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Photochemical and Photophysical Properties of Fac-Re(I) Tricarbonyl Complexes: A Comparison of Monomer and Polymer Species with −Re^I(CO)$_3$Phen Chromophores

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The photochemical and photophysical properties of a polymer containing nearly 200 pendant groups Re-(CO)$_3$(1,10-phenanthroline)$^+$ bonded to poly-(vynilpyridine)$_{600}$ and the related monomer pyRe(CO)$_3$(1,10-phenanthroline)$^+$ were investigated in solution phase. The yield of formation and the kinetics of decay of the MLCT excited state were found to be dependent on medium and laser power. MLCT excited states in the polymer undergo a more efficient annihilation and/or secondary photolysis than in the monomer. In the polymer, redox quenching of MLCT excited states by methyl viologen and by 2,2′,2″-nitrilotriethanol revealed the presence of intrastrand electron-transfer processes. These processes exhibited a complex kinetics. Mechanisms of the excited-state annihilation and electron-transfer processes in the polymer are proposed.

Introduction

Numerous studies have been concerned with the thermal and photochemical reactions of inorganic polymers in solid- and solution phase. Some interest in their photochemical and photophysical properties is driven by their potential technical applications to catalysis and optical devices.[1] For example, some monomeric XRe^I(CO)$_3$L complexes, where X = Br or Cl and L is a bis-monodentated or a bidentated azine, catalyze the photoreduction of CO$_2$. These photoprocesses involve the reduction of the Re(I) to azine charge-transfer excited state, MLCT, with a sacrificial reductant, e.g., 2,2′,2″-nitrilotriethanol = TEOA.[2] The irradiation of the Re(I) complexes with a high power single laser flash or with two sequential laser flashes of different wavelengths, ν and ν', in a previous work has shown that the luminescent MLCT state is photolyzed according to eq 1.[3]

$$\text{XRe(CO)}_3\text{L}_1\text{L}_2 \xrightleftharpoons[\text{h}\nu_{\text{ems}}]{\text{h}\nu} \text{MLCT} \xrightarrow{\text{h}\nu'} \text{XRe(CO)}_3\text{L}_1\text{L}_2^* \quad (1)$$

In XRe^I(CO)$_3$L$_1$L$_2$, L$_1$ and L$_2$ are the same or different azines

and XRe(CO)$_3$L$_1$L$_2$* is an excited-state positioned above the MLCT. The bimolecular annihilation, eq 2,

$$2 \text{ MLCT} \rightarrow \text{XRe(CO)}_3\text{L}_1\text{L}_2 \text{ XRe(CO)}_3\text{L}_1\text{L}_2^* \quad (2)$$
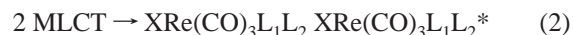
was slower than the unimolecular relaxations of the MLCT at those concentrations generated with large laser powers or with sequential laser irradiations.

We have applied ligand substitution reactions of the Re(I) complexes to the derivatization of a polymer backbone with pendant chromophores −Re^I(CO)$_3$L, (I). Incorporation of −Re^I-(CO)$_3$L$_1$L$_2$ chromophores into a polymer backbone can be used, in addition to the irradiation with high laser powers, to control the creation of excited states in close proximity. Such a large concentration of MLCT excited states may induce reactions of the chromophore that are different of those observed in diluted solutions of the excited state. In addition, medium effects resulting from the polymer's polyelectrolyte nature, may affect
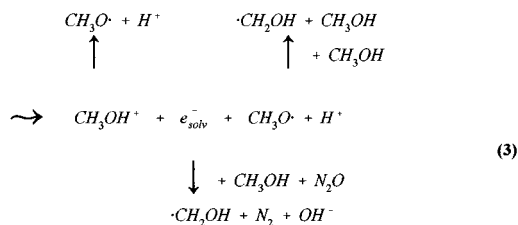
excited state reactions. Some of these effects were previously noticed in the photochemistry of Cu(II) complexes assembled in strands of polyacrylate.[4] The laser-flash induced photochemical processes of chromophores $-Re^I(CO)_3phen^+$ in the poly-(4-vynilpyridine) backbone, (I), are contrasted against those of the monomer $pyRe^I(CO)_3phen^+$ in this work.

