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Excited State Interactions in Electropolymerized Thin Films of Ru$^{\text{II}}$, Os$^{\text{II}}$, and Zn$^{\text{II}}$ Polypyridyl Complexes

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Emission from thin films of poly[Ru(vbpy)$_3$](PF$_6$)$_2$ (vbpy = 4-methyl-4′-vinyl-2,2′-bipyridine) prepared by reductive electropolymerization on ITO (Sn:In$_2$O$_3$) is dominated by time-dependent effects and dramatically reduced excited state lifetimes compared to related monomers. The origins of these effects have been investigated by photophysical measurements on a series of copolymeric films containing mixtures of the Zn$^{\text{II}}$, Ru$^{\text{II}}$, and Os$^{\text{II}}$ forms of poly[M(vbpy)$_3$](PF$_6$)$_2$. In copolymeric Ru$^{\text{II}}$ and Os$^{\text{II}}$ films, facile energy transfer occurs from Ru$^{\text{II}}$ to Os$^{\text{II}}$. Dilution of Ru$^{\text{II}}$ by Zn$^{\text{II}}$ in copoly-χ[Ru(vbpy)$_3$](PF$_6$)$_2$,$(1 - \chi)$[Zn(vbpy)$_3$](PF$_6$)$_2$ (χ = mole fraction of Ru$^{\text{II}}$) mixtures is accompanied by an increase in emission energy and average excited state lifetime. These results point to a quenching mechanism in poly[Ru(vbpy)$_3$](PF$_6$)$_2$ arising from facile energy transfer to low-energy, short-lived "trap sites". The trap sites may be created by electronic coupling between special pairs of adjacent complexes present in small amounts. The decrease in excited state lifetime at the trap sites is predicted qualitatively by the energy gap law for nonradiative decay.

Introduction

One of the characteristic features of polypyridyl complexes of Ru$^{\text{II}}$, Os$^{\text{II}}$, and Re$^{\text{I}}$ is the existence of low-lying metal-to-ligand charge transfer (MLCT) excited states with well-defined photophysical properties.[1] Procedures are available for forming thin polymeric films containing these complexes by oxidative[2] or reductive[3] electropolymerization. We report here the existence of novel self-quenching and energy transfer processes in films prepared by reductive electropolymerization of the vinyl-containing complexes [M(vbpy)$_3$]$^{2+}$ (M = Zn$^{\text{II}}$, Ru$^{\text{II}}$, Os$^{\text{II}}$; vbpy = 4-methyl-4′-vinyl-2,2′-bipyridine). The electrochemical properties of these films are well documented, but there have been no systematic studies of excited state properties. Electrochemiluminescence from poly[Ru(vbpy)$_3$](PF$_6$)$_2$ films has been reported.[4]

Experimental Section

The salts [Ru(vbpy)$_3$](PF$_6$)$_2$, [Zn(vbpy)$_3$](PF$_6$)$_2$, and [Os(vbpy)$_3$](PF$_6$)$_2$ were prepared as previously described.[3,5] All films were prepared in a nitrogen drybox on transparent ITO (Sn(IV)-doped In$_2$O$_3$, Delta Technologies, Limited) electrodes, with a platinum gauze as the counter electrode, in a two-electrode compartment cell by reductive electropolymerization in deaerated acetonitrile 0.1 M in [N(n-C$_4$H$_9$)$_4$](PF$_6$) (TBAH) with the complex or mixture of complexes at 1 mM. The electrodes was cycled through both bipyridine reductions, from 0 to −1.7 to 0 V vs SSCE at a scan rate of 50 mV s^{-1}. Composition and surface coverages were determined by integrating M$^{\text{III/II}}$ current−potential wave forms in slow scan cyclic voltammograms (ca. 10 mV s^{-1}) at 1.16 V vs SSCE for the Ru$^{\text{III/II}}$ couple and 0.76 V for Os$^{\text{III/II}}$ or for the first bpy$^{0/-}$ couple at −1.33 V. In the copolymerized Zn$^{\text{II}}$ and Ru$^{\text{II}}$ films, the composition in Zn$^{\text{II}}$, which is not electroactive, was verified by displacing the labile Zn$^{\text{II}}$ with Fe$^{\text{II}}$ and evaluating the Fe$^{\text{III/II}}$ wave of poly[Fe(vbpy)$_3$]$^{2+}$ at 1.06 V vs SSCE in acetonitrile containing 0.1 M TBAH. These results indicate that the ratio of Ru$^{\text{II}}$ to Zn$^{\text{II}}$ in the electropolymerization solution is maintained in the electropolymerized films. Typical electroactive surface coverages were $\Gamma = (0.11{-}4.7) \times 10^{-8}$ mol cm^{-2}, ~14−590 monomolecular layers.[3a] Film thicknesses of 60−2800 Å were measured by profilometry on dry films.

