

Contrasting Intrastrand Photoinduced Processes in Macromolecules Containing Pendant $-\text{Re}(\text{CO})_3(1,10\text{-phenanthroline})^+$: Electron versus Energy Transfer

M. R. Feliz[†] and G. Ferraudi^{*‡}

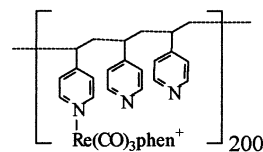
INIFTA-CICBA, Universidad Nacional de La Plata, 1900 La Plata, Argentina, and Radiation Laboratory, Notre Dame, Indiana 46556-0579

Received January 13, 2003

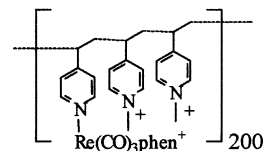
The photochemical and photophysical properties of the polymers $\{(\text{vpy}-\text{CH}_3^+)_2\text{-vpyRe}(\text{CO})_3(\text{phen})^+\}_{200}$ (vpy = vinyl pyridine, phen = 1,10-phenanthroline) have been investigated in solution phase and compared to those of a related polymer, $\{(\text{vpy})_2\text{-vpyRe}(\text{CO})_3(\text{phen})^+\}_{200}$, and monomer, $\text{pyRe}(\text{CO})_3(\text{phen})^+$. Irradiations at 350 nm induce intrastrand charge separation in the peralkylated polymer, a process that stands in contrast with the energy migration observed with $\{(\text{vpy})_2\text{-vpyRe}(\text{CO})_3(\text{phen})^+\}_{200}$. Electronically excited $-\text{vpyRe}(\text{CO})_3(\text{phen})^+$ chromophores and charge-separated intermediates react with neutral species, e.g., 2,2',2''-nitrilotriethanol, and anionic electron donors, e.g., SO_3^{2-} and I^- . The anionic electron donors react more efficiently with the metal-to-ligand charge transfer excited state of these polyelectrolytes than with the excited state of $\text{pyRe}(\text{CO})_3(\text{phen})^+$.

Introduction

Numerous studies have been concerned with thermal and photochemical reactions of inorganic polymers in solid and solution phases. Some interest in their photochemical and photophysical properties is driven by their potential applications to catalysis and optical devices.¹ Previous work has shown marked differences between the photochemical and photophysical properties of the monomer $\text{pyRe}(\text{CO})_3(1,10\text{-phenanthroline})^+$ and a related polymer, **A**, with nearly 200 pendant chromophores $-\text{Re}(\text{CO})_3(1,10\text{-phenanthroline})^+$ bonded to (vinylpyridine)₆₀₀.^{1a,2}



(A) : $\{[(\text{vpy})_2\text{-vpyRe}(\text{CO})_3\text{phen}]^+\}_{200}$



(B) : $\{[(\text{vpy}-\text{CH}_3^+)_2\text{-vpyRe}(\text{CO})_3\text{phen}]^+\}_{200}$

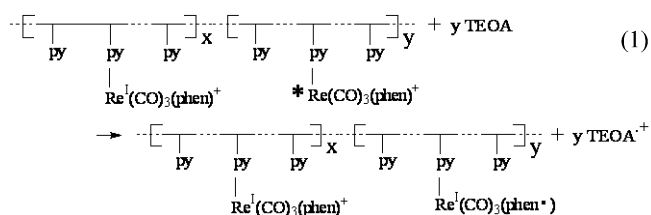
* To whom correspondence should be addressed. E-mail: ferraudi.1@nd.edu.

[†] INIFTA-CICBA.

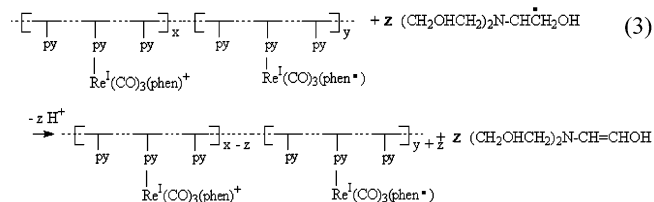
[‡] Radiation Laboratory.

- (1) (a) Wolcan, E.; Ferraudi, G. *J. Phys. Chem. A* **2000**, *104*, 9281. (b) Jones, W. E., Jr.; Hermans, L.; Jiang, B. In *Multimetallic and Macromolecular Inorganic Photochemistry*; Ramamurthy, V., Schanze, K. S., Eds.; Marcel Dekker Inc.: New York, 1999; Chapter 1, Vol. 4. (c) Ogawa, M. Y. In *Multimetallic and Macromolecular Inorganic Photochemistry*; Ramamurthy, V., Schanze, K. S., Eds.; Marcel Dekker Inc.: New York, 1999; Chapter 3, Vol. 4. (d) Worl, L. A.; Jones, W. E., Jr.; Strouse, G. F.; Younathan, J. D.; Danielson, E.; Maxwell, K. A.; Sykora, M.; Meyer, T. J. *Inorg. Chem.* **1999**, *38*, 2705. (e) Petersen, J. D. In *Supramolecular Photochemistry*; Balzani, V., Ed.; Reidel: Dordrecht, 1987; p 135. (f) Balzani, V.; Scandola, F. In *Supramolecular Photochemistry*; Ellis Harwood: Chichester, England, 1991; p 355. (g) Kaneko, M.; Tsuchida, E. *J. Polym. Sci.* **1981**, *16*, 397.
- (2) Abbreviations: vpy \equiv vinylpyridine, phen \equiv 1,10-phenanthroline, triflate \equiv CF_3SO_3^- , 2,2',2''-nitrilotriethanol \equiv TEOA, 2,2',2''-nitrilotriethane \equiv TEA.