(I) : {[(vpy)$_2$-vpyRe(CO)$_3$phen]$^+$ }$_{200}$
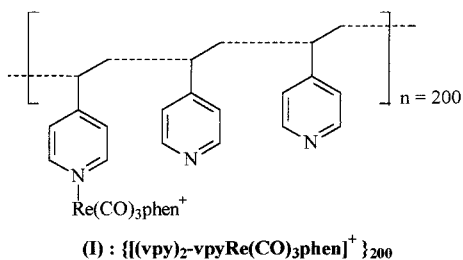
Experimental Section

Flash-Photochemical Procedures. Optical density changes occurring in a time scale longer than 10 ns, were investigated with a flash-photolysis apparatus described elsewhere. In these experiments, 20 ns flashes of 351 nm light were generated with a Lambda Physik SLL −200 excimer laser.[5] Time-resolved fluorescence experiments were carried out with a PTI flash fluorescence instrument. Solutions for the photochemical work were deaerated with streams of ultrahigh-purity N_2 before and during the irradiations. A flow-stop system ensured that fresh solution was brought to the reaction cell in experiments where the photodecomposition of the Re(I) complexes and/or formation of products interfered with the optical measurements. The concentrations of the complexes were adjusted to provide homogeneous concentrations of photogenerated intermediates within the volume of irradiated solution, i.e., optical densities equal to or less than 0.1 at 351 nm in a 1 cm optical path.

Pulse-Radiolytic Procedures. Optical pulse radiolysis measurements were carried out with a system and procedures similar to those described earlier.[6] Thiocyanate dosimetry was carried out before each experimental session. In this procedure, the output signal of a secondary emission monitor was calibrated against $(SCN)_2^-$ radical concentrations produced in the radiolysis cell by the electron pulse. A flow system was used to ensure that fresh solution was brought to the reaction cell between electron pulses. Solutions for the irradiation were prepared by adding the solid compounds to liquids previously deaerated with streams of O_2-free gases, i.e., N_2O and N_2. Radiolysis with ionizing radiation of CH_3OH and CH_3OH/H_2O mixtures have been reported elsewhere in the literature.[17,18] These studies have shown that pulse radiolysis can be used as a convenient source of e^-_{SLV} and $\cdot CH_2OH\cdot$ radicals according to eq 3.

$$CH_3O\cdot + H^+ \qquad \cdot CH_2OH + CH_3OH$$
$$\uparrow \qquad\qquad \uparrow \,\, + CH_3OH$$
$$\rightsquigarrow \quad CH_3OH^+ \, + \, e^-_{solv} \, + \, CH_3O\cdot \, + \, H^+$$
$$\downarrow \,\, + CH_3OH \, + N_2O$$
$$\cdot CH_2OH \, + \, N_2 \, + \, OH^-$$

$$(3)$$

Because e^-_{solv} and $\cdot CH_2OH$ have large reduction potentials, i.e., −2.8 V vs NHE for e^-_{solv} and −0.92 V vs NHE for $\cdot CH_2$-OH, they can be used for the reduction of coordination complexes and for the study of electron-transfer reactions. The yield of e^-_{solv} in CH_3OH ($G \approx 1.1$) is about a third of the G-value in the radiolysis of H_2O ($G \approx 2.8$).[7] In solutions where

e^-_{solv} was scavenged with N_2O,[12] the $\cdot CH_2OH\cdot$ radical appears to be the predominant product (yield > 90%) of the reaction between CH_3OH and $O^{\cdot-}$.

Steady-State Irradiations. The luminescence of the Re(I) complexes was investigated in an SLM-Aminco-8100 interfaced to a Dell 333P microcomputer.[8] The spectra was 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. $CF_3SO_3Re(CO)_3phen$ was prepared and purified by a literature procedure that involves the reaction of $ClRe(CO)_3phen$ with $AgCF_3SO_3$.[9] Reactions of $CF_3SO_3Re(CO)_3phen$ with pyridine and poly{4-vinylpyridine}$_{600}$, average FW 6×10^4, were respectively used in the preparations of [pyRe-(CO)$_3$phen]CF_3SO_3 and {[(vpy)$_2$-vpyRe(CO)$_3$phen]CF_3SO_3}$_{200}$, (I). In the synthesis of the latter, to a solution containing 33.4 mg of poly{4-vinilpyridine}$_{600}$ (5.55×10^{-7} mol) in 20 cm^3 of CH_2Cl_2 was slowly added by stirring 67 mg of $CF_3SO_3Re(CO)_3phen$ (1.11×10^{-4} mol) in 50 cm^3 of CH_2Cl_2. This stoichiometric relationship makes 200 $CF_3SO_3Re(CO)_3phen$ react with a similar number of pyridine groups of the ca. 600 present in the polymer. A yellow solid precipitated during the 9 h that the solution was refluxed under a blanket of N_2. The mixture was rotoevaporated to dryness; the resulting solid was redisolved in the minimum volume of CH_3CN, and the polymer was precipitated by the slow addition of ethyl ether. Yield 90%. Anal. Calcd. for {[(vpy)$_2$-vpyRe(CO)$_3$phen]CF_3SO_3}$_{200}$: C, 48.02; H, 3.11; N, 7.56. Found: C, 47.83; H, 3.20; N, 7.45. A literature procedure was followed for the preparation of the monomer [pyRe(CO)$_3$phen]CF_3SO_3. The purity of the resulting preparations was assessed by comparisons of the absorption spectrum, the emission spectrum and the emission lifetimes with those of a pure material available from a previous work.

