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Physical and Photophysical Properties of Rhenium(I) Tetracarbonyl Complexes

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The physical and photophysical properties of a series of rhenium(I) tetracarbonyl complexes $[Re(CO)_4(L\text{-}L)]CF_3SO_3$, where L-L = 2,2′-bipyrimidine (bpm), 4,4′-dimethyl-2,2′-bipyridine (dmb), 2,2′-bipyridine (bpy), and 1,10-phenanthroline (phen), are reported. The complexes displayed reductions but no oxidations within the +2 to −2 V vs SSCE electrochemical window. Electronic absorptions associated with $d\pi \rightarrow \pi^*$ transitions were observed between 300 and 400 nm; $\pi \rightarrow \pi^*$ transitions associated with the aromatic heterocyclic ligand were found at wavelengths <300 nm. Excitation at 355 nm resulted in the appearance of emission in solution at room temperature with emission quantum yields near 0.03 for the bpm, bpy, and dmb derivatives and 0.008 for the phen derivative. The bpy, dmb, and phen derivatives displayed structured emission located near 470 nm, while the bpm derivative displayed unstructured emission located near 521 nm. The complexes were photosensitive in methylene chloride, expelling one of the CO ligands. The photochemical quantum yields ranged from 0.03 to 0.9. Reductive quenching was observed with various methoxybenzene compounds and Cl^- ion verifying the high $[Re(CO)_4(L\text{-}L)^{+*/0}$ redox potentials calculated to be on the order of 1.5 V. An excited-state model assigning structured emission to a ^3LC state, unstructured emission to a ^3MLCT state, and photosubstitution to a $^3LF(dd)$ state or possibly the ^3MLCT state is proposed.

Introduction

Rhenium(I) carbonyl complexes comprise an important class of compounds that have been the object of photochemical and photophysical studies.[1] Rhenium pentacarbonyl halides ($Re(CO)_5X$) have been shown to emit at 25 K[2] and were found to undergo a stepwise dissociative loss of carbon monoxide to yield tetracarbonyl and tricarbonyl derivatives.[3] In the presence of monodentate ligands (L) or bidentate ligands (L-L), various types of tetracarbonyl and tricarbonyl complexes have been isolated.[4–15]

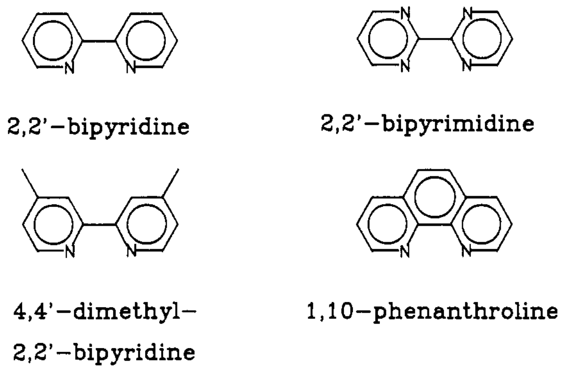

Figure 1. The L-L ligands 2,2′-bipyrimidine (bpm), 2,2′-bipyridine (bpy), 4,4′-dimethyl-2,2′-bipyridine (dmb), and 1,10-phenanthroline (phen).

Recently, complexes of the general formula $Re(CO)_3(L\text{-}L)X$ have been the focus of a large number of investigations owing to their attractive ground-state properties and high quantum emission efficiencies from the metal-to-ligand charge-transfer (MLCT) excited state.[4–12] It has been possible to vary L-L with a wide range of bidentate heterocyclic ligands and X with a number of monodentate ligands, demonstrating that the observed photophysics is controlled by the energy gap law.[11,13]

While research with rhenium(I) tricarbonyl complexes has blossomed, there is a relative dearth of information on the behavior of the tetracarbonyl analogues. To our knowledge, only a few compounds have been isolated. Among these are *trans*-$[Re(CO)_4(PPh_3)_2]^+$,[14] *cis*-$[Re(CO)_4(phen)]^+$,[15] and *cis*-$[Re(CO)_4(diphos)]^+$,[16] where phen is 1,10-phenanthroline. Recently, we reported the preparation of $[Re(CO)_4(bpm)]^+$, where bpm is 2,2′-bipyrimidine, and some of its physical and photophysical properties.[17] In this paper, we examine the behavior of a series of tetracarbonyl complexes of the type $[Re(CO)_4(L\text{-}L)]^+$, where the L-L ligands, as shown in Figure 1, are 2,2′-bipyrimidine (bpm), 2,2′-bipyridine (bpy), 4,4′-dimethyl-2,2′-bipyridine (dmb), and 1,10-phenanthroline (phen).

Experimental Section

Materials. $Re(CO)_5Cl$ was purchased from Pressure Chemical Co. and was used without further purification. The ligands 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), 4,4′-dimethyl-2,2′-bipyridine (dmb),

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Table I. Elemental Analyses and Percent Yields[a]

compound	%C calcd	%C found	%H calcd	%H found	%N calcd	%N found	% yield
$[Re(CO)_4(bpm)](CF_3SO_3)$	25.79	25.86	1.00	1.05	9.25	9.20	28.7
$[Re(CO)_4(bpy)](CF_3SO_3)$	29.85	29.74	1.34	1.37	4.64	4.62	46.1
$[Re(CO)_4(dmb)](CF_3SO_3)$	32.33	32.41	1.92	1.94	4.44	4.46	80.2
$[Re(CO)_4(phen)](CF_3SO_3)$	32.54	32.71	1.29	1.37	4.46	4.49	39.5

[a] Elemental Analyses were performed by Atlantic Microlabs, Norcross, GA.

and 2,2′-bipyrimidine (bpm) were purchased commercially and used without further purification. Methanol, acetonitrile, methylene chloride, and acetone were HPLC grade and were used without further purification.