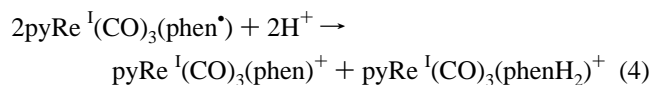
Annihilation processes and secondary photolysis of $\text{Re}(\text{I})$ to phen charge transfer excited states, $\text{MLCT}_{\text{Re} \rightarrow \text{phen}}$, in the polymer are more efficient than in the monomer. The reductive quenching of the $\{(\text{vpy})_2\text{-vpyRe}(\text{CO})_3(\text{phen})^+\}_{200}$ excited states by 2,2',2''-nitrilotriethanol, TEOA, is represented in eq 1 where the MLCT excited state is identified as $-\text{Re}(\text{CO})_3(\text{phen})^+$.



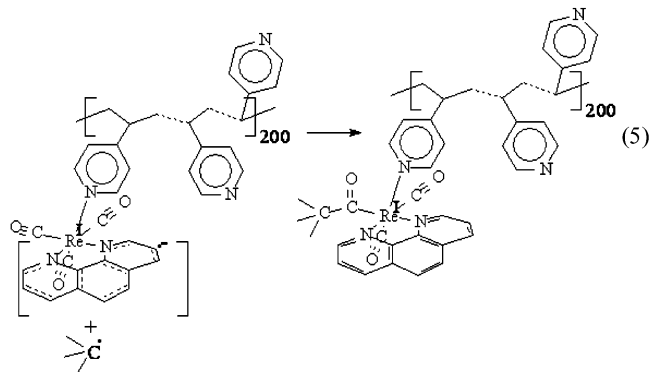
Radicals $(\text{CH}_2\text{OHCH}_2)_2\text{N}-\dot{\text{C}}\text{H}\cdot\text{CH}_2\text{OH}$, formed when TEOA is oxidized by the primarily generated $\text{TEOA}^{\bullet+}$ radicals in eq 2,³ reduce more $-\text{Re}(\text{CO})_3(\text{phen})^+$ chromophores in a polymer strand, eq 3.



By contrast to the polymer, the disproportionation of the monomeric Re(I) ligand-radical to form $\text{pyRe}(\text{CO})_3(\text{phenH}_2)^+$, eq 4, occurs with a rate comparable to those recorded for other Re(I) ligand-radical species.^{4–6}



Equations 1–3 were investigated with low conversions of the chromophores to $-\text{Re}(\text{CO})_3(\text{phen}^{\bullet})$ and bear some resemblance to those observed with other inorganic polymers in a solid or solution phase.^{7,8} By contrast to eqs 1–4, blue polymers containing alkyl–Re(I) chromophores were obtained with either high laser powers or relatively long steady state irradiations.⁹ It has been proposed that the product is formed by a reaction of the radicals with an activated carbonyl ligand, eq 5.



The striking differences between the photochemistries of $-\text{Re}(\text{CO})_3(\text{phen})^+$ in a monomer or pendants in a polymer

can be attributed to the high concentration of excited state created in the small volume of a macromolecule's strand. However, the excited state properties of a given chromophore are also dictated by the environment in which the excited state is created. Groups adjacent to the chromophore in the polymer backbone can be used to produce particular environs for the excited state. For example, the different environs that MLCT excited states will find in **A** and **B** may provide the means to control the rate of excited state reactions. In these regards, photoinduced intrastrand electron transfer processes in the peralkylated derivative **B** and its photoreactions have been investigated in this work and compared with the intrastrand energy transfer previously detected in the photophysics of the related polymer **A**.

Experimental Section

Flash-Photochemical Procedures. Optical density changes occurring in a time scale longer than 10 ns were investigated with a flash photolysis apparatus, FP, described elsewhere.^{4–6,8} In these experiments, 10 ns flashes of 351 nm light were generated with a Lambda Physik SLL-200 excimer laser or 1 ns flashes of 355 nm light were generated with a Continuum Powerlite Nd:YAG laser. The energy of the laser flash was attenuated to values equal to or less than 20 mJ/pulse by absorbing some of the laser light in solutions of $\text{Ni}(\text{ClO}_4)_2$ having the desired optical transmittance, $T = I/I_0$ where I_0 and I_t are respectively the intensities of the light arriving to and transmitted from the photolysis cell. The transmittance, $T = 10^{-\text{OD}}$, was routinely calculated by using the spectrophotometrically measured optical density, OD, of the solution. A right angle configuration was used for the pump and the probe beams. Concentrations of the complexes were adjusted to provide homogeneous concentrations of photogenerated intermediates over the optical path, $l = 1$ cm, of the probe beam. To satisfy this optical condition, solutions were made with an OD equal to or less than 0.4 over the 0.2 cm optical path of the pump. Time-resolved fluorescence experiments were carried out with a PTI flash fluorescence instrument.⁶ The excitation light was provided by a N_2 laser ($\lambda_{\text{em}} = 337$ nm, ca. 2 mJ/pulse) or by irradiation at 337 nm of suitable exciton dyes ($\lambda_{\text{em}} = 350$ or 457 nm with a 0.2 ns pulse width and ca. 0.2 mJ/pulse). Concentrations of the complexes were adjusted to optical densities equal to or less than 0.01 for a 1 cm optical path at 350 nm. All the solutions used in the photochemical work were deaerated with streams of ultrahigh-purity N_2 before and during the irradiations.