Aldrich poly{4-vinylpyridine}$_{600}$, average FW 6×10^4, and pyridine were used as received. The solvents were spectroquality grade and used without further purifications.

Results

Characterization of {[(vpy)$_2$-vpyRe(CO)$_3$phen]CF_3SO_3}$_{200}$. The polymer and the monomer [pyRe(CO)$_3$phen]CF_3SO_3 exhibited UV−vis spectra with similar features, but the extinction coefficients of the polymer, by comparison to the extinction coefficients of the monomer, corresponded to ∼200 chromophores, $-Re(CO)_3phen^+$, per formula weight of polymer. This load of Re(I) pendants was in good agreement with a calculation from the elemental analysis. Osmosis experiments with solutions of the Re(I) polymer and monomer in MeOH containing 20% v/v H_2O were followed by means of the changes in the optical density at 280 nm. Membranes with a 15×10^3 molecular weight cut off prevented the diffusion of the Re(I) polymer but allowed the monomer to diffuse freely through the membrane. The diffusion experiments demonstrated that $-Re(CO)_3phen^+$ groups were attached to the poly{4-vinylpyridine}$_{600}$ backbone. The polymer can be assigned the formal structure, (I), where pendant $-Re(CO)_3phen^+$ groups are randomly distributed along the strand of polymer with an average of two 4-vynilpyridine groups for each one coordinated to a Re(I) chromophore.

The same NMR spectrum of the polymer was recorded in CD_3CN and CD_3OD containing 20% v/v D_2O. This experimental observation suggests that the polymer backbone adopts the same conformation in both solvents, i.e., one that resembles a rigid rod and simultaneously supports a maximum separation between cationic groups. Similar configurations of the backbone have been found, for example, with a related Co(III) complex.[1f]
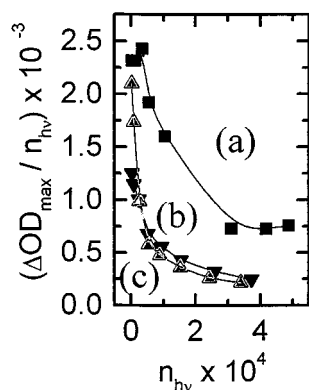
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Figure 1. Dependence of the MLCT excited-state quantum yield, ϕ_{MLCT} = $\Delta OD_{max}/n_{hv}$, on n_{hv} in, (a), the Re(I) monomer and, (b) and (c), the Re(I) polymer. Solutions of the Re(I) complexes in deaerated CH_3CN were used for measurements in curves (a) and (c) and solutions in $MeOH/H_2O$ for those in curve (b). The units of n_{hv} are Einstein L^{-1} flash^{-1}.
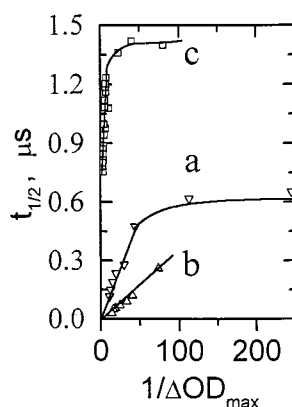
Figure 2. Dependence of the Re(I) monomer's, (a), and the Re(I) polymer's, (b) and (c), MLCT state $t_{1/2}$ on n_{hv}. Solutions in deaerated CH_3CN were used for measurements in curves (a) and (b) and solutions in $MeOH/H_2O$ for those in curve (c).

