polymer by evaporation, loss of the polymer from the surface when exposed to acetonitrile is negligible on the time scale for the photoelectrochemical experiments. The cell assembly was contained in an aluminum Faraday cage to minimize external electric noise. The polymer-coated surface was irradiated at the polymer side with monochromatic light from a Bausch and Lomb Model 33-88-66 double-grating monochromator with a 150-W xenon light source and Corn-

Table I. Absorption, Emission, and Lifetime Data at 298 K

complex ^a	solvent ^b	$\lambda_{\text{abs}}^{\text{max}}$, nm	$\lambda_{\text{em}}^{\text{max}}$, nm	τ° , ns
Ru(bpy) ₃ ²⁺	CH ₃ CN	453 ^d	605 ^d	860 ^d
	PC	453 ^e	608 ^e	929 ^e
Ru(bpy) ₂ (PVP) _{2/5} ²⁺	CH ₃ CN	460	611	20
	PC	460	613	68
Ru(bpy) ₂ (PVP) _{2/20} ²⁺	CH ₃ CN	460	609	20
	PC	460	612	44
Ru(bpy) ₂ (py) ₂ ²⁺	CH ₃ CN	457	606	500
	PC	457	608	

^a Ru(bpy)₃²⁺ and Ru(bpy)₂(py)₂²⁺ were used as the PF₆⁻ salts.

^b PC is propylene carbonate. ^c Uncorrected. ^d From ref 5.

^e From ref 22, note ref 23.

ing 3-74 filter to eliminate UV light. The light beam was sufficiently broad to illuminate the entire electrode surface. An orange luminescence was easily observable from the film upon irradiation. Photocurrents (*i*_{photo}) were measured with a Princeton Applied Research Model 173 potentiostat and were recorded on a Hewlett-Packard 7015B X-Y recorder. A bias of +0.5 V vs. SSCE was applied to the working (TiO₂) electrode to obtain maximum current collection efficiency. *i*_{photo} was measured as a function of excitation wavelength with a pulsed Moletron tunable dye laser as the light source. The laser beam was passed through a beam splitter, and the resultant 90° component of the laser pulse was focused onto a Moletron Model J302DW calibrated photodiode power meter. The excitation wavelength was swept on a point by point basis, with recording of both the photocurrent and the relative laser power output. Correction of the photocurrent for laser power variations gave the action spectrum shown in Figure 7.

Results

The excited-state lifetimes and absorption and emission spectra of Ru(bpy)₃²⁺, Ru(bpy)₂(py)₂²⁺, Ru(bpy)₂(PVP)_{2/5}²⁺, and Ru(bpy)₂(PVP)_{2/20}²⁺ were recorded in acetonitrile and propylene carbonate at 298 K. The contours of the spectra for the four compounds were very similar for either technique and shifted only slightly in wavelength with respect to each other. The absorption and emission maxima ($\lambda_{\text{abs}}^{\text{max}}$ and $\lambda_{\text{em}}^{\text{max}}$, respectively) are reported in Table I. The former measurements exhibit no dependence on the solvent, whereas $\lambda_{\text{em}}^{\text{max}}$ exhibits a slight shift to lower energy upon changing solvents from acetonitrile to propylene carbonate. A much more dramatic difference is observed between the lifetime values for the monomeric and polymeric complexes. Room-temperature lifetimes for the polymeric sites were approximately 10-40 times shorter than anticipated given the essential similarities between the coordination environments for the various luminophors.

Excited-state lifetimes were measured as a function of temperature by luminescence decay measurements following laser flash photolysis at 337 nm. The temperature dependence of the lifetime, $\tau^{\circ}(T)$, was fit to the equation^{5,6}

$$\tau^{\circ}(T)^{-1} = k_1 + k^{\circ} \exp(-\Delta E'/RT) \quad (1)$$

where k_1 is a composite rate constant that is the sum of the radiative (k_r) and nonradiative (k_{nr}) rates from the lowest charge-transfer excited-state (³CT) manifold (eq 2).^{15,16} It should

$$k_1 = k_r + k_{nr} \quad (2)$$

be noted that with this interpretation of the data k_r is actually the product of the efficiency of formation of ³CT following excitation into the MLCT singlet states, Φ_{isc} , and the actual radiative rate constant from ³CT, k_r' ; that is $k_r = \Phi_{\text{isc}} k_r'$. For Ru(bpy)₃²⁺, it is known that $\Phi_{\text{isc}} \sim 1.0$.²⁰ The state ³CT is actually a Boltzmann-populated series of triplet states. The states have appreciable singlet character because of spin-orbit coupling in-

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Table II. Excited-State Decay Parameters in Acetonitrile and Propylene Carbonate (PC) at 298 K^a

complex	solvent	$10^{-5}k_r, s^{-1}$	$10^{-5}k_{nr}, s^{-1}$	$\Delta E', cm^{-1}$	$10^{13}k^\circ, s^{-1}$	Φ_r	Φ_i
Ru(bpy) ₃ ²⁺	CH ₃ CN	0.72	4.8	3800	5.8	0.062	0.55
	PC	0.85	5.2	3270	0.36	0.071	0.47
Ru(bpy) ₂ (PVP) _{2/5} ²⁺	CH ₃ CN	0.57				0.0011	
	PC	0.46	9.6	3180	10	0.0020	0.96
Ru(bpy) ₂ (PVP) _{2/20} ²⁺	CH ₃ CN	0.95				0.0019	
	PC	0.27	5.3	2620	0.43	0.0018	0.96
Ru(bpy) ₂ (py) ₂ ²⁺	CH ₃ CN	0.0047				2.33×10^{-4}	
	PC	0.005				2.28×10^{-4}	

^a Parameters are defined in the text. ^b As cited, k_r is the product of the efficiency of formation of the emitting state upon photolysis, Φ_{isc} , and the true radiative efficiency of the emitting state k_r' ; $k_r = \Phi_{isc}k_r'$.

Table III. Photochemical Quantum Yields at 298 K^{a,b}

complex	Φ_i	$\Phi_p(d-d)$	Φ_p	$\Phi_p(O_2)^c$
Ru(bpy) ₃ ²⁺ ^d	0.76	0.089	0.068	0.039
Ru(bpy) ₂ (PVP) _{2/30} ²⁺ ^e	0.96	0.084	0.087	0.089
Ru(bpy) ₂ (py) ₂ ²⁺ ^d	0.61	~0.5	~0.3	

^a Explanations of the parameters are given in the text. ^b Quantum yields were determined under deaerated conditions unless noted. ^c Values for aerated solution. ^d In CH₂Cl₂, using the NCS⁻ salt for the determination of Φ_p ; from data in ref 5. ^e CH₃CN solution.

duced mixing with higher singlet states.¹⁶ The second term in eq 1 takes into account the existence of a d-d state which is thermally accessible from the lower CT state. $\Delta E'$ is then a measure of the gap in energy between the d-d state and ³CT and k° is an Arrhenius-type frequency factor which contains kinetic terms involving the formation and subsequent decay of the d-d state.