Steady state emission spectra were collected from electrodes mounted in a front face geometry on a SPEX F212 spectrofluorometer interfaced to a DM1B computer. Emission lifetime measurements were recorded by using a PRA LN1000 nitrogen laser (337 nm) as a pulsed source (3 Hz) to pump a PRA LN102/1000 tunable dye laser with dye coumarin 460. The excitation beam was focused to a 16 mm^2 spot on the film (40 μJ/pulse). The emission was focused onto the entrance slits of a Macpherson 272 monochromator, detected with a Hamamatsu R3896 PMT and transferred to a LeCroy 7200A digitizer inferfaced with a PC. A dichromate filter was used to remove scattered laser light. Time-resolved emission spectra were constructed by analysis of emission lifetime decay curves at wavelengths throughout the emission manifold from 580 to 760 nm at 5 nm intervals and were corrected for the spectral response of the detector. Low-temperature emission and lifetime data were recorded on film-coated electrodes. The ITO electrode with the electropolymerized film was placed in a glass tube, which was then immersed in an optical Dewar containing liquid nitrogen. Inside the glass tube containing the electrode, a flow of helium was maintained and the temperature monitored by a thermocouple placed next to the film. The electrodes could also be directly immersed into the liquid nitrogen; however, in some instances peeling of the electropolymerized film was observed.

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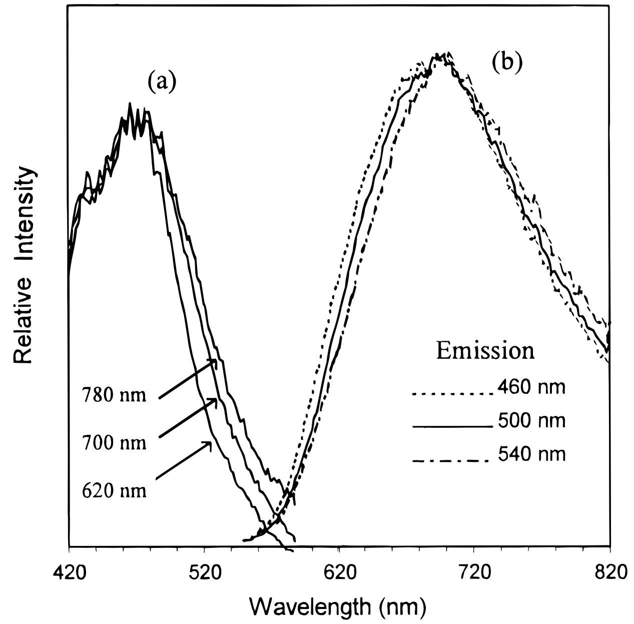


Figure 1. Excitation spectra (a) as a function of monitoring emission wavelength (620, 700, and 780 nm) and intensity normalized, steady state emission spectra (b) of ITO|poly[Ru(vbpy)$_3$](PF$_6$)$_2$ ($\Gamma = 2 \times 10^{-8}$ mol cm^{-2}) as a function of excitation wavelength (460, 500, and 540 nm) in deaerated acetonitrile.

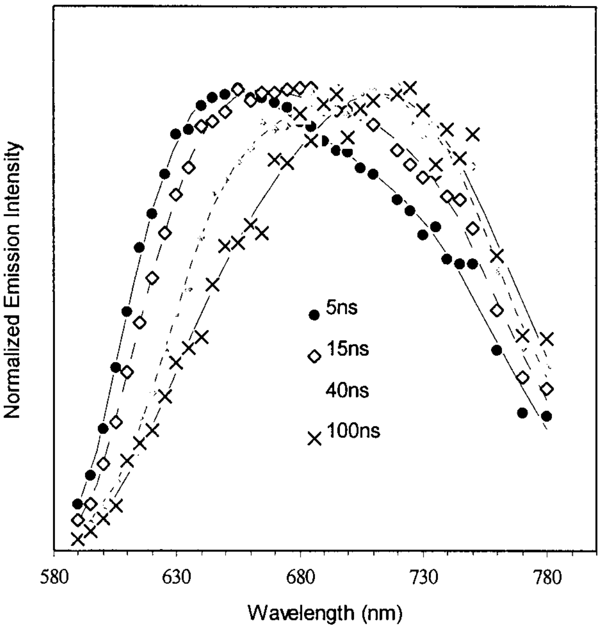


Figure 2. Intensity normalized, time-resolved emission spectra of ITO|poly[Ru(vbpy)$_3$](PF$_6$)$_2$ ($\Gamma = 1.7 \times 10^{-8}$ mol cm^{-2}) in air at 5, 15, 40, and 100 ns after initial pulsed laser excitation at 460 nm.