Photophysical Processes. The emission spectra of pyRe-(CO)$_3$phen$^+$ and {(vpy)$_2$-vpyRe(CO)$_3$phen$^+$}$_{200}$ in deaerated CH_3CN exhibited bands respectively centered at 560 and 565 nm with identical band shapes. Also, 351 nm laser flash irradiations of the monomer and polymer in deaerated CH_3CN produced nearly identical transient absorption spectra respectively assigned to the MLCT excited states. The spectra of the excited state, $\lambda_{max} \approx 460$ nm and $\lambda_{max} = 750$ nm, did not change with the number n_{hv} of 351 nm photons absorbed by either pyRe(CO)$_3$phen$^+$ or {(vpy)$_2$-vpyRe(CO)$_3$phen$^+$}$_{200}$. By contrast to this invariance of the MLCT spectra with n_{hv}, the quantum yield of the MLCT excited state, ϕ_{MLCT}, and its lifetime showed marked dependences on n_{hv} and the photogenerated concentration of MLCT excited state. The change in optical density ΔOD_{max}, determined at λ_{max} with a delay of 20 ns after the laser trigger, was considered proportional to the photogenerated concentration of the MLCT excited state and $\Delta OD_{max}/n_{hv}$ was regarded as a measure of ϕ_{MLCT} state, Figure 1, 2. Although the quantum yield was independent of n_{hv} for n_{hv} values that were below 20% of the total Re(I) concentration, it decreased monotonically above that limit, Figure 1a. Similar experiments with solutions of {(vpy)$_2$-vpyRe(CO)$_3$phen$^+$}$_{200}$ in CH_3CN, Figure 1b, or $MeOH/H_2O$ mixed-solvent, Figure 1c, showed that ϕ_{MLCT} decreased with n_{hv} and reached the same value of the monomer in the limit $n_{hv} = 0$.

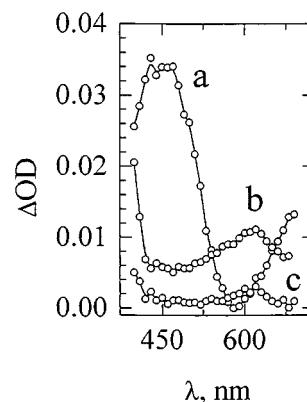The disappearance of the MLCT excited states in the monomer and in the polymer occurred with different reaction

Figure 3. Spectral changes in the irradiation of the Re(I) polymer in MeOH, (a) and (b) or CH_3CN, (c), with MV^{2+}. The spectrum of the MLCT excited state in (a) was measured with a 30 ns delay from the laser trigger. The $MV^{•+}$ spectrum in (b) and (c) was recorded with a 400 ns delay.

kinetics. In experiments with the polymer, the decay of the excited state was kinetically of a first order when n_{hv} was less than 17% of the total Re(I), Figure 2a,b. Linear inverse plots of the reciprocal of the change in optical density, ΔOD^{-1} vs time, and the linear dependence of $t_{1/2}$ on the MLCT concentration, ΔOD_{max}^{-1} in Figure 2, demonstrated that the rate of decay of the MLCT was kinetically of a second order on the MLCT concentration for larger values of n_{hv}. A similar study of the MLCT decay kinetics with the monomer established that traces were well fitted to a single exponential and that the lifetime, τ, of the exponential exhibited no dependence on MLCT concentration until n_{hv} corresponded to 30% of the Re(I) concentration, Figure 2c. These experimental observations showed that the process whose rate was kinetically of a second order in MLCT concentration contributed less to the excited-state decay in the monomer.

Redox reactions, in addition to the radiative and radiationless relaxations observed in deaerated CH_3CN, were detected with solutions of the MLCT excited state in MeOH or mixed solvents containing MeOH. In addition to a faster rate of decay in MeOH or MeOH−CH_3CN mixtures (Figure 2b), the spectrum recorded after the decay of the excited {(vpy)$_2$-vpyRe(CO)$_3$phen$^+$}$_{200}$ presented an absorption band with $\lambda_{max} = 550$ nm. This 550 nm absorption band is characteristic of the reduced Re(I) complex with a coordinated phen$^{•−}$ chromophore, see below.

Redox Quenching. The effect of the solvent on the oxidative quenching of the MLCT was investigated with 9.0×10^{-7} M solutions of {(vpy)$_2$-vpyRe(CO)$_3$phen$^+$}$_{200}$ in deaerated CH_3-CN or MeOH that also contained 1.0×10^{-3} M MV^{2+}. The spectrum of reduced methyl viologen, $MV^{•+}$, observed after the decay of the MLCT excited state showed that the yield of $MV^{•+}$ in MeOH solutions was five times larger than in CH_3CN, Figure 3. This experimental observation and the lifetimes in Figure 2 gave a ratio of the quenching rate constant in MeOH to the rate constant in CH_3CN that was between 6 and 7. However, the quenching rate constants measured from the optical density changes at 450 nm, $k = 4.3 \times 10^8$ M^{-1} s^{-1} in CH_3CN and $k = 2.1 \times 10^9$ M^{-1} s^{-1} in MeOH, differed by a factor of 5. The rate constant for the monomer's MLCT quenching was measured in flash photolysis of 1.8×10^{-5} M pyRe(CO)$_3$phen$^+$ in CH_3-CN containing 1.0×10^{-3} M MV^{2+} and with the same n_{hv} used in the experiments with {(vpy)$_2$-vpyRe(CO)$_3$phen$^+$}$_{200}$. The rate constant measured from the decay of the optical density at 450 nm, $k = 1.3 \times 10^9$ M^{-1} s^{-1}, was only three times larger than the one measured with the polymer.