Quantum yields for emission, Φ_r , were determined in both CH₃CN and propylene carbonate by comparing the observed emission intensities for the complexes at $\lambda_{em}(max)$ relative to previously measured values for Ru(bpy)₃²⁺ in the two solvents. Radiative rate constants, k_r , were calculated from eq 3, and

$$\Phi_r = k_r \tau^\circ \quad (3)$$

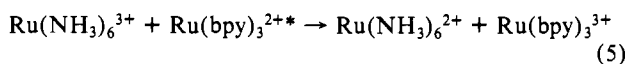
nonradiative rate constants for the decay of ³CT, k_{nr} , from eq 2. The photophysical parameters k_r , k_{nr} , $\Delta E'$, k° , and φ_r are listed in Table II.

The quantum yield for photochemical ligand loss, Φ_p , in one of the samples of Ru(bpy)₂(PVP)_{2/20}²⁺ was determined by monitoring the decay of luminescence intensity at $\lambda_{em}(max)$, as described in ref 5. The photoproduct, Ru(bpy)₂(PVP)_{2/20}(CH₃CN)²⁺, does not exhibit a detectable emission at room temperature. Values of Φ_p for the polymer sample were determined in both aerated and deaerated solutions and are compared in Table III with similar measurements for Ru(bpy)₃²⁺ and Ru(bpy)₂(py)₂²⁺. The additional quantities that appear in Tables II and III will be discussed later. They are (1) Φ_i , the quantum efficiency for population of the d-d state from ³CT, and (2) $\Phi_p(d-d)$, the efficiency of photosubstitution from the d-d state once it is reached.

Excited-state electron-transfer quenching and flash photolysis data have been acquired for excited states of the polymer complexes and for Ru(bpy)₃²⁺. TMPD, TMBD, and PTZ were employed as reductive quenchers in acetonitrile, where the net reactions are shown by the example in eq 4. The structures of



the quenchers are shown in Figure 1. Ru(NH₃)₆³⁺ was used as an oxidative quencher in aqueous, acidic solution as in eq 5. The



results of the quenching experiments are shown in Table IV. The data were plotted according to the Stern-Volmer equation

$$I^\circ/I = 1 + k_q \tau^\circ [Q] \quad (6)$$

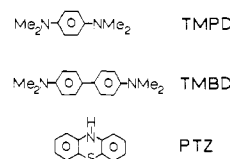


Figure 1. Structures and abbreviations for the reductive quenchers.

Table IV. Excited-State Electron-Transfer Quenching Rate Constants, k_q , at 298 K

complex	$k_q, M^{-1} s^{-1}$			oxidative quenching ^b Ru(NH ₃) ₆ ³⁺
	reductive quenching ^a			
	TMPD	TMBD	PTZ	
Ru(bpy) ₃ ²⁺	1.3×10^{10}	4.3×10^9	6.97×10^9	1.1×10^9
Ru(bpy) ₂ - (PVP) _{2/5} ²⁺	2.8×10^9	2.2×10^9	2.7×10^9	3.7×10^8
Ru(bpy) ₂ - (PVP) _{2/20} ²⁺	2.7×10^9		2.8×10^9	5.8×10^8

^a Acetonitrile solution. The structures of the reductive quenchers are shown in Figure 1. ^b 0.05 M HCl.

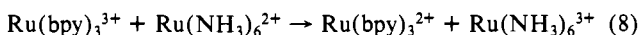
Table V. Back-Electron-Transfer Rate Constants from Flash Photolysis at 298 K

complex	$10^{-9}k_b, M^{-1} s^{-1}$	
	TMPD ^a	Ru(NH ₃) ₆ ³⁺ ^b
Ru(bpy) ₃ ²⁺	9.1	3.7 ^c
Ru(bpy) ₂ (PVP) _{2/5} ²⁺	0.91	0.1
Ru(bpy) ₂ (PVP) _{2/20} ²⁺	1.5	0.2

^a CH₃CN solution; Ru⁺ + TMPD⁺ → Ru²⁺ + TMPD. ^b 0.05 M HCl; Ru³⁺ + Ru(NH₃)₆²⁺ → Ru³⁺ + Ru(NH₃)₆³⁺. ^c From ref 17; in 0.1 M CF₃CO₂H.

where k_q is the experimental quenching rate constant, τ° is the excited-state lifetime for the emitting species, I° is the intensity of light emitted at a fixed wavelength in the absence of quencher, and I is the emitted intensity in solutions with added quencher. The plots were linear over a range of quencher concentrations and the intercepts were unity. k_q values were determined from the slopes of the lines resulting from plots of I°/I vs [Q]. Values of τ° listed in Table I were used for the quenching experiments in acetonitrile. In aqueous solution, τ° values were 580 ns for Ru(bpy)₃²⁺,⁵ 23 ns for Ru(bpy)₂(PVP)_{2/5}²⁺, and 29 ns for Ru(bpy)₂(PVP)_{2/20}²⁺.

Flash photolysis experiments were used to obtain rate constant data for the back-electron-transfer reactions that occur following quenching, e.g., eq 7 and 8. The results of the flash experiments



are summarized in Table V. For experiments in aqueous solution involving quenching by Ru(NH₃)₆³⁺, the post-flash buildup of either Ru(bpy)₃²⁺ or the metallopolymers as Ru(II) was followed at the $\lambda_{abs}(max)$ for the particular complex (see Table I). In acetonitrile, the decay of the oxidized quencher, TMPD⁺, was recorded at 615 nm. For the Ru(NH₃)₆³⁺ experiments, the systems were photochromic and the transient spectral changes were plotted