Results

Emission is observed from thin, electropolymerized films of poly[Ru(vbpy)$_3$](PF$_6$)$_2$ on ITO (460 nm excitation) in deaerated acetonitrile at $\lambda_{\max}^{\text{em}} = 690$ nm. Emission decays were nonexponential, but decay kinetics could be fit satisfactorily to the sum of two exponentials (eq 1) and the method of nonlinear least-squares by using a Marquardt algorithm.[6] Typical parameters were $\tau_1 = 19$ ns ($k_1 = 5.4 \times 10^7$ s^{-1}), $\tau_2 = 120$ ns ($k_2 = 8.4 \times 10^6$ s^{-1}), and $A = 0.80$ with an average lifetime, $\langle\tau\rangle$, of 39 ns (eq 2) with excitation at 460 nm and monitoring at 690 nm.

$$I(t) = A \exp(-t/\tau_1) + (1 - A) \exp(-t/\tau_2) \qquad (1)$$

$$\langle\tau\rangle = A\tau_1 + (1 - A)\tau_2 \qquad (2)$$

For a series of six films prepared on different days $\langle\tau\rangle$ varied from 32 to 52 ns, but the emission maximum remained constant. For individual films, no variation in the average lifetimes was noted as the laser power was increased from 20 to 100 μJ/pulse (laser spot size = 16 mm^2).

Emission decay kinetics were both excitation and monitoring wavelength dependent. In Figure 1 are shown intensity-normalized CW emission spectra for poly[Ru(vbpy)$_3$](PF$_6$)$_2$ on ITO obtained at three excitation wavelengths near and on the low-energy side of the MLCT absorption maximum at 468 nm. Also shown are excitation spectra recorded by monitoring the emission at 620, 700, and 780 nm. Excitation on the lower energy side of the MLCT absorption at 540 or 500 nm results in a loss in intensity on the high-energy side of the emission and a broadening on the low-energy side. As shown in Figure 2, a possible factor contributing to these observations is that emission from the films is time dependent with a shift in $\lambda_{\max}^{\text{em}}$ from 650 nm at 5 ns after the initial laser excitation pulse to 710 nm at 100 ns ($\Delta\bar{\nu}_{\max} = 1300$ cm^{-1}).

By contrast, for [Ru$^{\text{II}}$(dmb)$_3$]$^{2+}$ (dmb = 4,4′-dimethyl-2,2′-bipyridine), which is a model for the electropolymerized Ru$^{\text{II}}$ sites in the film,[3b,g] $\lambda_{\max}^{\text{em}} = 642$ nm, and the decay kinetics are exponential with $\tau = 950$ ns in deaerated acetonitrile.[7]

Emission lifetimes and maxima are essentially the same whether the films are immersed in CH$_3$CN or dry under a nitrogen atmosphere or in air. They are also independent of film thickness ($\Gamma = 0.11 \times 10^{-8}$ to 4.7×10^{-8} mol cm^{-2}) and of the underlying electrode material (ITO, gold, or silver). In bilayer films on ITO with a poly[Zn(vbpy)$_3$](PF$_6$)$_2$ inner layer ($\Gamma = 2 \times 10^{-8}$ mol cm^{-2}) the excited state properties of Ru$^{\text{II}*}$ are also unchanged. This experiment shows that electrode quenching does not contribute significantly to the shortened lifetimes, at least for a significant fraction of the sites. There are no low-lying excited states in [Zn(vbpy)$_3$](PF$_6$)$_2$, and in the structure ITO|poly[Zn(vbpy)$_3$](PF$_6$)$_2$/poly[Ru(vbpy)$_3$](PF$_6$)$_2$, the Zn$^{\text{II}}$ inner layer acts as a screen between the electrode surface and Ru$^{\text{II}*}$. For an ITO|poly[Ru(vbpy)$_3$](PF$_6$)$_2$ film at 100 K under helium, $\lambda_{\max}^{\text{em}} = 690$ nm. Excited state decay is still nonexponential with $\tau_1 = 52$ ns, $\tau_2 = 333$ ns, and $A_1 = 0.68$. $\langle\tau\rangle$ increases to 141 ns (460 nm excitation, 690 nm monitoring).

Emission was investigated in a series of copolymeric films prepared by electropolymerization of solutions containing varying ratios of [Ru(vbpy)$_3$](PF$_6$)$_2$ and [Zn(vbpy)$_3$](PF$_6$)$_2$ at a total concentration of 1 mM. In these films, the added [Zn(vbpy)$_3$](PF$_6$)$_2$ acts as a structurally equivalent, inert optical diluent. For all films examined there was no discernible change in the MLCT absorption maximum as a function of dilution. A broadening on the low-energy side of the band was observed in pure poly[Ru(vbpy)$_3$](PF$_6$)$_2$ compared to [Ru(dmb)$_3$](PF$_6$)$_2$ in CH$_3$CN. Attempts to correlate the degree of broadening with the extent of dilution by poly[Zn(vbpy)$_3$](PF$_6$)$_2$ in copolymeric films were unsuccessful due to the low absorptivities in the diluted films. In Table 1 are listed variations in $\langle\tau\rangle$, E_{em} ($\lambda_{\text{(ex)}} = 460$ nm), and relative integrated emission intensities, $\Phi_{\text{rel}}^{\text{em}}$,[9] as Ru$^{\text{II}}$ is diluted in Zn$^{\text{II}}$ to give copoly-χ[Ru(vbpy)$_3$](PF$_6$)$_2$,(1 − χ)[Zn(vbpy)$_3$](PF$_6$)$_2$, with χ the mole fraction of Ru$^{\text{II}}$. The increase in $\langle\tau\rangle$ with increasing Zn$^{\text{II}}$ is accompanied by an increase in emission energy and relative emission intensity. The variations in $\langle\tau\rangle$ and $\lambda_{\max}^{\text{em}}$ with the mole fraction of Ru$^{\text{II}}$ are illustrated in FIgure 3.