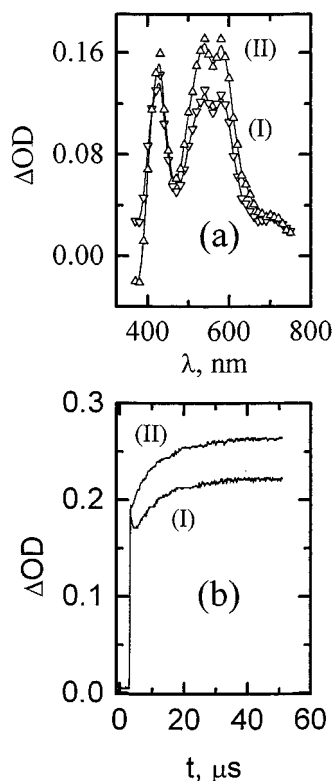**Figure 4.** Transient spectra, (a), in the quenching of the pyRe-(CO)$_3$phen$^+$ MLCT excited state with 0.73 M TEOA in CH$_3$CN. The spectra were respectively recorded with 30 ns, (I), and 40 μs, (II), delays from the laser irradiation. Traces, λ_{ob} = 460 nm, for the formation of pyRe(CO)$_3$(phen$^\bullet$) in (b) were recorded in solutions containing 0.073 M, (I), and 0.73 M, (II), TEOA.

Figure 5. Traces, λ_{ob} = 460 nm, for the formation and partial decay of $-$Re(CO)$_3$(phen$^\bullet$) in (a) were recorded in solutions of the Re(I) polymer containing 0.073 M, (I), and 0.73 M, (II), TEOA. Transient spectra, (b), recorded with 60 ns, (I), and 200 μs, (II), delays from the laser irradiation in similar experiments with 0.73 M TEOA in CH$_3$CN.

The reductive quenching of the MLCT excited state was investigated by flash photolysis of pyRe(CO)$_3$phen$^+$ and{(vpy)$_2$-vpyRe(CO)$_3$phen$^+$}$_{200}$ in deaerated CH$_3$CN containing TEOA in concentrations equal to or larger than 0.073 M. Identical concentrations of the Re(I) chromophore, [Re(I)] = 1.7 × 10^{-4} M, were used in solutions of the monomer and the polymer. Transient spectra, λ_{max} = 420, 550 nm and λ_{max} > 750 nm, recorded by flash photolysis and by the pulse radiolytic reduction of the complexes, see below, were assigned to Re(I) species with coordinated phen$^{\bullet-}$. In a 20 μs time scale, processes similar to those described in the literature reports, i.e., the additional formation of pyRe(CO)$_3$(phen$^\bullet$) due to reactions of excess Re-(I) complex with radicals from the TEOA oxidation, followed the photogeneration of pyRe(CO)$_3$(phen$^\bullet$), Figure 4.[3] The disappearance of the pyRe(CO)$_3$(phen$^\bullet$) spectrum at times longer than 0.1 s took place with a rate that was kinetically of a second order in accordance with the expected disproportionation of the radicals.