according to second-order, equal-concentration kinetics: $1/\Delta A$ vs. t , where ΔA is the change in absorbance at a given wavelength.¹⁸ Rate constants, k_b , were calculated from the slopes of the plots of $1/\Delta A$ vs. t , where the slope is equal to $k_b/l(\Delta\epsilon)$. l is the cell path length and $\Delta\epsilon$ is the molar extinction coefficient difference between reactants and products at the wavelength used. For $\text{Ru}(\text{bpy})_3^{2+}$, at 453 nm $\Delta\epsilon$ is $1.38 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ in water¹¹ and $1.42 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ in CH_3CN ;⁵ for the metallopolymers, $\Delta\epsilon$ at 460 nm is estimated to be $1.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ in both H_2O and CH_3CN from the known extinction coefficient of the analogous monomeric complex, $\text{Ru}(\text{bpy})_2(\text{py})_2^{2+}$.⁴ Kinetic plots from which rate data were obtained were linear for at least 2–3 half-lives. In the TMPD experiments, the systems were also photochromic but the time scale for the full return of the solution absorbance was much longer. Several minutes were required for the trace to return to the preflash base line. Repeated flashes eventually produced a steady-state buildup of TMPD^+ in the cell, as evidenced by the increasingly blue color of the solution, which is characteristic of the intense absorption of the radical cation. Therefore, only the first few flashes on a particular solution were used to obtain kinetic data. Attempts to fit the data to second-order, equal-concentration kinetics were unsuccessful; curved plots were obtained. Consequently, it was necessary to interpret the observed spectral changes using a second-order, unequal-concentration kinetics analysis.¹⁸ Linear plots of $\ln(\Delta A/\Delta A - A_\infty)$ vs. t (where A_∞ is the level to which the initial absorbance falls after the recombination of TMPD^+ and Ru^+) were then obtained. Rates of back-reaction were calculated from the slopes of the plots: slope = $k_b A_\infty / (\Delta\epsilon)l$. The value of $1.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ was used as $\Delta\epsilon$ for TMPD^+ at 615 nm.¹⁹

Front-face irradiation of a $\text{Ru}(\text{bpy})_2(\text{PVP})_{2/5}^{2+}$ ($\Gamma \approx 10^{-7} \text{ mol/cm}^2$) coated electrode at the absorbance maximum of the ruthenium complex resulted in the onset of a photocurrent that stabilized after 1.5 min to a value of 4.5 nA. Removal of the light source resulted in decay of the photocurrent, and the background current level was reached after 2.0 min. Addition of hydroquinone as a sensitizer to the electrolyte solution increased the photocurrent output to 17.5 nA. The photocurrent was reproducible between repeated on-off cycles and was stable during a constant irradiation for 20 min. Photocurrent-time curves are shown in Figure 6. The photoresponse of the coated semiconductor was monitored as a function of the wavelength of incident light. The resulting action spectrum shown in Figure 7 was found to have the same general shape as the absorption spectrum of the metallopolymer, exhibiting a peak at $\sim 460 \text{ nm}$, which is the value reported for the metallopolymer in solution (see Table I) or as a film.²

Discussion

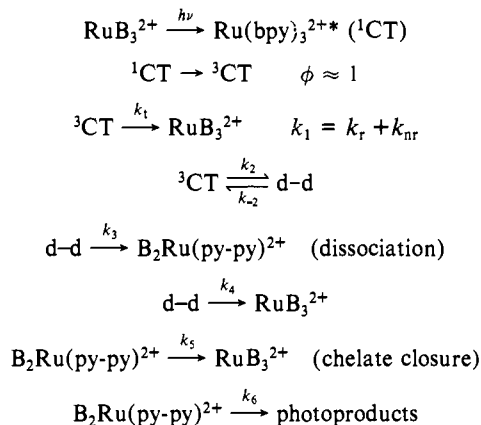
One of our major goals in the development of metallopolymeric materials is to transfer to them the desirable characteristics of monomeric ruthenium complexes. One of the features of note in the results reported here is that the photochemical and photophysical properties of the ruthenium sites bound to the PVP backbone do indeed bear a high degree of resemblance to their monomeric analogues $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Ru}(\text{bpy})_2(\text{py})_2^{2+}$. There are certain aspects of the excited-state properties of the metallopolymers that differ significantly from those of the monomers, but as noted below, they can be adequately rationalized in terms of a previously established model for the monomeric excited states.^{5,6}

The absorption and emission spectra of $\text{Ru}(\text{bpy})_3^{2+}$ and of similar poly(pyridyl) complexes of $\text{Ru}(\text{II})$, e.g., $\text{Ru}(\text{bpy})_2(\text{py})_2^{2+}$ and $\text{Ru}(\text{phen})_3^{2+}$ (phen is 1,10-phenanthroline), have been interpreted with use of a charge-transfer model.^{15,16} The main absorption bands in the visible region of the spectrum are assigned as metal to ligand charge transfer (MLCT), $d\pi(\text{Ru}) \rightarrow \pi^*(\text{bpy})$. The absorption is dominated by MLCT transitions to give states mainly singlet in character, ^1CT . The singlet states rapidly and

efficiently decay to a manifold of three or four closely spaced states that are lower in energy than ^1CT and are predominately triplet in character. Above 200 K, the low-lying manifold of states is populated according to Boltzmann statistics and can be treated as a single state, ^3CT . The use of pure spin labels is not entirely appropriate since spin-orbit coupling for the $d^5 \text{Ru}(\text{III})$ core has the effect of mixing the singlet and triplet states.^{15c,d,16} However, the lowest lying state(s) responsible for emission (^3CT) are still mainly triplet in character. The efficiency with which the lower, triplet states are populated following direct absorption into the higher singlet states is known to be ~ 1 for $\text{Ru}(\text{bpy})_3^{2+}$.²⁰

Following population of ^3CT , decay can occur by emission or radiationless decay, both of which return the complex to its ground state, or by thermal activation to a spectroscopically unobservable d-d state. Once formed, the d-d state undergoes decay to the ground state or ligand loss and net substitution.^{5,6} In an excited d-d state an electron occupies an antibonding, metal-based orbital, $(d\pi)^6 \rightarrow (d\pi)^5 d\sigma^*$. The expected structural consequences of electron occupation of $d\sigma^*$ include large distortions along the metal-ligand axes and weakening of the Ru-N bonds. From the results of quantum yield and lifetime studies⁵ on $\text{Ru}(\text{bpy})_3^{2+}$, $\text{Ru}(\text{bpy})_2(\text{py})_2^{2+}$, and $\text{Ru}(\text{phen})_3^{2+}$, it appears that, once formed, the d-d state either decays to the ground state or undergoes ligand loss to give a five-coordinate intermediate. Note the k_3 path in Scheme I. Following the formation of the intermediate, the nature of the lost ligand comes into play. A unidentate ligand (e.g., pyridine) is simply lost. For an initially chelated ligand like bpy, one end remains anchored by coordination at a second site at the metal so that chelate reclosure can come into play (k_5 in Scheme I). In competition with chelate ring closure is loss of the remaining end of the chelate to give net photosubstitution. The various photochemical and photophysical events that can occur following excitation are summarized in Scheme I with $\text{Ru}(\text{bpy})_3^{2+}$ as the example (B represents 2,2'-bipyridine and py-py a unidentate bpy ligand).