TABLE 1: Emission Properties of ITO|copoly-χ[Ru(vbpy)$_3$](PF$_6$)$_2$,(1 − χ)[Zn(vbpy)$_3$](PF$_6$)$_2$ in CH$_3$CN at 298 K[a]

		lifetime data				
$\chi_{Ru^{II}}$ [b]	λ_{max}^{em} [c]	A[d]	τ_1 (ns)	τ_2 (ns)	$\langle\tau\rangle$ (ns)[e]	Φ_{rel}^{em} [f]
1.0	690	0.8	19	118	39	1.0
0.8	685	0.86	33	152	50	1.1
0.7	685	0.85	35	168	55	1.8
0.6	680	0.83	40	193	66	3.8
0.5	675	0.82	48	229	81	5.2
0.4	670	0.78	55	276	103	7.5
0.3	660	0.73	56	268	113	7.9
0.2	650	0.72	59	279	120	7.1
0.1	635	0.56	88	333	197	7.1

[a] Film thickness were in the range (2−4) × 10^{-8} mol cm^{-2}. [b] Mole fraction of Ru^{II} sites in the copolymerized film, ±20%. [c] Corrected emission maxima ±3 nm. [d] Relative weighting factors for τ_1 and τ_2 normalized to 1; A = weighting for τ_1, $(1 - A)$ = weighting for τ_2. Error limits: $\tau_1 \pm 10\%$; τ_2 5%; $A \pm 10\%$. [e] Average lifetimes were calculated by using eq 2. [f] Integrated emission intensities relative to $\chi_{Ru^{II}} = 1.0$ (see ref 9).

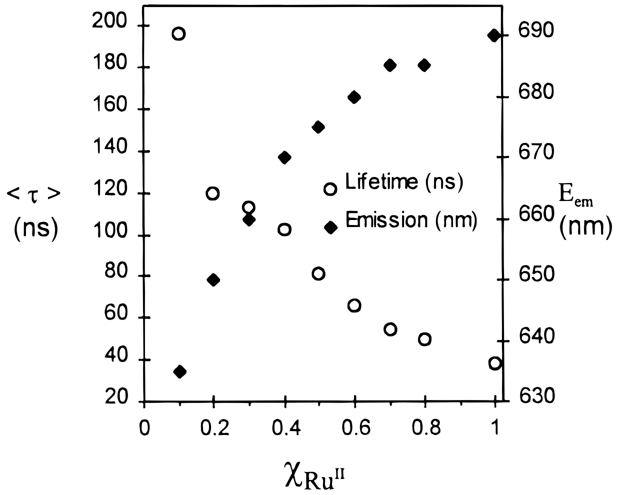


Figure 3. Plot of emission maximum (diamonds) and average excited state lifetimes (circles) as a function of $\chi_{Ru^{II}}$ for copolymerized films of copoly-χ[Ru(vbpy)$_3$](PF$_6$)$_2$,(1 − χ)[Zn(vbpy)$_3$](PF$_6$)$_2$.

Copolymerized films of poly[Ru(vbpy)$_3$](PF$_6$)$_2$ and poly-[Os(vbpy)$_3$](PF$_6$)$_2$ were also prepared. The Os^{II} complex is more easily oxidized (by 0.4 V), and its lowest lying MLCT excited state is ~0.4 eV below that of poly[Ru(vbpy)$_3$](PF$_6$)$_2$ (λ_{max}^{em} = 790 nm). Excitation of a film of composition ITO|copoly-0.73[Ru(vbpy)$_3$](PF$_6$)$_2$,0.27-[Os(vbpy)$_3$](PF$_6$)$_2$ throughout the visible results in emission only from Os^{II*} (λ_{max}^{em} = 760 nm, $\langle\tau\rangle \sim 15$ ns). The lifetime is within the time resolution of the experimental apparatus used. The emission spectrum is shown in Figure 4a. Included for comparison are emission spectra for ITO|poly[Ru(vbpy)$_3$](PF$_6$)$_2$ and ITO|poly-[Os(vbpy)$_3$](PF$_6$)$_2$, normalized for surface coverages as measured electrochemically. Os^{II*} decay in poly[Os(vbpy)$_3$](PF$_6$)$_2$ is also nonexponential with $\langle\tau\rangle < 15$ ns.

As shown by the inset in Figure 4b, the Ru^{II} and Os^{II} chromophores absorb different fractions of light throughout the visible with Ru^{II} the dominant light absorber in the mixed film 0.73 in Ru^{II}. These observations demonstrate the existence of facile Ru^{II*} → Os^{II} energy transfer. As illustrated in Figure 4c, energy transfer continues to occur even at 100 K.