Steady-State Irradiations. The luminescence of the Re(I) complexes was investigated in an SLM-Aminco-8100 interfaced to a Dell 333P microcomputer.⁶ The spectra were corrected for differences in instrumental response and light scattering. Solutions were deaerated with O_2 -free nitrogen in a gastight apparatus before recording the spectra.

Materials. The materials $[\text{pyRe}(\text{CO})_3(\text{phen})]\text{triflate}$, $\{[(\text{vpy})_2\text{-vpyRe}(\text{CO})_3(\text{phen})]\text{triflate}\}_{200}$ (**A**), and $\{[(\text{vpy}-\text{CH}_3^+)\text{-vpyRe}(\text{CO})_3(\text{phen})]\text{I}\}_{200}$ (**B**) were available from a previous work.^{1,8}

Solvents were spectroquality grade and used without further purifications.

Results

Solution Chemistry. The UV–vis spectrum of **A** and **B** in CH_3CN exhibited noticeable differences in the 400–500

(3) Kirch, M.; Lehn, J. M.; Sauvage, J. P. *Helv. Chim. Acta* **1979**, *62*, 1345.

(4) Feliz, M.; Ferraudi, G. *J. Phys. Chem.* **1992**, *96*, 3059.

(5) Feliz, M.; Ferraudi, G.; Altmiller, H. *J. Phys. Chem.* **1992**, *96*, 257.

(6) Guerrero, J.; Piro, O. E.; Wolcan, E.; Feliz, M. R.; Ferraudi, G.; Moya, S. A. *Organometallics* **2001**, *20*, 2842.

(7) Worl, L. A.; Jones, W. E., Jr.; Strouse, G. F.; Younathan, J. D.; Danielson, E.; Maxwell, K. A.; Sykora, M.; Meyer, T. J. *Inorg. Chem.* **1999**, *38*, 2705.

(8) Baxter, S. M.; Jones, W. E., Jr.; Danielson, E.; Worl, L.; Strouse, G.; Younathan, J.; Meyer, T. J. *Coord. Chem. Rev.* **1991**, *111*, 47 and references therein.

(9) Wolcan, E.; Ferraudi, G. J.; Feliz, M. R.; Gomez, R. V.; Mickelsons, L. *Supramol. Chem.* **2003**, *15*, 143.

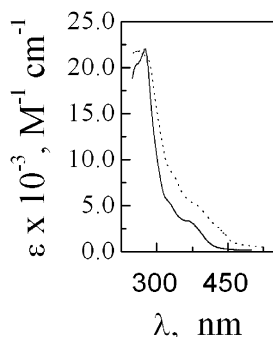


Figure 1. UV-vis spectra of **A** (—) and **B** (---) in CH_3CN . The extinction coefficients were calculated as $\text{OD}/[-\text{Re}(\text{CO})_3(\text{phen})^+]$, where $[-\text{Re}(\text{CO})_3(\text{phen})^+]$ is the concentration of $\text{Re}(\text{I})$ chromophore in the solutions of **A** or **B**.

nm region, i.e., in a region where the absorption bands due to the Re to phen charge transfer optical transitions are positioned, Figure 1. In order to make the spectrum of **A** comparable with the spectrum of **B** in the region of the $\text{Re}(\text{I})$ to phen charge transfer transitions, the extinction coefficients in Figure 1 were calculated on the basis of the concentration of $-\text{Re}(\text{CO})_3(\text{phen})^+$ chromophores. On the basis of this normalization, the charge transfer absorption band of **B** appears 30–50 nm red-shifted with respect to the similar absorption band in the spectrum of **A**. Differences were also observed between the emission spectra of **A** and **B** when deaerated solutions in CH_3CN of either polymer ($\approx 4 \times 10^{-5}$ M in $\text{Re}(\text{I})$ chromophore) were steady state irradiated at 350 nm. Since charge transfer transitions are sensitive to the environment, the distinct environments around the $-\text{Re}(\text{CO})_3(\text{phen})^+$ chromophores, respectively created by the pendants py and py- CH_3^+ in **A** and **B**, must be the cause of the differences in the absorption spectrum. In accordance with this proposition, the observed differences in the emission spectra suggest that distinctive environments of the electronically excited $\text{Re}(\text{I})$ chromophores in **A** and **B** affect the decay of the emissive excited state.