Scheme I



Interpretation of Results. As the data in Table I show, Ru-bpy excited states in the metallopolymers are spectroscopically similar to $\text{Ru}(\text{bpy})_3^{2+}$ and to $\text{Ru}(\text{bpy})_2(\text{py})_2^{2+}$. The correspondence in the absorption and emission spectra at room temperature indicates that energetically the relative positions of the ground and excited CT states are essentially the same in the monomers and polymers. There is no evidence for the appearance of new excited states in the polymers, and a Franck-Condon analysis²¹ of the bpy-based vibrational structure in low-temperature (77 K) emission spectra (see Figure 2) shows that there is essentially no difference in the distortion of the emitting state between the monomeric and polymeric samples, at least with regard to the 2(bpy) acceptor vibration.²² That the ruthenium sites on the polymer behave as

(20) Demas, J. N.; Taylor, D. G. *Inorg. Chem.* **1979**, *18*, 3177–9.

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(22) Caspar, J. V.; Meyer, T. J., submitted.

(23) E_{em} is converted from $\text{cm}^{-1} \times 10^3$ to eV by dividing by 8.066. Note: E_{em} is uncorrected for phototube response.

(18) Capellos, C.; Bielski, B. H. J. "Kinetic Systems"; Wiley-Interscience: New York, 1972; Chapter 5.

(19) Dressick, W. J., unpublished results.

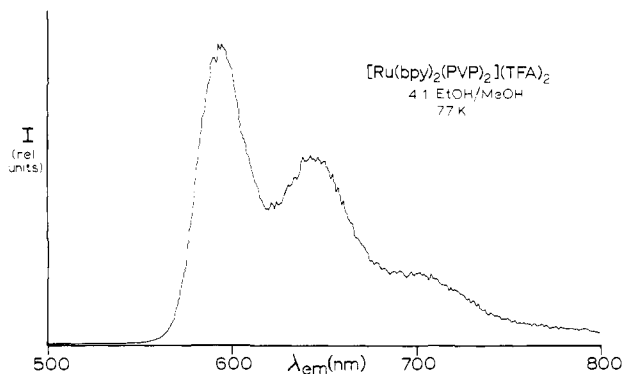


Figure 2. Emission spectrum of $\text{Ru}(\text{bpy})_2(\text{PVP})_{2/20}^{2+}$ in a 4:1 EtOH-MeOH glass at 77 K. TFA is the trifluoroacetate anion, CF_3CO_2^- .

isolated chromophores even in the sample of highest metalation, $\text{Ru}(\text{bpy})_2(\text{PVP})_{2/5}^{2+}$, is demonstrated by the lack of any noticeable shifts in either the absorption or the emission spectra compared to those of a sample of lower Ru content.¹ There are two striking observations of note in the behavior of the complexes as summarized in Table I. One is the apparently slow rate of radiative decay (k_r) from ^3CT in $\text{Ru}(\text{bpy})_2(\text{py})_2^{2+}$, which is reflected in a low value of Φ_r . However, it should be recalled that as defined here k_r is actually the product of the efficiency of formation of the excited state upon photolysis, Φ_{isc} , and the actual radiative rate constant for the emitting state, k_r' . The most reasonable explanation is that $\Phi_{\text{isc}} \ll 1$ even though $\Phi_{\text{isc}} \sim 1$ for $\text{Ru}(\text{bpy})_3^{2+}$.²⁰ The other unusual feature is the greatly diminished excited-state lifetimes for the chromophores when bound to the polymers. In acetonitrile, room-temperature lifetimes are 20 ns for samples of either metal loading.

To obtain insight as to the origin of the decrease in lifetime of the excited states in the metallopolymers, we carried out temperature-dependent lifetime measurements in propylene carbonate. The data were fit to eq 1 in order to determine the parameters k_1 , k^∞ , and $\Delta E'$. For the 2/20 polymer, the agreement between the experimental data and a line calculated by using values of k_1 , k^∞ and $\Delta E'$ in Table II is shown in Figure 3. As summarized in Table II, the temperature-dependent lifetime experiment gave values for k_1 , k^∞ , and $\Delta E'$ that are in the same range as those found for $\text{Ru}(\text{bpy})_3^{2+}$. The significant difference between $\text{Ru}(\text{bpy})_3^{2+}$ and the 2/20 polymer appears in the value of $\Delta E'$, which has its origin in the thermally activated transition from ^3CT to a low-lying d-d state. In the 2/20 polymer, the energy gap, $\Delta E'$, is significantly reduced in magnitude when compared to the monomer. One way to assess the importance of the variations in $\Delta E'$ on excited-state properties is to evaluate their effects on excited-state lifetimes at 25 °C. If all other constants remained the same, the decrease in $\Delta E'$ to 2620 cm^{-1} for $\text{Ru}(\text{bpy})_2(\text{PVP})_{2/20}^{2+}$ compared to $\Delta E' = 3270 \text{ cm}^{-1}$ for $\text{Ru}(\text{bpy})_3^{2+}$ (in propylene carbonate solvent) would cause a decrease in lifetime by a factor of 23. As a consequence of the lower $\Delta E'$ values for sites in the 2/20 polymer, the conversion efficiencies in Tables II and III for the thermally activated transition from ^3CT to the d-d state (ϕ_i) is close to unity for the polymer sample. The point is that for the 2/20 polymer, the decrease in lifetime for the excited-state sites is a result of the decreased energy gap for population of the d-d state. Once populated, the d-d state appears to undergo rapid decay to the ground state or photochemical ligand loss as noted below. From the data in Table II, the 2/5 polymer also undergoes efficient conversion from ^3CT to d-d. However, the more highly metallated polymer differs from $\text{Ru}(\text{bpy})_3^{2+}$ not in $\Delta E'$, since the values are nearly the same, but rather in the preexponential term k'^0 that is larger by ~ 30 for the sites in the polymer.