Discussion

The photophysical properties of polypyridyl complexes of Ru^{II} have been investigated in various rigid media. These include zeolites,[10] clays and layered inorganic solids,[11] sol−gel matrices,[12] and thin films.[13] Compared to the usual exponential decay behavior in solution, complex excited state decay kinetics are routinely observed in these environments. The polymeric films of interest here are no exception. They display some novel photophysical phenomena compared to solution, including a dramatic decrease in lifetime and time-dependent emission spectra which give rise to excitation- and wavelength-dependent decay kinetics.

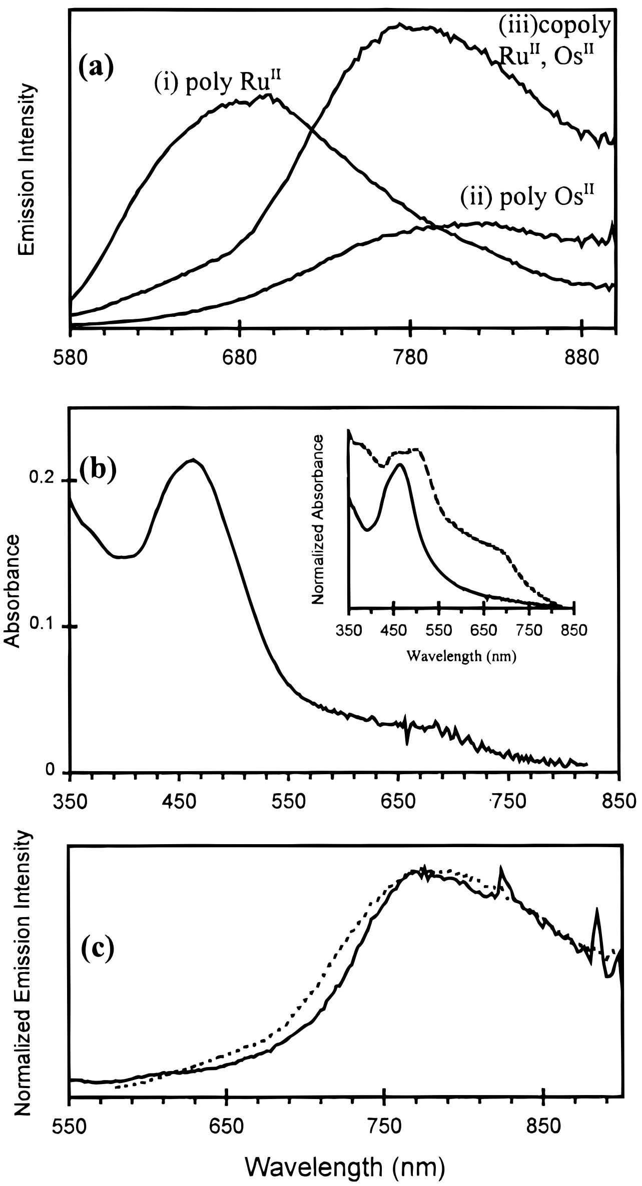


Figure 4. (a) Emission spectra from electropolymerized films on ITO immersed in acetonitrile and normalized for surface coverage from (i) ITO|poly[Ru(vbpy)$_3$](PF$_6$)$_2$, (ii) ITO|poly[Os(vbpy)$_3$](PF$_6$)$_2$, and (iii) ITO|copoly-0.73[Ru(vbpy)$_3$](PF$_6$)$_2$,0.27[Os(vbpy)$_3$](PF$_6$)$_2$. The excitation wavelength was 460 nm. (b) Absorption spectrum of ITO|copoly-0.73[Ru(vbpy)$_3$](PF$_6$)$_2$,0.27[Os(vbpy)$_3$](PF$_6$)$_2$ immersed in acetonitrile. $\Gamma = 4.83 \times 10^{-9}$ mol cm^{-2}. Inset: absorption spectra for (i) ITO|poly-[Ru(vbpy)$_3$](PF$_6$)$_2$ (solid line) and (ii) ITO|poly[Os(vbpy)$_3$](PF$_6$)$_2$ (broken line) normalized for surface coverage. (c) Emission spectra from ITO|copoly-0.73[Ru(vbpy)$_3$](PF$_6$)$_2$,0.27[Os(vbpy)$_3$](PF$_6$)$_2$; $\Gamma = 4.83 \times 10^{-9}$ mol cm^{-2} in air 298 K (broken line) and under helium at 100 K (solid line). The excitation wavelength was 460 nm.