Reduction of the polymer's excited states was effected in less than 30 ns by TEOA. This process was followed at times t > 25 μs by a growth of the $-$Re(CO)$_3$(phen$^\bullet$) spectrum that showed an additional reduction of $-$Re(CO)$_3$phen$^+$ groups in direct proportion to the TEOA concentration, Figure 5a. Further spectral changes took place in a 200 μs time scale, namely after the formation of $-$Re(CO)$_3$(phen$^\bullet$), Figure 5b. Because the spectra recorded between 200 and 300 μs and transient spectra generated in the disproportionation of pyRe(CO)$_3$(phen$^\bullet$) exhibited similar spectral features, it was related to the formation of two electron-reduced groups, $-$Re(CO)$_3$(phenH), in the polymer. It must be noted that the process leading to the formation of $-$Re(CO)$_3$ (phenH) in the polymer was 10 times faster than that of the disproportionation of the monomer's Re-
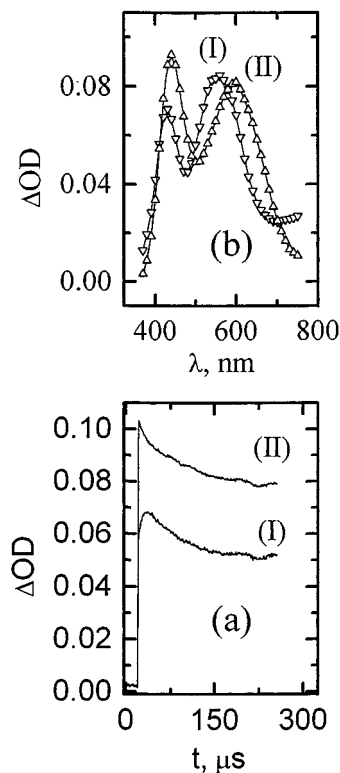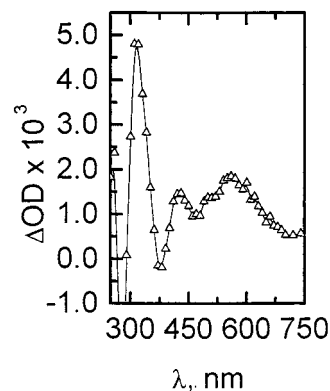

Figure 6. Transient absorption spectrum recorded in pulse radiolysis with a 100 μs delay after the irradiation of a, N$_2$-deaerated, 3 × 10^{-7} M polymer solution.

(I) ligand-radical and that oscillographic traces were fitted to a single exponential with a rate constant k = (1.10 ± 0.05) × 10^4 s^{-1} instead of the second-order kinetics observed with the monomer.

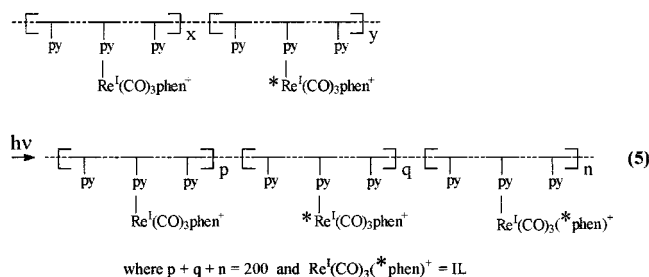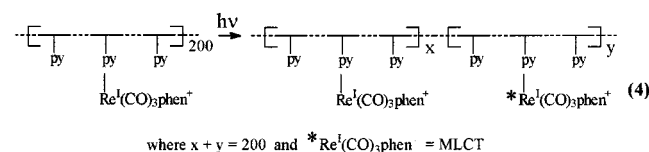The same experiments were conducted in a MeOH/H$_2$O, 20% v/v, mixed-solvent. Transient spectra of the monomer and polymer Re(I) ligand-radicals disappeared by processes that were kinetically of a second order in transient concentration. Ratios of the second-order rate constant to the extinction coefficient, k/ϵ = (7.1 ± 0.1) × 10^6 cm s^{-1} for the polymer and k/ϵ = (6.6 ± 0.5) × 10^6 cm s^{-1} for the monomer, were nearly independent of the number of absorbed 351 nm photons.

In either solvent, CH$_3$CN or MeOH/H$_2$O, the decay of the transient spectra was not complete, and the residual spectrum, similar to one recorded for the polymer's $-$Re(CO)$_3$(phen$^\bullet$), remained stable for several minutes after the irradiation.

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Pulse Radiolysis. The spectrum of $-Re(CO)_3(phen^{\bullet})$ was generated by a two-step process in pulse radiolysis of 3×10^{-7} M $\{(vpy)_2\text{-}vpyRe(CO)_3phen^+\}_{200}$ in MeOH deaerated with streams N_2 (Figure 6). The slower component of the $-Re(CO)_3\text{-}(phen^{\bullet})$ formation was the only reaction that was observed when solutions were deaerated with streams of N_2O instead of N_2. This slow process, $t_{1/2} \approx 30 \ \mu s$, was ascribed to the reduction of the complex by $^{\bullet}CH_2OH$ with very little efficiency, and the fast and more efficient reaction to the reduction of the polymer by e^-_{solv}.