There are at least two reasonable origins for the lowered $\Delta E'$ value for the 2/20 polymer. It was noted in a previous paper that from X-ray crystallographic data the N-Ru-N "bite" angle for a Ru-bpy link in $\text{Ru}(\text{bpy})_3^{2+}$ is 78.7° while from estimates based on molecular models the bite angle for a Ru(PVP)₂ grouping is

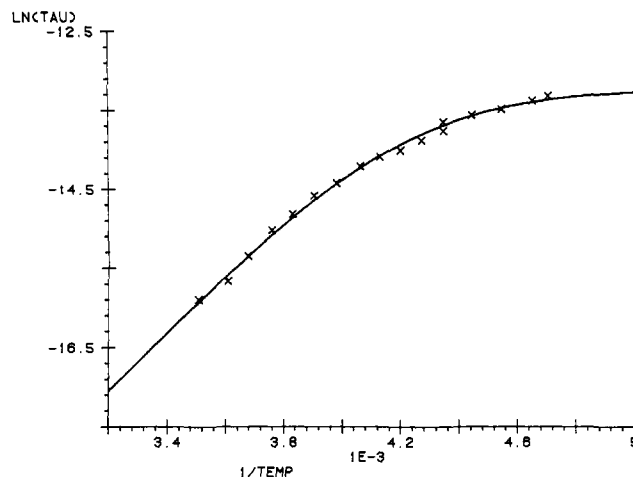


Figure 3. Temperature dependence of the lifetime of $\text{Ru}(\text{bpy})_2(\text{PVP})_{2/20}^{2+}$ in propylene carbonate. Data points (x) were fit to eq 1. The line shown in the figure was calculated by using a least-squares program and the values of k_1 , k^∞ , and $\Delta E'$ listed in Table II.

$\sim 73^\circ$.² The further lowering of ligand-metal-ligand bond angles from the 90° for O_h symmetry will cause a mixing of the purely $d\sigma^*$ (e_g) and $d\pi(t_g)$ orbitals of O_h symmetry. The net effect will be to stabilize some of the d-d excited states having the nominal configuration $(d\pi)^5d\sigma^*$, and a stabilization relative to the low-lying MLCT state(s) would cause a lowering of $\Delta E'$. The same effect may be operative in complexes of Os(II) and Ru(II) containing the 2,2',2''-terpyridine ligand, where the planar trpy ligand does not span 180° and unusually short lifetimes and/or surprisingly efficient ligand loss have been observed.^{7a}

The second possible origin for the decreased $\Delta E'$ values lies in the known solvent dependence of the energy gap between the ^3CT and d-d states.²² For $\text{Ru}(\text{bpy})_3^{2+}$, $\Delta E'$ varies from 3820 cm^{-1} in *N,N'*-dimethylformamide solution to 3180 cm^{-1} in pyridine. As can be seen from the data, effects of solvent changes on $\Delta E'$ for $\text{Ru}(\text{bpy})_3^{2+}$ can be quite large, which suggests a second possible explanation for the decreased $\Delta E'$ values for the metallopolymer excited states. In the "dilute" metallopolymer sample the lowered value of $\Delta E'$ may be a consequence of the local "pyridine-like" environment of the ruthenium sites caused by the presence of nearby pyridyl groups for the PVP backbone. In the more highly loaded sample, $\text{Ru}(\text{bpy})_2(\text{PVP})_{2/5}^{2+}$, the excited-state environment is necessarily less pyridine-like. The polymer structure should be more open and the excited-state environment more like the external solvent, which is propylene carbonate. These predictions are qualitatively correct in that $\Delta E'$ is larger in $\text{Ru}(\text{bpy})_2(\text{PVP})_{2/5}^{2+}$ (3180 cm^{-1}) than for the less highly loaded sample (2620 cm^{-1}), which is the relative order of $\Delta E'$ for $\text{Ru}(\text{bpy})_3^{2+}$ in propylene carbonate and pyridine.

Photochemical Properties. The lifetime results show that d-d states play an important role in defining the photophysical properties of the metallopolymer excited states in solution. In the monomeric excited states the d-d states are also the apparent origin of the observed photochemical ligand loss. Photosubstitution occurs for the metallopolymers, and as shown by the data in Table III the room-temperature efficiency for ligand loss (Φ_p) is between the values found for $\text{Ru}(\text{bpy})_2(\text{py})_2^{2+}$ and $\text{Ru}(\text{bpy})_3^{2+}$. In terms of innate reactivity from the d-d state, the more fundamental parameter is $\Phi_p(\text{d-d})$, the quantum yield for ligand loss following population of the d-d state. $\Phi_p(\text{d-d})$ can be calculated from the observed quantum yield for net ligand loss and the efficiency for the $^3\text{CT} \rightarrow \text{d-d}$ conversion (ϕ_i) as shown in eq 9. The $^3\text{CT} \rightarrow$

$$\Phi_p = \phi_i \Phi_p(\text{d-d}) \quad (9)$$

$$\phi_i = \frac{k'}{k_1 + k'} \quad k' = k^\infty \exp(-\Delta E'/RT) \quad (\text{note eq 1}) \quad (10)$$

d-d conversion efficiency can be calculated from the quantities k_1 and k' (eq 10). Calculated values for ϕ_i and $\Phi_p(\text{d-d})$ as well

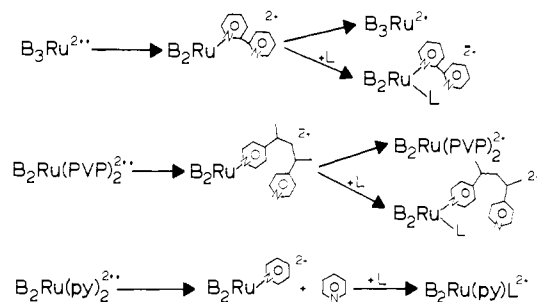


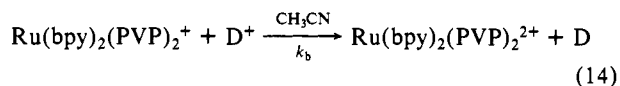
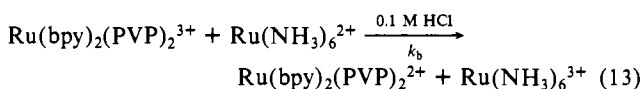
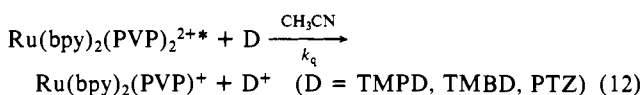
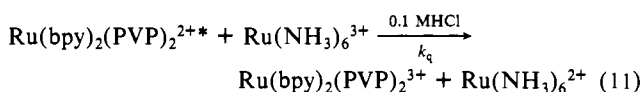
Figure 4. Schematic representation showing relative chelate ring reclosure abilities for photochemical intermediates for (top) $\text{Ru}(\text{bpy})_3^{2+}$, (middle) $\text{Ru}(\text{bpy})_2(\text{PVP})_2^{2+}$, and (bottom) $\text{Ru}(\text{bpy})_2(\text{py})_2^{2+}$. The reactant L is a solvent molecule or anion in the vicinity of the photoreactive site.

as experimentally determined values for Φ_p are reported in Tables II and III. Although there is some variation in the solvents used for the comparisons, the overall conclusions are clear. Quantum yields for the $^3\text{CT} \rightarrow \text{d-d}$ transition at room temperature are all relatively high with 61% of the excited state decay in $\text{Ru}(\text{bpy})_2(\text{py})_2^{2+}$ in CH_2Cl_2 occurring from the d-d state and 96% for $\text{Ru}(\text{bpy})_2(\text{PVP})_2^{2+}$ in propylene carbonate. Efficiencies for ligand loss from the d-d state, $\Phi_p(\text{d-d})$, show that the d-d states for $\text{Ru}(\text{bpy})_2(\text{PVP})_2^{2+}$ in CH_3CN and for $\text{Ru}(\text{bpy})_3^{2+}$ in CH_2Cl_2 have the same reactivity. These values are in turn ~ 6 times lower than $\Phi_p(\text{d-d})$ for the bis(pyridine) complex.