Time-Resolved Spectroscopy. To investigate the time-resolved emission of **B**, 7.2×10^{-7} M deaerated solutions of the polymer ($\approx 1.4 \times 10^{-4}$ M in $\text{Re}(\text{I})$ chromophore) in CH_3CN were flash irradiated at 350 nm. The oscillographic traces collected in experiments where the emission was monitored over a wide range of wavelengths, $550 \leq \lambda_{\text{ob}} \leq 610$ nm, were fitted to a biexponential decay, $A_1 \exp -t/\tau + A_2 \exp -t/\tau'$. The lifetimes calculated for the decay of the emission at $\lambda_{\text{ob}} = 580$ nm were $\tau = 50 \pm 3$ ns and $\tau' = 1.45 \pm 0.08$ μs , and the relation of the preexponential factors was $A_1/A_2 = 0.5$, Figure 2. A minor dependence of τ' on λ_{ob} was also observed but was more pronounced in the decay of the transient absorption spectrum described below. In addition, the biexponential decay of the luminescence of **B** contrasts with the single exponential decay of the electronically excited chromophores in **A** ($\tau = 0.86 \pm 0.05$ μs) and in the monomer $\text{pyRe}(\text{CO})_3(\text{phen})^+$ ($\tau = 2.17 \pm 0.01$ μs).¹

Three well differentiated steps were observed in the decay of the transient absorption spectrum recorded 10 ns after a deaerated solution containing 7.2×10^{-7} M of **B** ($\approx 1.4 \times 10^{-4}$ M in $\text{Re}(\text{I})$ chromophore) in CH_3CN was flash irradiated

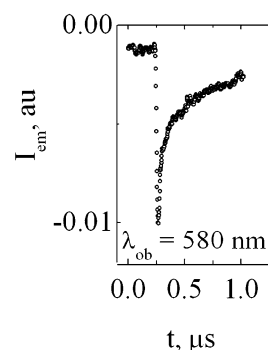


Figure 2. A typical trace for the decay of the 580 nm luminescence recorded when a deaerated solution of **B** ($\approx 1.4 \times 10^{-4}$ M in $\text{Re}(\text{I})$ chromophore) in CH_3CN was flash irradiated at 350 nm.

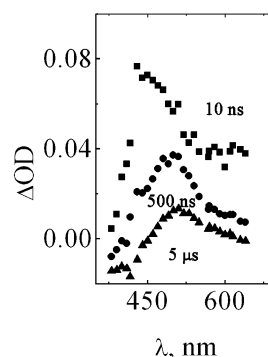


Figure 3. Transient spectra recorded in the 350 nm flash irradiation of deaerated solutions 7.2×10^{-7} M in **B** ($\approx 1.4 \times 10^{-4}$ M in $\text{Re}(\text{I})$ chromophore) in CH_3CN . The delays from the laser irradiation are indicated in the figure.

at 350 nm, Figure 3. A broad absorption band with a maximum at 450 nm was observed in the transient spectrum recorded with delays (from the 10 ns flash irradiation) equal to or less than 2 μs . The transient absorption spectrum underwent a partial biexponential decay with a lifetime, $\tau = 48 \pm 2$ ns, independent of the monitoring wavelength and τ' increasing from 1.12 ± 0.06 μs ($\lambda_{\text{ob}} = 410$ nm) to 2.08 ± 0.06 ($\lambda_{\text{ob}} = 600$ nm). An average value, $\langle \tau' \rangle = 1.7 \pm 0.3$ μs , was calculated from the values collected between 410 and 600 nm. The lifetimes of the transients are nearly the same calculated for the time-resolved luminescence and must be related to the decay of excited states. Therefore, the lifetimes from the transient absorption spectra were assigned to the decay of the IL and the $\text{MLCT}_{\text{Re-phen}}$ excited states, as was in the case of some monomeric $\text{Re}(\text{I})$ complexes.^{1,6} By contrast to the photo behavior of the monomeric $\text{Re}(\text{I})$ complexes, an additional transient was observed after the decay of the excited states of **B**. The long-lived transient, poly-(LL), fulfills the spectroscopic and kinetic conditions of a displacement of charge through the strand of polymer, i.e., one that occurs during the decay of the MLCT and induces the creation of a $\text{Re}(\text{II})$ center at a distance from the $\text{phen}^{\bullet-}$ ligand radical. The absorption spectra recorded with delays longer than 2 μs showed a maximum at 500 nm, i.e., where a $\text{phen}^{\bullet-}$ ligand radical coordinated to $\text{Re}(\text{I})$ instead of $\text{Re}(\text{II})$ has its absorption maximum.^{1,6} The kinetics of the optical density change, investigated between 370 and 520 nm, showed that the formation of the radical and the