Tetraethylammonium chloride ((TEA)Cl), purchased from Aldrich, was purified by the procedure of Urri, Elias, and Schift[18] and stored in a vacuum oven. Tetrabutylammonium hexafluorophosphate was purchased from Southwestern Analytical Chemical, Inc., and stored in a vacuum oven. The quenchers, 1,4-dimethoxybenzene, 1,2,3-trimethoxybenzene, and anisole, were purchased commercially and used without further purification. Silver trifluoromethanesulfonate (silver triflate) and silver hexafluorophosphate were purchased commercially, stored in a vacuum desiccator, and used without further purification. The gases, argon, carbon monoxide, and nitrogen, were obtained from Linde.

Preparation of $[Re(CO)_4(L\text{-}L)](CF_3SO_3)$. $Re(CO)_5Cl$ (0.200 g, 5.53×10^{-4} mol) was dissolved in 40 mL of methylene chloride. Silver triflate (0.150 g, 5.84×10^{-4} mol) dissolved in 10 mL of methylene chloride was added to the solution containing rhenium. The mixture was allowed to stir at room temperature in the dark for 18 h. A AgCl precipitate formed, was removed by filtration, and then was washed with 15 mL of methylene chloride. The filtrate was placed in a round-bottom flask containing L-L, where L-L = bpm (0.140 g, 8.85×10^{-4} mol), bpy (0.095 g, 6.08×10^{-4} mol), dmb (0.110 g, 5.97×10^{-4} mol), or phen (0.110 g, 6.10×10^{-4} mol). The mixture was then allowed to stir for 8 h under argon at room temperature in the dark to yield a green luminescing solution. The solution was evaporated to approximately 20 mL with a rotary evaporator, and hexane was added to precipitate the product. Elemental analyses and percent yields for these compounds are listed in Table I.

Measurements. Visible/UV measurements were recorded with a Perkin-Elmer Model 3840 diode array spectrophotometer. Uncorrected emission spectra and luminescence intensity measurements were recorded using a Hitachi Perkin-Elmer Model 650-40 fluorescence spectrophotometer. Corrected emission spectra were obtained on a SPEX Fluorolog Model 212 spectrofluorometer. A flow system that consisted of 50 mL of a CO- or Ar-purged solution connected to a Cole-Palmer Masterflex L/S Easy-Load pumphead and fluorescence flow cell (path length = 10 mm, volume = 0.5 mL, flow rate = 8–10 mL/min) was used in the luminescence measurements. Cyclic voltammograms were obtained with a three-electrode system consisting of a Pt-disk working electrode, a Pt-wire counter electrode, and a saturated sodium chloride calomel reference electrode (SSCE). Electrochemistry was carried out with a PAR 173 potentiostat in conjunction with a PAR 175 programmer. The voltammograms were recorded with an IBM 7424 X-Y recorder.

Emission lifetimes were acquired using a Photochemical Research Associates Model LN1000 pulsed N_2 laser and a PRA LN102 dye laser as the excitation source. The analog signal from the photomultiplier tube was digitized with a LeCroy transient digitizer system employing either a 6880A or TR8828C transient recorder. The LeCroy 6010 controller was interfaced to an IBM PS/2 Model 60 computer via a National Instrument GPIB IEEE bus and controlled by Catalyst software supplied by LeCroy. Radiative lifetimes were calculated by the program LIFETIME written in C utilizing an algorithm designed to fit the data to a single-exponential decay. The program calculated a straight-line fit of a plot of the difference between the sample and the background vs time. The data were presented in exponential format, and calculations were performed on data between two cursors positioned randomly on the measured decay curve. The lifetimes and correlation coefficients were continuously displayed on the screen to provide an indication of the linearity of the plot. Data yielding the best correlation coefficients were selected.

Emission quantum yields were calculated by a comparison to rhodamine B using eq 1,[19] where ϕ_{em} is the experimental emission quantum yield, I_0 and A_0 are respectively the emission intensity and absorbance of rhodamine B at the excitation wavelength, I_s and A_s are respectively the emission intensity and absorbance of the sample at the excitation wavelength, and ϕ is the emission quantum yield of rhodamine B (0.69 at λ_{ex} = 355 nm in ethanol at 25 °C).[20]

$$\phi_{em} = (I_s/I_0)(A_0/A_s)\phi \qquad (1)$$

Stern–Volmer quenching constants were determined by luminescence or emission lifetime changes. Intensities (and lifetimes) were corrected for dilution using eq 2, where I_r and V_r

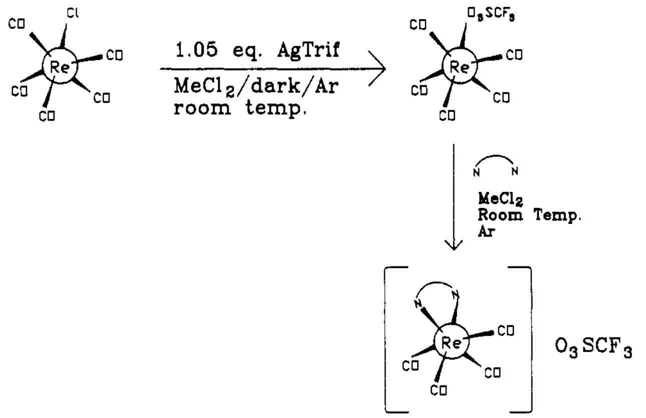
$$I_{cor} = I_r[(V_r + V_q)/V_r] \qquad (2)$$

are respectively the emission intensity (or lifetime) and the solution volume prior to adding the quencher, V_q is the volume of the quencher, and I_{cor} is the corrected intensity (or lifetime). Plots of I_0/I (or τ_0/τ) vs quencher concentration were constructed, and Stern–Volmer constants (K_{SV}) were determined from the slopes. The quenching rate constant was then determined by dividing K_{SV} by τ_0.