Discussion

Relative to $pyRe(CO)_3phen^+$, the incorporation of the $-Re(CO)_3phen^+$ chromophore in a poly(vinylpyridine) polymer backbone has little effect on the photophysical processes of the MLCT excited state when these complexes are irradiated with low photonic fluxes, i.e., steady-state photolysis or laser irradiations with $n_{hv} < 5$ mJ/pulse $\approx 5 \times 10^{-6}$ Einstein L^{-1} pulse^{-1}. This experimental observation and the similarity of the monomer and polymer absorption spectra suggest that electronic interactions between Re(I) chromophores in the polymer are negligible. A rigid rod conformation of the polymer backbone that supports maximum separation between cationic pendants accounts for these spectroscopic and photochemical properties. By contrast to the irradiations with low photonic fluxes, the photophysics of the MLCT in the Re(I) monomer is different of the one observed with the Re(I) polymer when irradiations are carried out with laser powers $n_{hv} \geq 5$ mJ/pulse. In the Re(I) monomer, the quantum yield of the MLCT excited state, ϕ_{MLCT}, remains constant until there is a significant depletion of the ground-state population, i.e., $n_{hv} \leq 3.5 \times 10^{-5}$ Einstein L^{-1} pulse^{-1} in Figure 1. The decrease of ϕ_{MLCT} with n_{hv} occurs earlier than expected for the depletion of the ground state in the Re(I) polymer. However, absorption of light by MLCT excited states in the polymer to form intraligand excited states, IL, accounts for the functional dependence of ϕ_{MLCT} on n_{hv}, eq 4, 5.

$$\text{where } x + y = 200 \text{ and } {}^*Re^I(CO)_3phen = MLCT \quad (4)$$

$$\text{where } p + q + n = 200 \text{ and } Re^I(CO)_3({}^*phen)^+ = IL \quad (5)$$

Because the IL excited state is shorter lived than the MLCT excited state, the decay represented in eq 6 is faster than the instrument's 20 ns response, and it was manifested only by a photogenerated concentration of MLCT smaller than the expected one.

The observed oxidation of MeOH in laser irradiations of $\{(vpy)_2\text{-}vpyRe(CO)_3phen^+\}_{200}$ lends support to the proposition that excited states positioned above the MLCT are created via secondary photolysis or annihilation processes. Indeed, it has been established in previous literature reports that MLCT excited

$$(6)$$
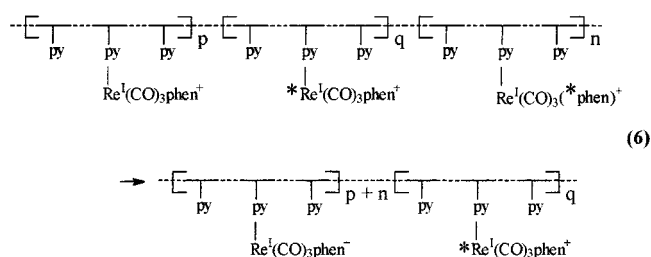
states of $pyRe(CO)_3phen^+$ and related Re(I) complexes are unable to oxidize MeOH and that excited states more reactive than the MLCT are produced by biphotonic processes.[3b] To a certain extent, this mechanism resembles one that accounts for the multiphoton, multielectron photochemistry of a soluble polymer of Ru(II).[1c]

A fast intrastrand annihilation of MLCT excited states also provides a good rationale for the functional dependence of ϕ_{MLCT} on n_{hv}. In this mechanism, the rapid curvature of ϕ_{MLCT} with n_{hv} in Figure 1 requires that a large fraction of photogenerated excited states vanishes within the 20 ns laser pulse. If excited Re chromophores are close neighbors and have the right spatial orientation within the strand of polymer, they may undergo a fast annihilation within that period of time. This fast annihilation process can create IL excited states that are placed at higher energies and that are more reactive than the parent MLCT excited state.