decay of the MLCT excited states are simultaneous processes. Indeed, the shift of the absorption maximum from 450 to 500 nm and the decay of the MLCT_{Re→phen} excited state, followed at 410 nm, have nearly the same lifetimes, $\approx 1.55 \pm 0.07 \mu\text{s}$. The disappearance of the poly-(LL) transient spectrum, ascribed mainly to the phen^{•-} ligand radical, was followed by means of the optical density change, ΔOD , at 500 nm. It was fitted to a single exponential, $\Delta\text{OD} = \Delta\text{OD}_0 \exp -t/\tau''$, with a lifetime $\tau'' = 8.0 \mu\text{s}$. In agreement with the a separation of charge in the MLCT first and in a charge-separated intermediate later, the flash irradiation induced a prompt bleach of the optical density at $\lambda_{\text{ob}} = 380 \text{ nm}$, i.e., the region of the Re(I) to phen charge-transfer absorption band in **B**. The single exponential fitted to the recovery of 370 nm optical density has a lifetime, $\tau \approx 7.7 \pm 0.7 \mu\text{s}$, very close to the value reported above for the decay of the poly-(LL) intermediate with $\lambda_{\text{max}} = 500 \text{ nm}$. In flash luminescence experiments carried out under similar experimental conditions, no luminescence between 300 and 600 nm could be observed in the time scale corresponding to the final decay of the transient spectrum. The absence of a long-lived luminescence with an $\sim 8.0 \mu\text{s}$ lifetime confirms that the transient spectrum must be assigned to a reaction intermediate instead of an excited state. Since the spectral changes in the longest time scale are in accordance with those of a species containing separated Re(II) and phen^{•-} radical moieties, it is possible to account for the decay kinetics by considering that the separated Re(II) and phen^{•-} moieties undergo charge annihilation processes within the strand of polymer.

It was demonstrated that the formation of poly-(LL) was not related to a redox reaction of the excited states with the solvent by using solutions containing $7.2 \times 10^{-7} \text{ M}$ of **B** ($\approx 1.4 \times 10^{-4} \text{ M}$ in Re(I) chromophore) in a 50% (v/v) CH₃-OH/CH₃CN mixed solvent. Time-resolved spectral changes similar to those seen when the solvent was CH₃CN, Figure 3, were observed when deaerated solutions in the mixed-solvent were flash photolyzed at 350 nm.

Quenching Reactions. The experiments communicated above revealed some distinct photochemical properties of pyRe(CO)₃(phen)⁺ and the polyelectrolytes **A** and **B**. To investigate how the different environments of the chromophores, i.e., the presence of pyridinium versus pyridine groups, affected the reactivity of the MLCT_{Re→phen}, the excited state reactions were investigated with solutions of **A** and **B**, $\approx 1 \times 10^{-6} \text{ M}$ in polyelectrolyte, containing counterions more reactive than triflate. In order to have adequate solubilities of the polyelectrolytes and their counterions, the solutions for the photochemical work had to be prepared in a 50% (v/v) CH₃OH/CH₃CN mixed solvent. Solutions where the concentration of I⁻ or SO₃²⁻ was increased from 1.0×10^{-4} to $1.0 \times 10^{-2} \text{ M}$ showed a progressive quenching of the -Re(CO)₃(phen)⁺ luminescence in **A** or **B**. By contrast, very little quenching of the pyRe(CO)₃(phen)⁺ luminescence was observed with solutions containing concentrations of the chromophore and the counterions similar to those of **A** and **B**. In flash fluorescence experiments with **A** and **B**, the lifetimes for the decay of the

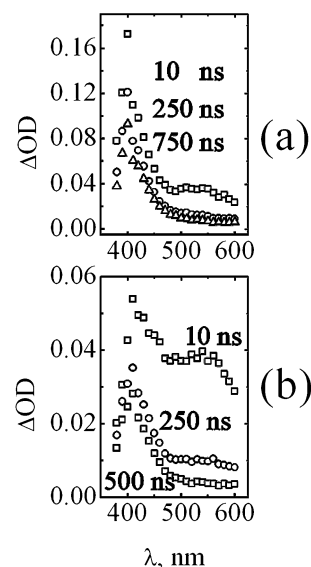


Figure 4. Transient spectra observed in the reaction of I⁻ ($1.2 \times 10^{-2} \text{ M}$ top and $1.3 \times 10^{-3} \text{ M}$ bottom) with electronically excited **B**. The transients were recorded in the 350 nm flash irradiation of $7.2 \times 10^{-7} \text{ M}$ (**B**) ($\approx 1.4 \times 10^{-4} \text{ M}$ in Re(I) chromophore) in deaerated CH₃CNCH₃OH (50% v/v). The delays from the laser irradiation are indicated by the side of the spectra.

luminescence decreased with I⁻ concentration. To find the reason for the quenching of the -Re(CO)₃(phen)⁺ luminescence, transient absorption spectra were recorded with various delays after the 350 nm flash irradiation of solutions having 1.2×10^{-2} or $1.3 \times 10^{-3} \text{ M}$ I⁻, Figure 4. While the prompt spectrum observed after the flash irradiation of the solution with $1.3 \times 10^{-3} \text{ M}$ I⁻ exhibited some of the features of the electronically excited chromophores, Figure 4b, the spectra recorded with longer delays or with a solution containing I⁻ in higher concentrations agreed with the literature spectrum of I₂⁻, Figure 4. Concentration of the I₂⁻ product per flash was calculated from the OD change at 400 nm, and the values of the **A** change were recorded on a time scale where the decay of I₂⁻ was insignificant, e.g., delays $1.0 \leq t \leq 10 \mu\text{s}$ after the flash irradiation. In accordance with a redox reaction of I⁻ with the electronically excited Re(I) pendant, concentrations of flash-generated I₂⁻ increased with I⁻ concentration, Figure 5. Oscillographic traces, $\lambda_{\text{ob}} = 400 \text{ nm}$, showing the decay of I₂⁻ were fitted to linear inverse plots, ΔOD^{-1} versus t , inset to Figure 5. It was concluded that the decay of I₂⁻ is kinetically second order under the experimental conditions used for these experiments. The rate constant, $2k = 8.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ at an ionic strength $I \approx 1 \text{ M}$ at the strand of polyelectrolyte, was calculated from the ratio of the rate constant to the extinction coefficient, $2k/\epsilon = 6.2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ at $\lambda_{\text{ob}} = 400 \text{ nm}$, and the literature value of the I₂⁻ extinction coefficient, $\epsilon = 1.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at such a wavelength.¹⁰ It is possible to associate the decay of I₂⁻ with the reoxidation of the phen^{•-} ligand-radicals that remain coordinated to Re(I) after the quenching of the MLCT_{Re→phen} excited state.