The apparent quenching of Ru^{II*} in the films is intrinsic, independent of film thickness and the nature of the underlying electrode material. Photophysical properties are essentially the same for poly[Ru(vbpy)$_3$](PF$_6$)$_2$ on ITO or with a poly[Zn-(vbpy)$_3$](PF$_6$)$_2$ inner layer, showing that electrode quenching does not contribute to the decreases in lifetime to any appreciable degree. Given the high concentration of chromophores in the electropolymerized films (~1.6 M),[3a] self-quenching by triplet−triplet excited state annihalation may play a role.[14] However, the independence of $\langle\tau\rangle$ over a range of relatively low laser powers shows that, although such effects may exist, they do not play a significant role in further shortenening the already diminished lifetimes, at least under our experimental conditions.[15] Oxidative or reductive quenching of $\mathrm{Ru^{II}}$* by neighboring ground state $\mathrm{Ru^{II}}$ is thermodynamically unfavorable and not expected to play a role. A referee suggested the possibility of charge-trapped $\mathrm{Ru^{III}}$ acting as quencher, but the films are prepared under strongly reducing conditions, and $\mathrm{Ru^{III}}$ quenching would not cause the observed time-dependent emission shifts. It is clear from the emission properties of the ~7:3 mixed $\mathrm{Ru^{II}}$ and $\mathrm{Os^{II}}$ film that at least local energy transfer in the film can be facile, although in this case it is favored by ~0.4 eV (eq 3).

$$\mathrm{Ru^{II}, Os^{II} \rightarrow Ru^{II}*, Os^{II} \rightarrow Ru^{II}, Os^{II}*} \qquad (3)$$

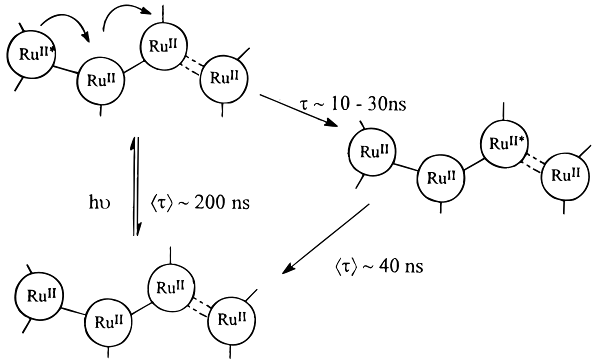
Evidence concerning the microscopic origin of the film quenching effect comes from the observation of the time-dependent, red-shifted emission (Figure 2) and the increase in $\langle\tau\rangle$ and E_{em} as $\mathrm{Ru^{II}}$ is diluted with $\mathrm{Zn^{II}}$ (Table 1 and Figure 3). In the most dilute ITO|copoly-χ[Ru(vbpy)$_3$](PF$_6$)$_2$,(1 − χ)[Zn(vbpy)$_3$](PF$_6$)$_2$ film with $\chi_{\mathrm{Ru^{II}}} = 0.1$, $\langle\tau\rangle = 197$ ns, and $\lambda_{\max}^{\mathrm{em}} =$ 635 nm. As $\chi_{\mathrm{Ru^{II}}}$ increases, there is a steady decrease in $\langle\tau\rangle$, E_{em}, and $\Phi_{\mathrm{rel}}^{\mathrm{em}}$ up to $\chi_{\mathrm{Ru^{II}}} = 0.7$. At $\chi_{\mathrm{Ru^{II}}} > 0.7$, E_{em} and $\langle\tau\rangle$ still decrease with $\chi_{\mathrm{Ru^{II}}}$, but the effect is less dramatic.

Any interpretation of the lifetime data must take into account both the time dependence of the emission and its shift to lower energy. In this context, the increase in $\lambda_{\max}^{\mathrm{em}}$ from 690 to 635 nm ($\Delta\bar{\nu}_{\max} = 1255$ cm^{-1}) as $\mathrm{Ru^{II}}$ is diluted with $\mathrm{Zn^{II}}$ is significant. This is not a simple medium effect. [Zn(bpy)$_3$]$^{2+}$ and [Ru(bpy)$_3$]$^{2+}$ are isomorphous structurally. [Zn(bpy)$_3$](ClO$_4$)$_2$ has been used as an inert crystalline host for excited state studies on ruthenium polypyridyl complexes.[16] The average immediate environment near $\mathrm{Ru^{II}}$ is expected to remain nearly the same as $\mathrm{Ru^{II}}$ is replaced with $\mathrm{Zn^{II}}$ in the polymer films.

Similar concentration effects have been noted for [Ru(bpy)$_3$]$^{2+}$ in micelles, clays, and other heterogeneous media.[11b,i,g,17] Red-shifted emissions were observed with increasing concentrations of [Ru(bpy)$_3$]$^{2+}$ and variously interpreted as arising from steric, electrochemical, or covalent modifications induced by the matrix. For high concentrations of [Ru(bpy)$_3$]$^{2+}$ incorporated in layered zirconium phosphate, host interactions and interactions with neighboring complexes were invoked to explain red-shifted absorption and emission maxima and decreased excited state lifetimes.[11b] Dramatically red-shifted MLCT absorption bands (~40 nm) have been noted at high loading levels of [Ru(bpy)$_3$]$^{2+}$ in zeolite Y cages.[10b,18] Dutta and coworkers[10b] also observed decreased average excited state lifetimes and emission quantum yields in zeolites although in this case no shift in emission energy was observed as a function of concentration. One possibility suggested was that interactions between the bipyridine ligands of neighbors caused enhanced excited state deactivation of [Ru(bpy)$_3$]$^{2+*}$ by ground state [Ru(bpy)$_3$]$^{2+}$.