As concluded in the earlier study, which dealt with monomer photochemistry,⁵ the higher apparent reactivity of the d-d states for $\text{Ru}(\text{bpy})_2(\text{py})_2^{2+}$ may be largely in the irreversible loss of the pyridine ligand. In contrast to the case for $\text{Ru}(\text{bpy})_3^{2+}$ and the polymer-bound excited states there is no possibility for the d-d state of $\text{Ru}(\text{bpy})_2(\text{py})_2^{2+}$ to recapture a lost ligand by chelate reclosure. By contrast, there is a close similarity in values of $\Phi_p(\text{d-d})$ between the metallopolymer excited state and $\text{Ru}(\text{bpy})_3^{2+}$. The similarity suggests that, as in $\text{Ru}(\text{bpy})_3^{2+}$, at the ruthenium site bound to the polymer "chelate ring closure" can also occur due to the relatively high concentration of unbound pyridyl groups in the local environment. In essence, photosubstitution at metal sites in the polymer is inhibited because following ligand loss an efficient chelate closure step exists past the metal-ligand bond-breaking step. The net effect is a decrease in Φ_p compared to that for the monomeric analogue, $\text{Ru}(\text{bpy})_2(\text{py})_2^{2+}$. A schematic attempt to illustrate the reclosure (in)abilities of the various complexes is shown in Figure 4.

The use of aerated as opposed to deaerated acetonitrile solutions has no effect on the values obtained for Φ_p for the metal complex sites in the metallopolymers. The absence of quenching by O_2 , which is significant for $\text{Ru}(\text{bpy})_3^{2+}$, is a consequence of the decreased lifetimes for the metallopolymer excited states since excited-state decay is short on the time scale of diffusional quenching by O_2 .

Excited-State Electron-Transfer Reactions. Both oxidative (eq 11) and reductive (eq 12) excited-state electron-transfer reactions



of the metallopolymeric excited states were studied by the

Stern-Volmer quenching technique. The back-electron-transfer reactions of the redox products of the quenching step were also studied (eq 13 and 14) by conventional flash photolysis.

Our interests in the redox properties of the metallopolymeric excited states were twofold. The first was to continue the comparisons in excited-state properties with related monomeric excited states. The second was in the implications such a study could have for energy conversion processes. The quenching step (eq 11 and 12) converts excited-state energy into stored redox energy. The storage is transient because of back electron transfer (eq 13 and 14), which is a recombination event leading to evolution of heat. A series of approaches based on organized media or using hydrophobic or surfactant derivatives of the reagents involved have been studied as means of slowing down or avoiding back electron transfer.²⁴ Our thought was that it might be possible to influence favorably the relative magnitudes of k_q and k_b by taking advantage of the polycationic nature of the polymers.

The results in Tables IV and V clearly show that the ruthenium sites on the metallopolymers do take part in excited-state electron-transfer processes and can act as either electron donors or acceptors. We have not been able to acquire sufficient quenching data to estimate directly¹² redox potentials for the excited-state couples $E^\circ[\text{Ru}(\text{bpy})_2(\text{PVP})_2^{3+/2+*}]$ and $E^\circ[\text{Ru}(\text{bpy})_2(\text{PVP})_2^{2+*/+}]$. Redox potentials can however be estimated from spectral and electrochemical data. With use of the emission energy, E_{em} (see Table I), as a reasonable approximation for the 0-0 energy of the excited state¹² and the formal potentials for oxidation¹² and reduction²⁵ of the metallopolymer (recorded vs. SSCE as a film coated onto a Pt electrode in 0.1 M TEAP in CH_3CN ²⁶), the excited-state potentials can be calculated as

$$\begin{aligned} E^\circ(\text{Ru}^{3+/2+*}) &\cong E^\circ(\text{Ru}^{3+/2+}) - E_{em} \\ &= 1.24 - 2.03 \\ &= -0.79 \text{ V} \end{aligned}$$

$$\begin{aligned} E^\circ(\text{Ru}^{2+*/+}) &\cong E^\circ(\text{Ru}^{2+*/+}) + E_{em} \\ &= -1.39 + 2.03 \\ &= 0.64 \text{ V} \end{aligned}$$

These estimates are similar in value to those reported for $\text{Ru}(\text{bpy})_2^{2+}$ in CH_3CN : $E^\circ[\text{Ru}(\text{bpy})_3^{3+/2+*}] = 0.81 \text{ V}$; $E^\circ[\text{Ru}(\text{bpy})_3^{2+*/+}] = 0.77 \text{ V}$ vs. SSCE.

Beyond the simple fact that the quenching of the polymeric complexes is possible, there are some interesting features to note in the data of Tables IV and V. In acetonitrile solution, values for rates of reductive quenching of the PVP complexes are all between 2×10^9 and $3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The values are somewhat lower than the values obtained for quenching of $\text{Ru}(\text{bpy})_3^{2+}$ by the same reductants and are substantially slower than the diffusion-controlled limit for the quenchers in CH_3CN ($\sim 2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$).¹² The same falloff in rate constant for oxidative quenching in water is also observed where the diffusion-controlled limit for 2+ and 3+ ions in 0.1 M HCl is $(3-5) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The failure to observe a larger relative decrease in 0.1 M HCl is somewhat unexpected. In sufficiently acidic solution (pH < 3.5), PVP is known to be protonated.²⁷ In acidic solution the polymer becomes an even more highly charged polyelectrolyte, consisting of both Ru-complex and pyridinium sites. Since the quenching reaction involves a 3+ oxidant, $\text{Ru}(\text{NH}_3)_6^{3+}$, a more dramatic electrostatic effect might have been expected. In fact, given that the relative rate decreases in acetonitrile and acid are of the same magnitude, the presence of neighboring pyridinium sites may have

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(25) Calvert, J. M., unpublished results.