Beer's law studies were used to determine absorption coefficients by serial dilution methods. Solutions for electrochemistry contained 0.1 M TBAH in various solvents. Samples for determining emission lifetimes and Stern–Volmer constants were adjusted to 0.1 absorbance unit at λ_{ex} = 355 nm and were purged with nitrogen, argon, or carbon monoxide. The solution containing the quencher was added to the solution containing the rhenium complex via a 10-μL syringe.

Curve fitting and linear regression analyses were effected using an IBM PS/2 Model 60 computer employing Graph Pad or Quattro software.

Scheme I



Results

Preparation of Compounds. An outline of the rhenium tetracarbonyl synthesis is given in Scheme I. The approach was to remove coordinated chloride from $Re(CO)_5Cl$ rather than replace Cl with CO in $Re(L\text{-}L)(CO)_3Cl$ under high CO pressures as reported in the past.[14] The removal of chloride from $Re(CO)_5Cl$ was effected by use of silver triflate, $Ag(CF_3SO_3)$, in methylene chloride, yielding $[Re(CO)_5(CF_3SO_3)]$. The silver chloride that formed was easily removed from the solution by filtration. Silver triflate was used rather than $AgPF_6$, since PF_6^- in methylene chloride reportedly oxidizes to $PO_2F_2^-$ in the presence of rhenium(I).[21]

$[Re(CO)_5(CF_3SO_3)]$ was stable and was isolated and used in subsequent reactions for preparing the tetracarbonyl complexes.

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Table II. Vibrational CO Stretching Frequencies for $[Re(CO)_4(L\text{-}L)](CF_3SO_3)^a$

L-L	ν(CO),^{b} cm^{-1}			
bpm	2129	2029	2009	1974
bpy	2127	2030	1999	1945
dmb	2099	1982	1956	1922
phen	2120	2015 (sh)	2003	1970
bpm^c		2033	1906 (sh)	1899

^{a} Nujol mulls, 23 ± 1 °C. ^{b} Error = ±2 cm^{-1}. ^{c} $Re(bpm)(CO)_3Cl$; ref 7.

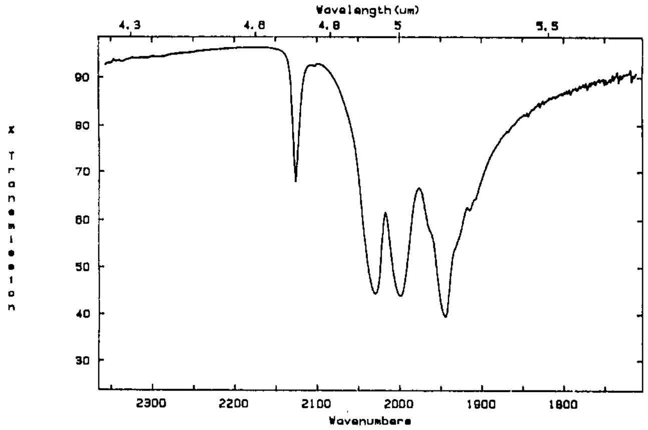

Figure 2. Infrared spectrum of $[Re(CO)_4(bpy)](CF_3SO_3)$ in Nujol mull.

The $CF_3SO_3^-$ ligand was an excellent leaving group. Thus, upon addition of a stoichiometric quantity of a bidentate ligand (a 2-fold excess was used with bpm to minimize formation of bimetallic species), the triflate and a neighboring carbonyl ligand were displaced, resulting in formation of $[Re(CO)_4(L\text{-}L)]^+$ complexes which were isolated as $CF_3SO_3^-$ salts. The $CF_3SO_3^-$ anion was present in solution after displacement from the coordination sphere of rhenium and served as the counterion for isolating the rhenium cation.

Carbonyl Stretching Frequency. The carbonyl stretching frequencies are listed in Table II, and the spectrum of $[Re(bpy)(CO)_4](CF_3SO_3)$ is shown in Figure 2. Four vibrational modes were found for the complexes in the 2200–1900-cm^{-1} region. The four CO vibrations were expected on the basis of those found for $W(bpy)(CO)_4$, which were assigned as an A_1 (2010 cm^{-1}), a B_1 (1900 cm^{-1}), another A_1 (1874 cm^{-1}), and a B_2 (1832 cm^{-1}) mode.[22] The presence of the mode at 2100 cm^{-1} in Figure 2 distinguishes the tetracarbonyl complexes from the tricarbonyl analogues, which show only the lower energy vibrations.[4,7] This high-energy vibration is near the carbonyl stretching frequency for gaseous CO (2155 cm^{-1}), indicating that there is only weak π-bonding interaction between rhenium and one or more of the CO ligands. This is consistent with the crystal structure of the $[Re(bpm)(CO)_4]^+$ cation, where the trans CO ligands had Re–C bond lengths of 2.025 Å whereas the CO ligands trans to bpm had Re–C bond lengths of 1.928 Å.[17]

Electronic Absorption Spectra. The visible/UV spectra were examined in acetonitrile and the results are listed in Table III. The assignment of the $d\pi \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions were made by comparison to those found in $Re(bpm)(CO)_3Cl$.[7] The molar absorptivities were on the order of 10^3 M^{-1} cm^{-1} for $d\pi \rightarrow \pi^*$ transitions and on the order of 10^4 M^{-1} cm^{-1} for $\pi \rightarrow \pi^*$ transitions. The absorption spectrum of $[Re(CO)_4(bpm)]^+$ is shown in Figure 3A. Typically, there are two $\pi \rightarrow \pi^*$ transitions for all complexes. One of the two bands appears as a shoulder on the band with the larger molar absorptivity. Figure 3B illustrates the electronic spectrum of $[Re(CO)_4(bpy)]^+$, which shows larger molar absorptivities of the $d\pi \rightarrow \pi^*$ bands than $[Re(CO)_4(bpm)]^+$. Larger molar absorptivities for $d\pi \rightarrow \pi^*$ transitions were also observed for $[Re(CO)_4(dmb)]^+$.