One explanation for the time-dependent, red-shifted emission in poly[Ru(vbpy)$_3$](PF$_6$)$_2$ is that it arises from two distinct emitting sites that are kinetically coupled by energy transfer. One site emits at high energy (650 nm) and one at low energy (710 nm) consistent with the time-resolved emission spectra in Figure 2. In this interpretation energy transfer occurs from the higher to the lower. (Given the expected inhomogeneities in local film structure, each emitting site probably consists of a distribution of sites having slightly different emission energies and lifetimes.)

SCHEME 1



The higher energy emitters are the majority sites. The minority “trap sites” emit at lower energy and are shorter-lived. Energy transfer from high- to low-energy emitters occurs on a time scale comparable to but shorter than the lifetime(s) of the majority emitters. This explains the time dependence of the emission spectrum as a consequence of energy transfer and conversion of the high-energy emitter to the low-energy emitter. Based on $\langle\tau\rangle \sim 200$ ns for $\mathrm{Ru^{II}}$* highly diluted in poly[Zn(vbpy)$_3$](PF$_6$)$_2$ ($\chi_{\mathrm{Ru^{II}}} = 0.1$), $\langle\tau\rangle \sim 200$ ns for the majority emitter. From the variation of the emission maximum with time at room temperature (Figure 2), energy transfer occurs on a time scale of 10−30 ns. The lifetime of the low-energy emitter is $\langle\tau\rangle \sim 40$ ns (Table 2).

The proposed kinetic model is illustrated in Scheme 1. In this model it is necessary to invoke rapid $\mathrm{Ru^{II}* \rightarrow Ru^{II}}$ energy transfer through the film to the low-energy, minority trap sites by energy transfer self-exchange. (Under the conditions used in the lifetime experiments there is no evidence for multiphoton effects.) This conclusion is consistent with the observation of rapid ($\tau < 15$ ns) $\mathrm{Ru^{II}* \rightarrow Os^{II}}$ energy transfer in the copolymerized $\mathrm{Ru^{II}}$ and $\mathrm{Os^{II}}$ films, although energy transfer in this case is favorable by ~0.4 eV (eq 3).

There is independent spectroscopic evidence concerning the trap sites. MLCT absorptions are broadened on the low-energy side in poly[Ru(vbpy)$_3$](PF$_6$)$_2$ films. This provides evidence for ground state electronic interactions (indicated by the double broken lines in Scheme 1) perhaps in regions of the film where adjacent sites are tightly packed.

These sites also appear to be the red emitters. This is shown by the enhanced red emission with low-energy MLCT excitation in Figure 1. From the time-resolved emission in Figure 2, emission energies for the high- and low-energy emitters are at ~15 400 and ~14 100 cm^{-1}. If this difference arises largely from $\mathrm{Ru^{II}}$* interactions with $\mathrm{Ru^{II}}$ in the trap sites, the magnitude of this interaction is significant (~1300 cm^{-1}).

An orbital basis for electronic coupling exists by π,π^*(bpy) mixing between adjacent sites. This could be induced by interpenetration of the polypyridyl ring systems in regions where there is tight packing. There is structural and spectroscopic evidence for such effects in other systems.[10b] $\pi-\pi^*$ coupling and partial electron donation from the $d\pi^5\pi^{*1}$ excited state to the $d\pi^6$ ground state may contribute to this excited state−ground state interaction.

Based on the model in Scheme 1, the dilution effects contribute to both $\langle\tau\rangle$ and E_{em}. Dilution of $\mathrm{Ru^{II}}$ by $\mathrm{Zn^{II}}$ reduces the number of interacting $\mathrm{Ru^{II}}$- - -$\mathrm{Ru^{II}}$ pairs and lowers the number of trap sites. Dilution also breaks the energy transfer chains for intrafilm energy transfer by $Ru^{II}* \rightarrow Ru^{II}$ exchange (Scheme 1).

Other interpretations of these data are possible. The time-dependent, red-shifted emisions may reflect the dynamic formation of trap sites arising from excited state−ground state interactions between neighboring molecules as governed by polymer motions. Such effects are observed in thin films of organic polymers and interpreted as evidence for excimer formation brought about by segmental motion of polymer chains once an excited state is formed.[19] This type of response is expected to be strongly temperature dependent and unlikely for the Ru^{II} films studied here. There is evidence for ground state electronic interactions in the absorption spectra; *i.e., the trap sites are performed*. Further, the emission energy maximum is the same at both 100 and 298 K. Polymer motions are expected to be frozen at 100 K, and emission would occur at higher energy from an unrelaxed excited state frozen in the local orientational polarization of the ground state.