(10) Hugh, G. L. *Optical Spectra of Nonmetallic Inorganic Transient Species in Aqueous Solution*; nat. stand. ref. data ser.; NSRDS-NBS 69, 1981 and references therein.

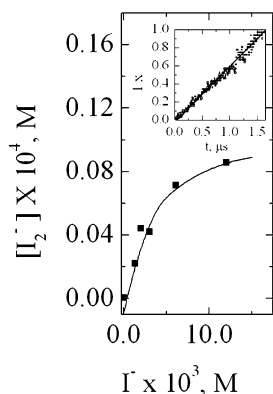


Figure 5. Concentrations of I_2^- from the reaction of I^- with electronically excited **B** are shown as a function of the I^- concentration. The 350 nm flash photolyzed solution also contained 7.2×10^{-7} M **B** ($\approx 1.4 \times 10^{-4}$ M in Re(I) chromophore) in deaerated CH_3CN/CH_3OH (50% v/v). The I_2^- concentrations were calculated from the ΔOD observed 250 ns after the laser irradiation at 400 nm. The inset shows an inverse plot of the optical density change at 400 nm for the back electron-transfer reaction of I_2^- .

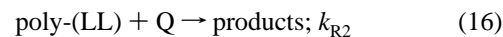
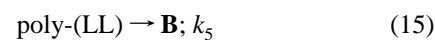
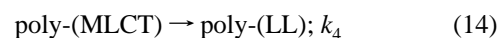
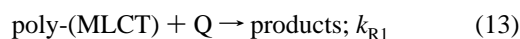
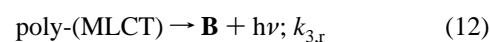
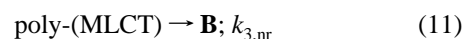
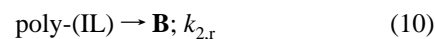
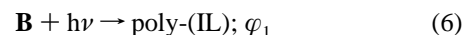
Other excited state reductants, i.e., 10^{-3} M SO_3^{2-} , 0.1 M TEOA, or 0.1 M TEA, react with the electronically excited chromophores. The transient absorption spectra, recorded when flash photolyzed solutions of **A** or **B** contained one of these quenchers, have the spectral features previously attributed to a Re(I)-coordinated phen $^{\bullet-}$ radical.^{1,6} Therefore, we concluded that a reductive quenching of the $MLCT_{Re-phen}$ excited state in **A** or **B** led to the spectroscopic changes. The concentrations of I^- and SO_3^{2-} in their redox reactions with the electronically excited Re(I) chromophores of **A** and **B** were ca. 2 orders of magnitude smaller than those required for the quenching of the electronically excited $pyRe(CO)_3(phen)^+$. A reason for this larger efficiency is a more favorable electrostatic interaction between the anionic quenchers and the cationic polyelectrolytes.

A complete kinetic study of the reactions of the excited polymer with oxidants was hindered by limitations that optical conditions and the solubilities of the reactants imposed in these experiments. However, the oxidation of poly-(LL) by tetracyanoethylene, TCE, was observed under a limited range of TCE concentrations. Solutions of the triflate salt of **B** containing 1×10^{-6} M in polyelectrolyte and 1.0×10^{-4} M to 1.0×10^{-3} M TCE were flash irradiated at 350 nm. The disappearance of poly-(LL) with a lifetime $\tau \approx 2 \mu s$ was observed at $\lambda_{ob} = 500$ nm.

Discussion

The experimental observations in this work and in recent literature reports show that Re(I) sensitizers imbedded in polymeric structures provide routes for new photoinduced reactions that could be more efficient than those available to the monomeric moieties.^{1a,6} Some of the routes appear to be controllable by the environs that surround the chromophore, e.g., the Re(I) chromophores in **A** and **B**. Since there are sharp differences between the photobehavior of **B** and the literature reported photobehavior of **A**,^{1a} the 350 nm photochemistry of **B** will be discussed first and the differences between the photobehavior of **A** and **B** will be rationalized at the end.

Photophysics of the Electronically Excited B. The results of time-resolved and steady state experiments can be properly modeled on the basis of eqs 6–16 which are an abbreviated form of those shown in the scheme.