Table III. Visible/UV Spectral Data for $[Re(CO)_4(L\text{-}L)](CF_3SO_3)$ Complexes in Acetonitrile^a

L-L	$\lambda(d\pi \rightarrow \pi^*)$ $(\epsilon)^b$		$\lambda(\pi \rightarrow \pi^*)$ $(\epsilon)^b$	
bpm		319 (3.2×10^3)		246 (3.2×10^4)
bpy	315 (1.50×10^4)	305 (1.42×10^4)		244 (2.57×10^4)
dmb	315 (1.59×10^4)	305 (1.56×10^4)		252 (2.71×10^4)
phen	357 (2.14×10^3)	340 (2.37×10^3)	272 (3.56×10^4)	250 (1.99×10^4)
bpm^c	384 (2.7×10^3)	310 (3.4×10^3)	260 (sh)	232 (2.3×10^4)

^{a} T = 23 ± 1 °C. ^{b} λ in nm, error ± 1 nm; ϵ in M^{-1} cm^{-1}, error ± 1 in last digit. ^{c} $Re(bpm)(CO)_3Cl$; ref 7.

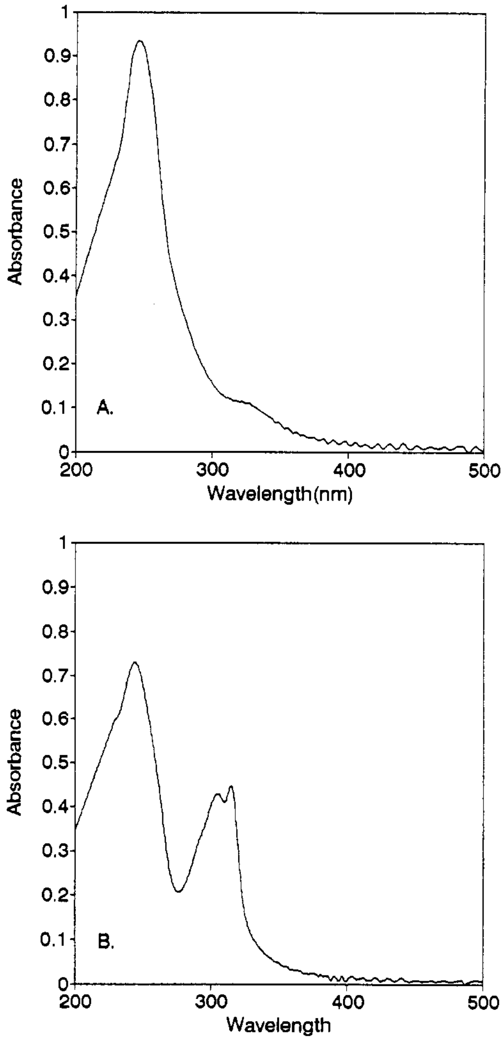

Figure 3. Visible/ultraviolet spectra of (A) $[Re(CO)_4(bpm)](CF_3SO_3)$ (3.16×10^{-5} M in acetonitrile) and (B) $[Re(CO)_4(bpy)](CF_3SO_3)$ (2.77×10^{-5} M in acetonitrile).

Electrochemistry. Redox processes were investigated by cyclic voltammetry, and the results are summarized in Table IV. Also listed for comparison are redox potentials of uncoordinated ligands. Only reductions of the complexes were observed in acetonitrile; no oxidations were found within the solvent window from 0 to +2.0 V vs SSCE. The first reduction was quasireversible. The i_a/i_c ratio was nearly 1, and a plot of the square root of the sweep rate vs ΔE_p, where $\Delta E_p = E_{p,ox} - E_{p,red}$, had intercepts somewhat greater than the 56 mV expected for a reversible, one-electron-transfer process.[23] The second reduction process was irreversible. Similar reduction processes were observed with rhenium(I)

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[22] Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; John Wiley and Sons: New York, 1986.

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Table IV. Redox Potentials for Ligands (L-L) and [Re(CO)$_4$(L-L)](CF$_3$SO$_3$) Compounds[a]

	redn pot., V		$E_{1/2}^{+*/0}$, V
[Re(CO)$_4$(bpm)]$^+$	−0.87 (75)	−1.86[b]	1.51
[Re(CO)$_4$(bpy)]$^+$	−1.22 (80)	−1.53[b]	1.55
[Re(CO)$_4$(dmb)]$^+$	−1.30 (80)	−1.50[b]	1.49
[Re(CO)$_4$(phen)]$^+$	−1.20 (90)	−1.55[b]	1.50
bpm	−1.80[c]		
bpy	−2.18[c]		
dmb	−2.24[c]		
phen	−2.04[c]		

[a] In 0.1 M TBAH in acetonitrile; V vs SSCE (error ±0.02 V); T = 23 ± 1 °C; values are $E_{1/2}$ unless otherwise noted; values in parentheses are ΔE_p; scan rate = 200 mV/s. [b] Values are E_p; irreversible. [c] Kawanishi, Y.; Kitamura, N.; Tazuke, S. *Inorg. Chem.* **1989**, *28*, 2968.