The trap sites could have a different origin. They might be introduced as an impurity in the Ru^{II} sample or be produced during the formation of the films by electropolymerization. The energies of Ru^{II}(polypyridyl) MLCT excited states are known to vary systematically as the energies of the π^*(polypyridyl) acceptor level and the ancillary ligands are varied.[7,20] A possibility is that the low-energy sites contain an unreacted vinyl group. This is feasible, but the magnitude of the shift between the high- and low-energy emitters in the film (1300 cm^{-1}) is considerably greater than that between $[Ru(dmb)_3]^{2+}$ (λ_{max}^{em} = 642 nm) and $[Ru(dmb)_2(vbpy)]^{2+}$ (λ_{max}^{em} = 670 nm) in deaerated CH_3CN (650 cm^{-1}).[7] They are models for fully and partially polymerized film sites.

The decreased average lifetimes for the trap sites is expected based on the energy gap law for nonradiative decay.[20−22] Since the film-based emission is weak, $k_{nr} \gg k_r$ and $k_{nr} \sim \tau^{-1}$, where k_r and k_{nr} are the radiative and nonradiative decay rate constants. k_{nr} is predicted to vary with the energy gap, E_0, as

$$\tau^{-1} \sim k_{nr} \propto \exp[-(\gamma E_0/\hbar\omega)] \quad (4)$$

$$\gamma = (\ln E_0/S\hbar\omega) - 1 \quad (5)$$

This relationship incorporates mode averaging with $\hbar\omega$ the quantum spacing for an average ν(bpy) mode that acts as the dominant energy acceptor. (This is an average of a series of ν(vbpy) modes from 1000 to 1600 cm^{-1}.) The quantity S is the electron-vibrational coupling constant. It is related to the square of the difference in equilibrium displacement between the excited and ground states.

For the most dilute copolymeric Ru^{II} and Zn^{II} film ($\chi_{Ru^{II}}$ = 0.1) quenching effects are minimized, and $\langle\tau\rangle$ = 197 ns with $E_0 \sim E_{em}$ = 15 800 cm^{-1}. At $\chi_{Ru^{II}}$ = 1.0, E_{em} = 14 500 cm^{-1}. By assuming that the term $\gamma/\hbar\omega$ stays relatively constant as the Ru^{II}/Zn^{II} ratio is varied and with E_0 = 14 500 cm^{-1}, it is possible to estimate an average lifetime for films with $\chi_{Ru^{II}}$ = 1.0. by using eq 4. This gives $\langle\tau\rangle$ = 51 ns, which is near the experimental value of $\langle\tau\rangle \sim 40$ ns. *This is important since it demonstrates that, at least qualitatively, the decrease in lifetime in the films concentrated in Ru^{II} can be accounted for as largely an energy gap effect*. The decrease in energy gap is caused by the presence of preformed trap sites which are stabilized by excited state−ground state electronic interactions.

A number of points remain to be resolved in accounting for the photophysical properties of these films. One is further elucidation of the trap sites and the possible role of the electropolymerization conditions on their occurrence. Another is to establish in greater detail the transport properties of the films. Our initial observations prove the existence of facile intrafilm energy transfer which continues even at 100 K. The possibility exists for long-range energy transfer in these films. Another point is the use of the simple biexponential model to describe excited state decay. This treatment allows qualitative comparisons between different polymer films but offers limited physical insight. Other, more explicit models, such as those described by Fayer and co-workers to account for excited state transport and trapping in concentrated dye solutions and polymers may be more profitably exploited to explain the time-dependent phenomena that we observe.[23]

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(9) Emission efficiencies were measured relative to poly$[Ru(bpy)_3](PF_6)_2$ and calculated by $\Phi_{rel}^{em} = \Phi^{em}/\Phi_{Ru^{II}}^{em} = (I_i/I_{Ru^{II}})(A_{Ru^{II}}/A_i)$. In this equation Φ_{rel}^{em} is the relative emission intensity of the unknown film of integrated emission intensity (I_i) and absorbance (A_i) compared to poly$[Ru(bpy)_3](PF_6)_2$ ($\Phi_{Ru^{II}}^{em}$), with an integrated intensity $I_{Ru^{II}}$ and absorbance $A_{Ru^{II}}$. The relative intensities were normalized such that $\Phi_{Ru^{II}}^{em} = 1$.

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$$^3Ru(bpy)_3{}^{2+}* + {}^3Ru(bpy)_3{}^{2+}* \rightarrow Ru(bpy)_3{}^{+} + Ru(bpy)_3{}^{3+}, \quad \Delta G^\circ \sim -1.6\ \text{eV}$$

or energy transfer to give a singlet excited state which rapidly crosses to the triplet[14b]

$$^3Ru(bpy)_3{}^{2+}* + {}^3Ru(bpy)_3{}^{2+}* \rightarrow {}^1Ru(bpy)_3{}^{2+}* + Ru(bpy)_3{}^{2+}, \quad \Delta G^\circ \sim -1.5\ \text{eV}$$

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