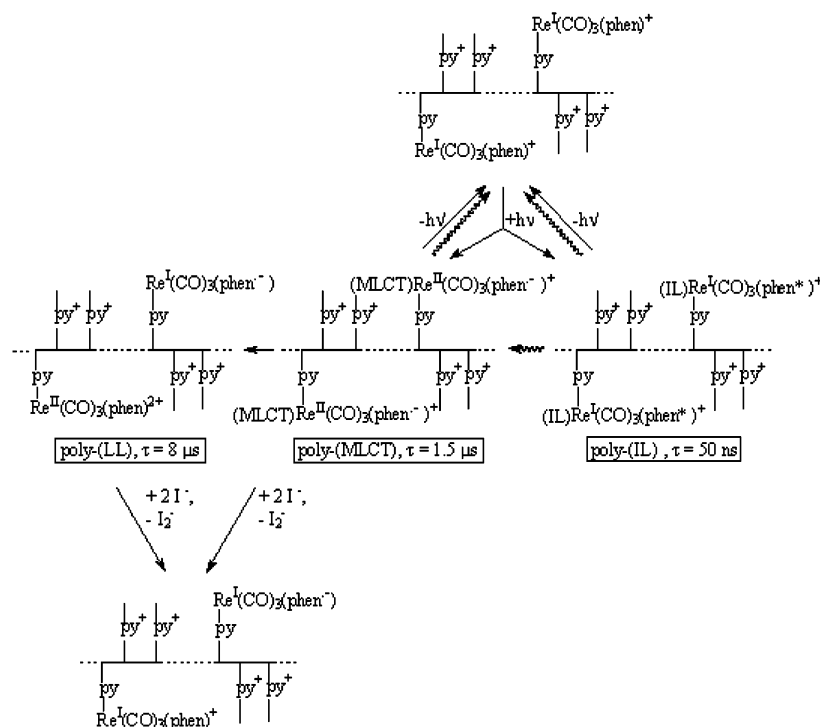


The species poly-(IL) and poly-(MLCT) represent strands of **B** populated with different excited states. They are generated with quantum yields φ_1 and φ_2 by the absorption of light, eqs 6 and 7, and decay via radiative, eqs 10 and 12, and radiationless, eqs 9 and 11, processes. On the basis of the experimental observations, the transformation of the poly-(MLCT) into the poly-(LL) intermediate has to be represented as a process that is kinetically first order in the excited chromophores. If pairs of excited chromophores are converted to poly-(LL) as radicals are converted to products in a geminate pair, the population of excited states in poly-(MLCT) must decay exponentially in time. It is also possible that MLCT excited states in the strand are placed in different environments and undergo bimolecular transformations to LL with different rates.¹¹ A convolution function describing the overall decay of the excited state concentration will approximately have the shape of an exponential. Although the dependence of the lifetime on λ_{ob} is consistent with an assortment of decay rates, the possibility of pairs of excited states decaying exponentially in time cannot be ruled out.

In addition, poly-(LL) and poly-(MLCT) undergo electron transfer reactions with a reactant Q, eqs 13 and 16. Integration of the rate equations derived for the mechanism in eqs 6–16 with $[\text{poly}-(IL)]_0$ and $[\text{poly}-(MLCT)]_0$ being the flash-generated concentrations of poly-(IL) and poly-(MLCT) gives the following relationships for the emission

(11) Experimental observations with polymers containing two different pendants, $-ReI(CO)_3(2, 2'-bipy)$ and $-ReI(CO)_3(phen)$, in a strand are also consistent with the existence of specific environments for the Re(I) chromophores. Wolcan, E.; Feliz, M. R.; Ferraudi, G. Work in progress.

Scheme 1



intensity, eq 17, and the quotient of pre-exponential factors, eq 18, when the quencher, Q, concentration is $[Q] = 0$.

$$I_{\text{em},T} = I_{\text{em},0} \left[\frac{\rho}{1+\rho} e^{-t/\tau} + \frac{1}{1+\rho} e^{-t/\tau'} \right] \quad (17)$$

$$\frac{A_1}{A_2} = \frac{\frac{k_{2r}}{k_{3r}} + \frac{k_1 \tau \tau'}{\tau - \tau'}}{[\mathbf{B}^{*'}]_0 - \frac{k_1 \tau \tau'}{\tau - \tau'}} = \rho, \quad \tau = (k_1 + k_{2,\text{nr}} + k_{2,r})^{-1}, \text{ and}$$

$$\tau' = (k_4 + k_{3,\text{nr}} + k_{3,r})^{-1} \quad (18)$$

Insertion of the experimental result $A_1/A_2 \approx 0.5$ in eqs 17 and 18 gives the expression for the emission intensity, eq 19.

$$I_{\text{em},T} = I_{\text{em},0} [0.33e^{-t/\tau} + 0.66e^{-t/\tau'}] \quad (19)$$