Table V. Excited-State Emission Maxima, Emission Quantum Yields, Emission Lifetimes, and Photosubstitution Quantum Yields of [Re(CO)$_4$(L-L)](CF$_3$SO$_3$) in Methylene Chloride under CO at Room Temperature[a]

L-L	λ_{em}^{cor} [b]	ϕ_{em}[c,d]	τ_0, μs[d]	ϕ_p[e]
bpm	521	0.037	0.75	0.5
bpy	448, *476*, 506	0.031	4.7	0.3
dmb	444, *473*, 505	0.033	2.3	0.9
phen	*459*, 489, 525	0.008	3.8[f]	0.05

[a] T = 23 ± 2 °C; λ_{ex} = 355 nm. [b] In nm (error ±1 nm); dominant peak is italicized. [c] Emission quantum yield. [d] Error is ±10%. [e] Photosubstitution quantum yield. [f] 4.9 μs under Ar.

tricarbonyl complexes containing bidentate heterocyclic ligands and were assigned to the reversible reduction of the coordinated bidentate heterocyclic ligand followed by the irreversible reduction of the rhenium(I) center.[7] The redox assignments for the rhenium(I) tetracarbonyl complexes studied here are illustrated in eqs 3 and 4.

$$[\mathrm{Re^I(CO)_4(L\text{-}L)}]^+ + e^- \rightleftarrows [\mathrm{Re^I(CO)_4(L\text{-}L^-)}] \quad (3)$$

$$[\mathrm{Re^I(CO)_4(L\text{-}L^-)}] + e^- \rightleftarrows [\mathrm{Re^0(CO)_4(L\text{-}L^-)}]^- \quad (4)$$

As noted from the data in Table IV, the reduction of the coordinated ligand occurs at a potential 0.8–1.0 V more positive than that of the free ligand. In the past, this has been attributed to electrostatic lowering of the energy of the π^* orbital(s) on the ligand by the positive charge of the metal center.[23] Compared to [Ru(bpy)$_3$]$^{2+}$, which undergoes reduction at −1.3 V vs SSCE,[24] [Re(CO)$_4$(bpy)]$^+$ is reduced at a more positive potential. This can be rationalized, since the 2+ charge on ruthenium is shared by three ligands whereas the 1+ charge on rhenium interacts with only one bpy ligand.

Luminescence Properties. Emission data obtained at 298 °C are listed in Table V. The data were collected in a flow cell under a CO atmosphere in order to deter photodecomposition. With the exception of [Re(CO)$_4$(bpm)](CF$_3$SO$_3$), the tetracarbonyl complexes showed structured emission, as illustrated by [Re(CO)$_4$(bpy)](CF$_3$SO$_3$) in Figure 4A. The excited-state lifetimes of the complexes with structured emission were 2–4 μs in methylene chloride at room temperature. The high-energy peak occurred near 450 nm with vibrational progressions on the order of 1300–1400 cm^{-1}. Structured emission, as previously observed in rhenium tricarbonyl complexes, was assigned to a ^{3}LC ($^3\pi$–π^*) process.[4,13]

The nonstructured emission spectrum of [Re(CO)$_4$(bpm)]$^+$ is shown in Figure 4B. The radiative lifetime was 800 ns, a factor of 4 or 5 less than those of the structured emitters. Nonstructured emission was previously observed for rhenium tricarbonyl complexes and was assigned to ^{3}MLCT-based emission.[4,13]

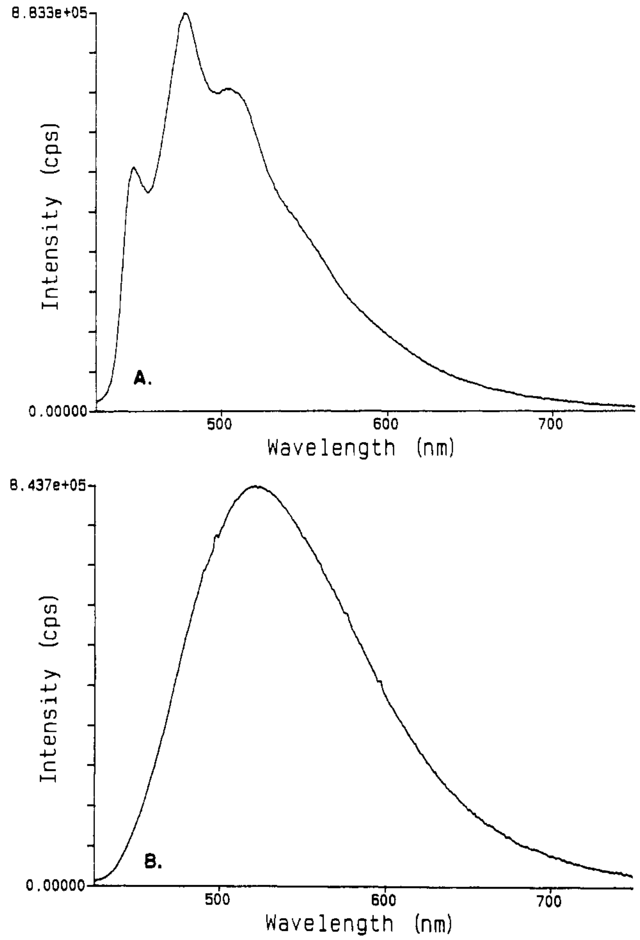

Figure 4. Emission spectra of (A) [Re(CO)$_4$(bpy)](CF$_3$SO$_3$) and (B) [Re(CO)$_4$(bpm)](CF$_3$SO$_3$) in methylene chloride at room temperature. λ_{ex} = 355 nm.

The emission quantum yields were about 0.03 for the complexes and did not correlate with emission lifetimes. The variance suggests that there may be more than one decay channel available for excited-state energy loss.