(26) It has been demonstrated that potentials measured for complexes as polymer films are nearly identical with those for the same material in homogeneous solution.¹² The formal potentials, E° , reported here were determined by cyclic voltammetry of the complex as a film coated onto a Pt-disk electrode. Potentials were measured with 0.1 M TEAP/ CH_3CN as electrolyte and are reported vs. the sodium chloride calomel electrode (SSCE).

(27) Kirsch, Y. E.; Komarova, O. P. *Polym. Sci. USSR (Engl. Transl.)* **1976**, *18* 223-8.

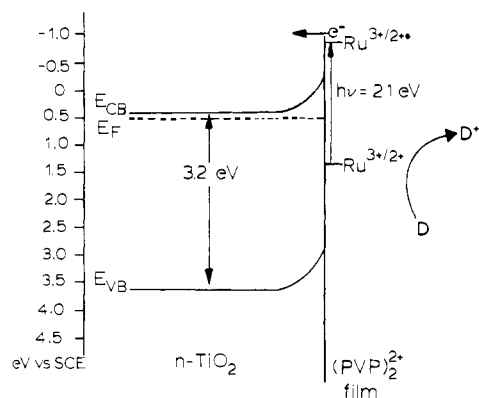


Figure 5. Schematic energy diagram of the relative placement of redox levels for the ground- and excited-state couples in the metallopolymers relative to the semiconductor energy levels of $n\text{-TiO}_2$. The extent of band bending is unknown under the conditions of the experiment. A bias of +0.5 V was applied to the electrode in the photoelectrochemical experiment. D represents the electron-transfer donor hydroquinone, which was used as a "sensitizer" to reduce Ru(III) sites in the film to Ru(II).

little bearing on the rate of $\text{Ru}(\text{NH}_3)_6^{3+}$ quenching. The origin of the rate decrease in both cases may be a decreased accessibility of the excited state in the polymeric environment.

The back-reaction rate constants from flash photolysis in both water and acetonitrile also exhibit a decrease compared to the data for $\text{Ru}(\text{bpy})_3^{2+}$. The magnitudes of the decrease in k_b parallel the decreases found for k_q , suggesting that the decreased accessibility of the redox sites bound to PVP may be responsible for slowing down both electron-transfer rate constants.

An unusual feature of the flash photolysis experiments using TMPD as quencher was the buildup of TMPD^+ after the flash and its relatively slow decay to TMPD. From the flash experiments it could be estimated that $\sim 30\%$ of the reducing equivalents produced by quenching are temporarily stored in the solution resulting in a buildup of TMPD^+ . With time (minutes), these redox equivalents are scavenged by TMPD^+ , which is a weak oxidant, $E^\circ(\text{TMPD}^{+/0}) = 0.12 \text{ V}$ at 25°C in CH_3CN vs. SSCE,¹² and the solution is photochromic. After a series of flashes, TMPD^+ builds up in the solution permanently. We are currently investigating the point further since, in principle, the apparent inhibition of the back-reaction may ultimately be utilizable for the production of H_2 .

Photoelectrochemical Properties. One difficulty with the polymeric complexes described here in terms of energy conversion processes in solution is the short lifetimes of their excited states. An alternate approach to utilizing the polymers is as visible photosensitizing films on a large band gap semiconductor such as $n\text{-TiO}_2$. There is an extensive background in this area based on both organic or inorganic chromophores adsorbed or coated onto semiconductor surfaces.²⁸ Especially notable in the context of the present work is the recent report of Ghosh and Spiro on electropolymerized complexes of Ru.²⁹ With a suitable arrangement of the energy levels between the dye and semiconductor, the semiconductor can function as a rapid, irreversible electron-transfer quencher of a surface-confined excited state.

One of the attractive characteristics of the Ru-PVP complexes is their ability to form films on various surfaces. With this ability, the properties of the metallopolymers can be studied on surfaces

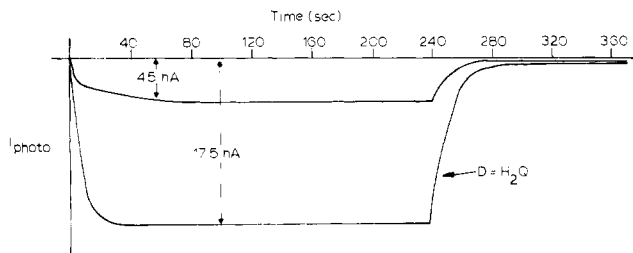


Figure 6. Photocurrents obtained by irradiating a $\text{Ru}(\text{bpy})_2\text{-(PVP)}_{2/5}^{2+}$ -coated $n\text{-TiO}_2$ electrode with visible light ($\lambda = 450 \pm 3 \text{ nm}$). The electrolyte was 0.1 M TEAP/ CH_3CN and the electrode area 0.25 cm^2 . The excitation beam was blocked at $t = 240 \text{ s}$ in order to observe photocurrent decay. The lower curve ($i_{\text{photo}} = 17.5 \mu\text{A}$) was recorded in the presence of $\sim 0.1 \text{ M}$ hydroquinone (H_2Q) as supersensitizer.

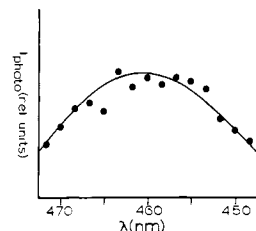


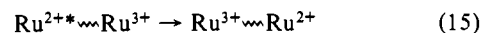
Figure 7. Wavelength-dependent photocurrents for $\text{Ru}(\text{bpy})_2\text{-(PVP)}_{2/5}^{2+}$ -coated $n\text{-TiO}_2$ electrodes. The electrolyte was 0.1 M TEAP/ CH_3CN and the light source was a pulsed, tunable dye laser. See Experimental Section for details. A curve that best fit the data (\bullet) was drawn by eye.

as well as in solution. Clark and Sutin have shown that $\text{Ru}(\text{bpy})_3^{2+}$ in homogeneous solution can be used to sensitize $n\text{-type TiO}_2$ to visible light.^{28a} Given the similarity in the photophysical properties of the metallopolymers and $\text{Ru}(\text{bpy})_3^{2+}$, $n\text{-TiO}_2$ was chosen in an attempt to obtain sensitized photocurrents with the electrode coated with a film of the polymer. Although the results obtained here are preliminary in nature, they are of interest in the context of the photoredox properties of the polymers.

The relative positions of the relevant redox levels of the semiconductor and metallopolymers are shown schematically in Figure 5. Although the extent of band bending under our experimental conditions is unknown, it seems clear that oxidative quenching of the excited state by electron transfer to the conduction band of the semiconductor is allowed energetically.