Excited chromophores that are disfavored by reason of their position for a fast annihilation or do not undergo a secondary photolysis will be observed at times longer than the 20 ns laser irradiation. Flash photolysis shows that the rate of decay of this remanent excited state population is kinetically of a second order in the overall MLCT concentration. Because diffusive motions of the polyelectrolyte are much slower than those of the observed decay of excited states, the second-order kinetics indicates that mechanisms by which the energy moves through the strand of polymer are available. Various mechanisms of intramolecular energy transfer have been proposed for organic polymers.[10] In a mechanism, energy hopping in the strand may form pairs of excited chromophores that undergo annihilations. The process could involve excited states of the uncomplexed pyridine pendants.[11] It is also possible that energy can be transferred between remotely placed excited chromophores. These events will leave, therefore, one chromophore in the ground state and the other in an upper intraligand excited state, IL.
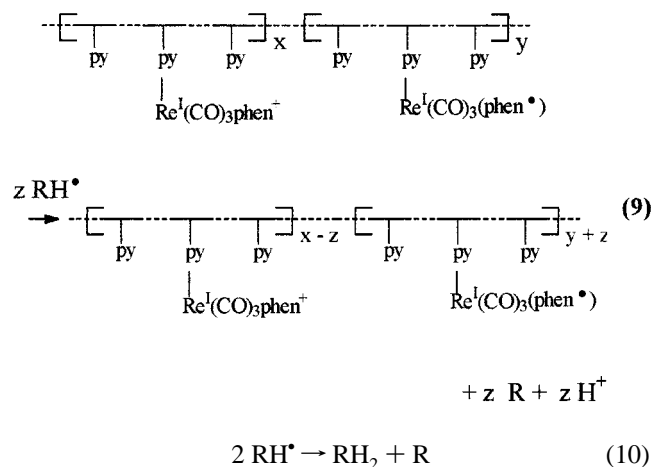
To a certain extent, medium effects were observed in the excited-state redox quenching by MV^{2+} or TEOA. The reductive quenching of the $\{(vpy)_2\text{-}vpyRe(CO)_3phen^+\}_{200}$ excited state by TEOA is represented in eq 7.

$$(7)$$
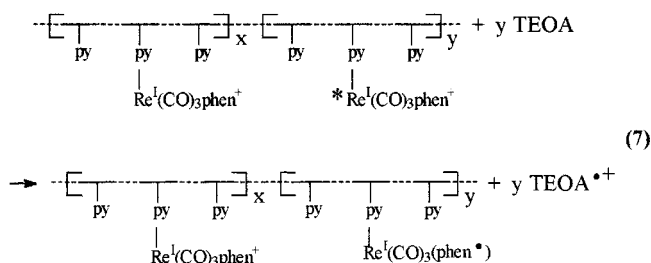
Flash photolysis shows that an additional formation of Re(I) ligand radical must follow eq 7.

Radicals $RH^{\bullet}$ that are formed by the oxidation of TEOA, eq 8,[12] must react with $-Re(CO)_3phen^+$ chromophores in the polymer, eq 9, in competition with a fraction of radicals that

undergo the reported disproportionation reaction, eq 10.

$$TEOA^{\bullet+} + TEOA \rightarrow TEOA + RH^{\bullet} + H^+ \qquad (8)$$

$$z\ RH^{\bullet}$$

(9)

$$+ z\ R + z\ H^+$$

$$2\ RH^{\bullet} \rightarrow RH_2 + R \qquad (10)$$

Flash photolysis experiments show that a fraction of the photogenerated radicals $RH^{\bullet}$ also reduce excess $pyRe(CO)_3phen^+$ to $pyRe(CO)_3(phen^{\bullet})$.

The disproportionation of the monomer Re(I) ligand-radical to form $pyRe(CO)_3phenH_2^+$, eq 11, occurs with a rate comparable to those recorded for other Re(I) ligand-radical species.[3b,c]

$$2\ pyRe^I(CO)_3(phen^{\bullet}) + 2\ H^+ \rightarrow$$
$$pyRe^I(CO)_3phen^+ + pyRe^I(CO)_3(phenH_2)^+ \quad (11)$$
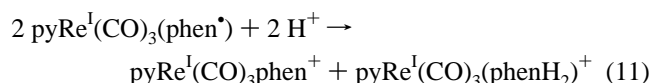
By contrast to the disproportionation of the monomer radical, a partial decay of Re(I) ligand-radicals in the polymer to form $-Re(CO)_3phenH_2^+$ has rate laws in CH_3CN and in $MeOH/H_2O$ solvents that are respectively of a first and a second order on ligand-radical concentration.

Because the same products are formed in both solvents, it is proposed that the reduction of $-Re(CO)_3(phen^{\bullet})$ groups proceeds via two sequential processes, one being kinetically of a first order and the other being kinetically of a second order. In CH_3CN, the former process is the rate determining step whereas the rate determining step in $MeOH/H_2O$ is the later process. The process that exhibits a first-order rate law can be related to the formation of additional vicinal $-Re(CO)_3(phen^{\bullet})$ groups that disproportionationate in a reaction similar to the monomer in eq 11. When formation of vicinal $-Re(CO)_3(phen^{\bullet})$ groups is

fast, electron transfer between such groups is the rate determining step. Because a residual concentration of $-Re(CO)_3(phen^{\bullet})$ survives several minutes, the reactions of $RH^{\bullet}$ leave some of these groups in isolation for either the transfer or the acceptance of electrons. The demise of these residual Re(I) ligand-radicals must occur by a slower disproportionation process that possibly demands larger diffusive displacements of polymer strands in a time scale of minutes.

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