Photosubstitution. The rhenium(I) tetracarbonyl complexes were unstable in solution upon steady-state excitation and underwent photosubstitution. The photosubstitution quantum yields are presented in Table V. The emission spectra of the rhenium(I) tetracarbonyl complexes changed as a function of irradiation time. The spectral changes of the rhenium(I) tetracarbonyl complexes that occurred were followed for [Re(CO)$_4$(phen)]$^+$ and are illustrated in Figure 5. Under steady-state photolysis at 355 nm, the emission maximum at 460 nm decreased in intensity and a new maximum of greater intensity appeared at ~550 nm. An isobestic point was observed at 498 nm indicative of smooth conversion of one species into another. Experimental evidence suggests the process occurring can be understood by eq 5.

$$[\mathrm{Re(CO)_4(phen)}]^+ + \mathrm{CF_3SO_3}^- \rightarrow [\mathrm{Re(CO)_3(phen)(CF_3SO_3)}] + \mathrm{CO} \quad (5)$$

The product [Re(CO)$_3$(phen)(CF$_3$SO$_3$)] was independently synthesized by the reaction of [Re(CO)$_3$(phen)Cl] with Ag(CF$_3$SO$_3$) in CH$_2$Cl$_2$. The AgCl was formed was removed by filtration, and [Re(CO)$_3$(phen)(CF$_3$SO$_3$)] was isolated from the filtrate. It gave a satisfactory elemental analysis[25] and had an emission maximum at 565 nm when excited at 355 nm. At room

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(24) Rillema, D. P.; Allen, G.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 1617.

(25) Anal. Calcd: C, 32.06; H, 1.35; N, 4.67. Found: C, 31.78; H, 1.28; N, 4.61.

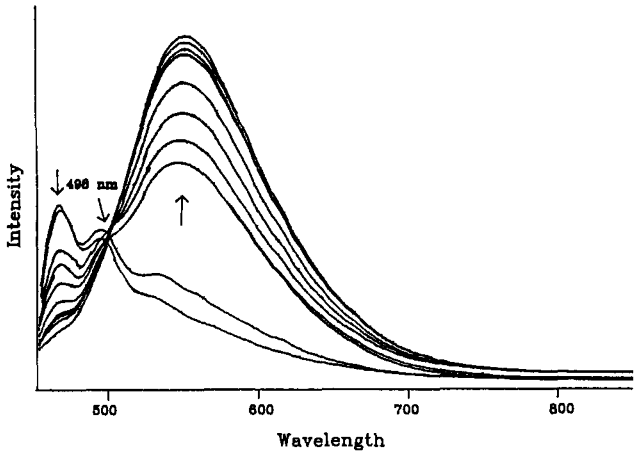

Figure 5. Spectral changes associated with the steady-state photolysis of $[Re(CO)_4(phen)](CF_3SO_3)$ in methylene chloride. $\lambda_{ex} = 355$ nm.

temperature in CH_2Cl_2, it had an emission quantum yield of 0.044 and an excited-state lifetime of 883 ns. The emission quantum yield is larger for $[Re(CO)_3(phen)(CF_3SO_3)]$ than for $[Re(CO)_4(phen)]^+$, in agreement with the increase in luminescence intensity as the reactant was converted to product. The quantum yield for the photosubstitution process in eq 5 was 0.048. Clearly, the ability of the complex to expel CO in favor of the weak-field $CF_3SO_3^-$ ligand indicates the photolability of the tetracarbonyl complexes which followed the order $[Re(CO)_4(dmb)]^+ > [Re(CO)_4(bpm)]^+ > [Re(CO)_4(bpy)]^+ > [Re(CO)_4(phen)]^+$.

Luminescence Quenching. Estimates of excited-state redox potentials for the $[Re(CO)_4(L\text{-}L)]^{+*/0}$ couples obtained by subtracting the ground state $E_{1/2}$ value for the $[Re(CO)_4(L\text{-}L)]^{+/0}$ couple from the emission energy maximum in electronvolts are listed in Table IV. The large, positive values indicate that $[Re(CO)_4(L\text{-}L)]^+$ complexes should be powerful photooxidants. This possibility was examined for $[Re(CO)_4(bpm)]^{+*}$ with several alkoxybenzene compounds known to undergo oxidative electron-transfer quenching.[26]

Stern–Volmer quenching studies were performed with 1,4-dimethoxybenzene, 1,2,3-trimethoxybenzene, 1,3,5-trimethoxybenzene, and anisole, and the results are listed in Table VI. Stern–Volmer constants (K_{SV}) were determined from plots of I_0/I vs [Q] (the alkoxybenzene quencher concentration) and ranged from 542 to 2338 M^{-1}. The calculated k_q values ($k_q = K_{SV}/\tau_0$) ranged from 1.4×10^9 to 5.8×10^9 M^{-1} s^{-1}. An example of the reaction sequence of $[Re(CO)_4(bpm)]^{+*}$ with 1,3,5-trimethoxybenzene (TMB) is shown in eqs 6–8. The photoreaction involves formation

$$[Re(CO)_4(bpm)]^+ \xrightarrow[h\nu]{} [Re(CO)_4(bpm)]^{+*} \qquad (6)$$

$$[Re(CO)_4(bpm)]^{+*} + TMB \xrightarrow[k_q]{} [Re(CO)_4(bpm)] + TMB^+ \qquad (7)$$

$$[Re(CO)_4(bpm)] + TMB^+ \xrightarrow[k_{bet}]{} [Re(CO)_4(bpm)]^+ + TMB \qquad (8)$$

of two highly reactive species, $[Re(CO)_4(bpm)]$ and TMB^+, which undergo rapid back electron transfer to re-form starting materials. Formation of TMB^+ was detected by laser flash photolysis techniques,[27] and the back electron transfer monitored at 600 nm ($\epsilon \simeq 4220$ M^{-1} cm^{-1}) for TMB^+ gave a value of $k_{bet} = 2.2 \times 10^{10}$ M^{-1} s^{-1}.[27]