As mentioned earlier, illumination of a thick ($\sim 10^{-7} \text{ mol/cm}^2$) coating of the metallopolymers on TiO_2 results in an easily visible orange luminescence from the film. The energy of the emission is consistent with that observed for the complex in solution and indicates that gross photophysical properties (e.g., absorption and emission energies) are maintained in the film environment.

Front-face, visible irradiation of the polymer-coated electrode ($\Gamma \approx 10^{-7} \text{ mol/cm}^2$) exposed to a 0.1 M $(\text{NEt}_4)(\text{ClO}_4)$ -acetonitrile solution gave a detectable and reproducible oxidative photocurrent, i_{photo} (Figure 6). The anodic nature of i_{photo} is consistent with electron transfer having occurred to the conduction band of the semiconductor from excited states in the metallopolymers. That the chromophoric sites in the film are the origin of the photocurrents is confirmed by the action spectrum (plot of i_{photo} vs. irradiation wavelength) shown in Figure 7. In the action spectrum a maximum appears which is very close to the $\lambda(\text{max})$ in the absorption spectrum of the chromophore. One characteristic of the photoprocess as described is that, with time, the Ru(II) sites in the film are converted into Ru(III). Conversion to Ru(III) causes a decrease in the photocurrent level both because of the depletion of the Ru(II) chromophores in the film and possibly because of quenching by neighboring Ru(III) sites (eq 15).



Because of problems associated with the eventual buildup of Ru(III), photocurrent measurements were also made in the presence of an electron donor known to reduce Ru(III) sites rapidly

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to Ru(II). As expected, irradiation of the coated semiconductor in the presence of added hydroquinone (~ 0.1 M) to the electrolyte solution resulted in an increase in the observed photocurrents in this case by a factor of 4. Under these conditions, i_{photo} was stable for a period of at least 20 min of photolysis.

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Synthesis, Molecular Structure, and Exchange Coupling in the Alternatingly Bridged and Alternatingly Spaced Linear-Chain Compound *catena*-Dichloro(3,6-dithiaoctane)copper(II)

Marilyn M. Olmstead, W. Kenneth Musker, Leonard W. Ter Haar, and William E. Hatfield*

Contribution from the Departments of Chemistry, The University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27514, and The University of California at Davis, Davis, California 95616. Received March 9, 1982

Abstract: The crystal and molecular structure of the compound dichloro(3,6-dithiaoctane)copper(II), Cu(C₂H₅SC₂H₄SC₂H₅)Cl₂, has been determined from single-crystal, three-dimensional X-ray diffraction counter data. The compound crystallizes as dark green needles in space group *P* $\bar{1}$ with *Z* = 2 and having unit cell dimensions *a* = 7.832 (4) Å, *b* = 7.929 (5) Å, *c* = 9.803 (6) Å, α = 69.71 (4)°, β = 71.36 (4)°, and γ = 77.84 (4)°. The observed and calculated densities are 1.71 (298 K) and 1.76 (140 K) g cm⁻³, respectively. The structure was refined by full-matrix least-squares techniques to a conventional *R* value of 0.048. Formula units of the compound stack along the *a* axis to form an alternatingly spaced chain in which the copper(II) ions are six-coordinate. Two chloride ligands and two sulfur atoms from the bidentate thioether constitute the equatorial plane with a sulfur atom and a chloride ion from adjacent monomeric units loosely bound in the two axial positions. Copper-chloride bond distances are 2.264 (1) and 2.230 (1) Å within the equatorial plane, and the copper-chloride interatomic distance to the axial chloride is 3.234 (1) Å. Equatorial copper-sulfur bond distances are 2.311 (1) and 2.327 (1) Å. The copper-copper distance in the Cu₂Cl₂ planar unit is 4.406 (1) Å, and the Cu-Cl-Cu' bridging bond angle is 93.1 (1)°. The copper-sulfur interatomic distances that propagate the chain are 3.361 (2) Å, the copper-copper separation in the planar Cu₂S₂ portion of the chain is 4.679 (1) Å, and the Cu-S''-Cu'' bridging bond angle is 109.3 (1)°. The magnetic susceptibility of this unique chain exhibits a maximum at 4.2 K that is indicative of an antiferromagnetic intrachain exchange coupling interaction between the alternatingly spaced and alternatingly ligand-bridged copper(II) ions. The best fit of the magnetic susceptibility data by alternating chain theory for *S* = 1/2 ions yields values for the exchange coupling constant and the alternation parameter of -2.73 cm⁻¹ and 0.69, respectively, using the EPR *g* value of 2.084.

Although organic compounds with alternatingly spaced linear-chain structures have been known and studied extensively for many years,¹ exchange-coupled transition-metal compounds with analogous structures and comparable magnetic properties have received much less attention. The most thoroughly studied transition-metal compound which exhibits alternating Heisenberg antiferromagnetic behavior is Cu(NO₃)₂·2.5H₂O,² and it is important to note that the compound has a ladder-like structure at room temperature.³ Other examples of compounds that are known to have alternating chain structures include the pyrazine-bridged binuclear copper acetate chain, [Cu₂(OAc)₄pyr]_n,⁴ and the carcinostatic and carcinolytic agent [3-ethoxy-2-oxobutylaldehyde bis(thiosemicarbazone)]copper(II), Cu-KTS.^{5,6} On the basis of their magnetic properties the following compounds have been suggested to have alternatingly spaced linear-chain structures at low temperatures: the form of tetrathiafulvalenium bis[*cis*-(1,2-bis(trifluoromethyl)ethylene-1,2-dithiolato)]cuprate(II), which results from a spin Peierls transition at 12 K,⁷ *catena*-bis(μ -bromo)bis(*N*-methylimidazole)copper(II),⁸ and *catena*-bis(μ -chloro)bis(4-methylpyridine)copper(II).^{9,10} These latter three compounds have uniformly spaced linear-chain structures at room temperature.¹¹⁻¹³

We have found that *catena*-dichloro(3,6-dithiaoctane)copper(II), Cu(3,6-DTO)Cl₂, has an alternatingly spaced structure at

140 K and exhibits magnetic properties that may be explained by Heisenberg alternating chain exchange theory. The results of our studies are reported in this article.

Experimental Section

Preparation and Characterization of *catena*-Dichloro(3,6-dithiaoctane)copper(II). A solution of CuCl₂ in methanol was prepared by dissolving 0.755 g of CuCl₂ in 250 mL of methanol (0.0224 M). A solution of the dithioether was prepared by dissolving 2.25 g of 3,6-dithiaoctane (K & K Laboratories, Inc., Hollywood, CA) in 250 mL of

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* Address correspondence to this author at the University of North Carolina.