In accordance with eq 19, the lifetimes calculated from the time-resolved luminescence experiments must be $\tau = (k_1 + k_{2,\text{nr}} + k_{2,r})^{-1} \approx 50 \text{ ns}$ and $\tau' = (k_{3,\text{nr}} + k_{3,r} + k_4)^{-1} \approx 1.45 \mu\text{s}$. With exclusion of the formation of the LL intermediate, the photophysical processes of the IL and $\text{MLCT}_{\text{Re} \rightarrow \text{phen}}$ excited states in the scheme resemble those reported in the literature for **A**.^{1a,9} On the basis of the luminescence results, the IL and $\text{MLCT}_{\text{Re} \rightarrow \text{phen}}$ excited states are simultaneously generated with the absorption of 350 nm light. The short-lived decay of the luminescence, $\tau \approx 50 \text{ ns}$, is spectroscopically and kinetically consistent with the decay of an IL excited state placed above the $\text{MLCT}_{\text{Re} \rightarrow \text{phen}}$. Previous works have shown that IL excited states undergoes competitive decays to the lower lying $\text{MLCT}_{\text{Re} \rightarrow \text{phen}}$ and to the ground state.⁴⁻⁶ The subsequent process with a lifetime $\tau' \approx 1.45 \mu\text{s}$ is kinetically and spectroscopically consistent

with the relaxation of the $\text{MLCT}_{\text{Re} \rightarrow \text{phen}}$. Indeed, the 1.45 μs lifetime is nearly the same lifetime of the $\text{MLCT}_{\text{Re} \rightarrow \text{acceptor}}$ in a related monomeric complex.⁶ The subsequent process has a lifetime, $\tau'' = 8.0 \mu\text{s}$, and it is too slow to be ascribed to the room temperature radiationless relaxation of an excited state in a tricarbonyl Re(I) complex. A charge-separated species with a Re(II) chromophore and a reduced phen, i.e., a phen⁻ radical separated of the Re(II) metal center, provides a better rationale for the transient absorbing with a $\lambda_{\text{max}} \approx 500 \text{ nm}$ and a lifetime, $\tau'' = 8.0 \mu\text{s}$. Such a species, see Scheme 1, must be produced by a remote displacement of charge within the strand of polymer, i.e., a reaction that competes with the radiative and radiationless relaxations of the $\text{MLCT}_{\text{Re} \rightarrow \text{phen}}$.

Contrasting Photoprocesses of A and B. The most evident difference between the photophysics of **B** and **A** is that a remote charge transfer operates in the former while excited state annihilations processes, due to energy migration in the strand of polymer, are favored in the latter. It is expected that the different intrastrand processes are a consequence of the different environmental conditions respectively created around the $\text{MLCT}_{\text{Re} \rightarrow \text{phen}}$ by the pyridine and pyridinium pendants. Migration of energy in **A** can be expected to be a collisional process, i.e., a Dexter's exchange mechanism,¹² requiring that two Re(I) pendants come to a close proximity. Intrastrand encounters of this nature must be hindered in **B** because of electrostatic interactions between the cationic Re(I) and pyridinium pendants. However, pathways for a remote electron transfer could be available in **B**. The formation of LL through these paths can be fast enough to compete with the relaxation of the $\text{MLCT}_{\text{Re} \rightarrow \text{phen}}$ excited state. Absence of delayed luminescence with an 8.0

(12) Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 836.

μs lifetime shows that back-electron transfers in LL to restore the $\text{MLCT}_{\text{Re} \rightarrow \text{phen}}$ or generate other luminescent excited states are inefficient processes. Therefore, the lifetime of LL must be controlled by the radiationless decay to the ground state. Since the donor–acceptor distances for the charge migration in the decay of LL to the ground state or to the $\text{MLCT}_{\text{Re} \rightarrow \text{phen}}$ are nearly the same, it cannot be the reason for the difference between the reaction rate constants of these two processes.¹³

Quenching experiments indicate that Re(I) chromophores in **A** and **B** must be inside the positive electrostatic field of the strand. Indeed, the anionic reactants, I^- or SO_3^{2-} , are more efficient electron transfer quenchers of the $\text{MLCT}_{\text{Re} \rightarrow \text{phen}}$ luminescence in **A** and **B** than they are for the excited state of $\text{pyRe}(\text{CO})_3(\text{phen})^+$. Relative to the monomeric complex, the enhanced efficiency of the quenchers must be due to stronger electrostatic interactions between the reactants, with the anions possibly located in the double layer of the polyelectrolyte. When the electron transfer quenching was followed by means of the concentration of the I_2^- product, the charge-separated species with a longer lifetime, $\tau'' = 8 \mu\text{s}$, than the $\text{MLCT}_{\text{Re} \rightarrow \text{phen}}$ excited state, $\tau' = 1.5 \mu\text{s}$, appears

(13) Moser, C. C.; Keske, J. M.; Warncke, K.; Farid, R. S.; Dutton, P. L. *Nature* **1992**, 355, 79.

to be reduced by I^- , eq 23. Moreover, the mechanism, eqs 6–16, predicts that the I_2^- concentration will approach the limiting value $[\mathbf{B}^*]_0 + [\mathbf{B}^{*\prime}]_0$, i.e., the trend seen in Figure 5 for the dependence of the I_2^- concentration on I^- .

Conclusion

The different photoreactions of **A** and **B** suggest that a more diverse photobehavior should be attained when pyridine and or pyridinium pendants are replaced by ionic electron donor/acceptors. Diverse molecular architectures can be devised in order to induce photoreactions that are atypical in the photochemistry of the isolated pendants. Among the various photoinduced processes of these newer macromolecules, there are sequential multielectron processes of practical and theoretical interest.

Acknowledgment. G.F. acknowledges support from the Office of Basic Energy Sciences of the U.S. Department of Energy. This is contribution NDRL-4403 from the Notre Dame Radiation Laboratory. G.F. also wishes to acknowledge travel support from the NSF, Grant INT97-26738.

IC030012W