Table VI. Stern–Volmer and Quenching Rate Constants for the Reaction of $[Re(CO)_4(bpm)]^{+*}$ with Various Alkoxybenzene Compounds[a]

quencher	$E_{1/2}(Q/Q^+)$, V[b]	K_{SV}, M^{-1} [c]	$10^{-9}k_q$, M^{-1} s^{-1} [c]
1,4-dimethoxybenzene	1.34	2338	5.8
1,2,3-trimethoxybenzene	1.42	963	2.4
1,3,5-trimethoxybenzene	1.49	1277	3.2
anisole	1.79	542	1.4

[a] In acetonitrile; $T = 25 \pm 1$ °C; $\lambda_{ex} = 355$ nm ($A_{355} = 0.1 \pm 0.01$). [b] Bard, A. J. *Encyclopedia of Electrochemistry of the Elements*; Marcel Dekker, Inc.: New York, 1978; Vol. XI, p 292. [c] Values are ±10%.

On the basis of redox potentials ($E_{1/2}(Q/Q^+) = 1.76$ V compared to $E_{1/2}[[Re(CO)_4(bpm)]^{*/0}] \simeq 1.51$ V), the rate constant for the reaction of $[Re(CO)_4(bpm)]^{+*}$ with anisole should be less than diffusion controlled. Compared to those of the other quenchers which have diffusion-controlled rates, the quenching rate constant for the anisole reaction is only slightly smaller. The reason for this is unclear; although, the excited-state redox potential estimates are based on irreversible redox couples and may have led to lower limit estimates of $[Re(CO)_4(L\text{-}L)]^{+*/0}$ potentials.

Quenching by Cl^- was also investigated. The reaction of $[Re(CO)_4(bpm)]^{+*}$ with Cl^- was studied in acetonitrile by following changes both in luminescence intensity and in excited-state lifetime as Cl^- was added to the solution. As shown in Figure 6, the quenching process was dynamic; similar Stern–Volmer constants were obtained by luminescence and lifetime changes. The redox potential for the reaction $Cl^- \rightarrow Cl + e^-$ in acetonitrile is reported to be less than 1 V.[28] If redox quenching is playing a role, then a possible mechanism is as outlined in eqs 9–12. As noted from the sequences of reactions, formation of the

$$[Re(CO)_4(bpm)]^+ \xrightarrow[h\nu]{} [Re(CO)_4(bpm)]^{+*} \qquad (9)$$

$$[Re(CO)_4(bpm)]^{+*} + Cl^- \rightarrow ([Re(CO)_4(bpm)]^{+*},Cl^-) \qquad (10)$$

$$([Re(CO)_4(bpm)]^{+*},Cl^-) \rightarrow ([Re(CO)_4(bpm)],Cl) \qquad (11)$$

$$([Re(CO)_4(bpm)],Cl) \rightarrow [Re(CO)_4(bpm)]^+ + Cl^- \qquad (12)$$

solvated ion pair (eq 10) is followed by electron transfer (eq 11), and then the reduced and oxidized species separate according to eq 12, giving back the original starting materials. Flash photolysis techniques were used in an attempt to find evidence for formation of $Cl^\bullet$, which has a characteristic absorption at 335 nm.[29] However, the transient was not observed.[30] Therefore, the dominant reaction pathway may be back electron transfer within the solvent cage, re-forming $[Re(CO)_4(bpm)]^+$ and Cl^-.

Discussion

Preparation General Properties. The emphasis of our work is the design of solar energy photocatalysts based on transition metal complexes. In the work reported here, we have turned our attention to a class of high-energy emitters, rhenium(I) tetracarbonyl complexes. These were previously ill characterized due to difficult synthetic strategies used for their preparation. The preparative methods reported here, removal of Cl^- from $Re(CO)_5Cl$ with $Ag(CF_3SO_3)$ in methylene chloride followed by

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(26) Ballardini, R.; Varani, G.; Indelli, M. T.; Scandola, F.; Balzani, V. *J. Am. Chem. Soc.* **1978**, *100*, 7219.

(27) These experiments were performed at UNC—Chapel Hill using a Spectra Physics Nd:YAG laser system.

(28) Bard, A. J. *Encyclopedia of Electrochemistry of the Elements*; Marcel Dekker: New York, 1973; Vol. 1.

(29) Chateauneuf, J. E. *Chem. Phys. Lett.* **1989**, *164*, 577.

(30) These experiments were carried out by Guillermo Ferraudi at the Notre Dame Radiation Laboratory using a picosecond laser system.

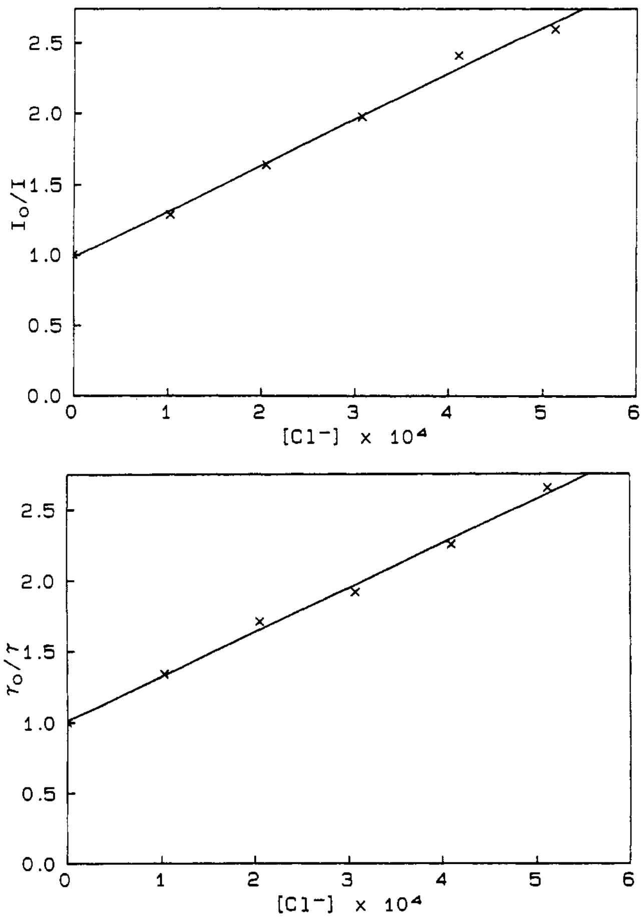

Figure 6. Stern–Volmer plot of (top) luminescence changes and (bottom) lifetime changes of $[Re(CO)_4(bpm)]^+$ with chloride ion as a quencher. The solvent was acetonitrile, degassed with argon. $T = 25$ °C.

reaction with the desired bidentate ligand, readily led to formation of the desired complexes.

The tetracarbonyl complexes have proven to be unstable species both in the solid state and in solution. In the solid state, the complexes undergo thermal rearrangements resulting in uncharacterizable products. Consequently, it was necessary to reprepare the complexes before each physical and photophysical measurement. In solution, the complexes were stable in the dark, but their large photosubstitution quantum yields indicate their extreme sensitivity to light at wavelengths <400 nm. The complexes undergo CO ligand loss which involves ejection of one of the axial CO ligands. The product in the photosubstitution reaction of $[Re(CO)_4(phen)]^+$ with $CF_3SO_3^-$ in methylene chloride gave the same emission spectrum as $[Re(CO)_3(phen)(CF_3SO_3)]$, verifying the mechanism (eq 5) for the substitution process.

Electronic Absorption and Luminescence Properties. As noted under Results, the low-energy absorption spectra for $[Re(CO)_4(bpy)]^+$ and $[Re(CO)_4(dmb)]^+$ differed from those of $[Re(CO)_4(phen)]^+$ and $[Re(CO)_4(dmb)]^+$. The "$d\pi \rightarrow \pi^*$" transitions for the former were sharp and more intense than those of the phen or bpm analogues. According to the Franck–Condon principle,[31] the relatively sharp intense transitions are indicative of a small change in internuclear distance between the ground-state and excited-state species. Normally, $d\pi \rightarrow \pi^*$ transitions are broad, indicative of rather large internuclear bond distance changes between the oxidized metal and the reduced ligand. Broad low-energy absorption spectra were obtained with rhenium(I) tricarbonyl analogues[7,13] and with $[Re(CO)_4(phen)]^+$ and $[Re(CO)_4(bpm)]^+$. Thus the $d\pi \rightarrow \pi^*$ transitions in $[Re(CO)_4(bpy)]^+$ and $[Re(CO)_4(dmb)]^+$ may be masked. The emission spectra certainly are in accord with this explanation.

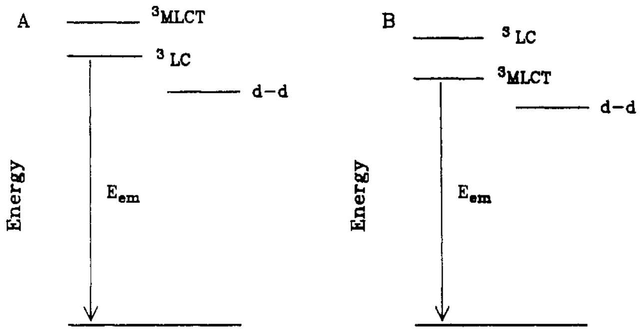

Figure 7. Ground-state–excited-state energy scheme for (A) ³LC emitters and (B) ³MLCT emitters.

Emission manifolds of $[Re(CO)_4(phen)]^+$, $[Re(CO)_4(bpy)]^+$, and $[Re(CO)_4(dmb)]^+$ were structured, while the one for $[Re(CO)_4(bpm)]^+$ was unstructured. The structured emission for the corresponding rhenium tricarbonyl complexes resembled emission from bpy, dmb, and phen;[4c] the nonstructured emission occurred for $[Re(CO)_4(bpm)]^+$ at lower emission energy than that for the other tetracarbonyl complexes and was also broad. In earlier work on rhenium tricarbonyl complexes, molecules undergoing emission that was structured were designated ³LC emitters; those with unstructured emission manifolds were assigned as ³MLCT emitters.[4c] More recently, Demas and co-workers[13] have examined the room- and low-temperature luminescence from $Re(CO)_3(L\text{-}L)X$, where L-L = bpy or phen and X = substituted pyridines or quinolines, and found that the emission can be switched from ³MLCT to ³LC phosphorescence on cooling from room temperature to 77 K. They attributed this behavior to the fact that the energy of the ³MLCT state can be raised as the temperature is lowered and brought above the energy of the ³LC state. On the basis of these prior results, emission decay from the excited states of the tetracarbonyl complexes can be explained using Figure 7. In Figure 7A, the ³LC state is populated and structured emission is observed; in Figure 7B, the ³MLCT state is populated and unstructured emission is observed.

Experimentally, we were unable to assign the photosubstitution process to population of the ³LF or ³MLCT state, where the ³LF state would lie at an energy level comparable to (or below) those of the lowest lying ³LC or ³MLCT states. Argument can be raised for weakened CO bonding in both cases. Labilization of ligands upon population of a ³LF state is well documented. One might also argue that CO loss could result from populating a ³MLCT excited state. Oxidation of the metal center should weaken π bonding to CO, and since CO is bonded largely by π bonding, labilization by a dissociative mechanism may follow. Alternatively, an associative pathway in which the oxidized metal center is more prone to attract an anionic ligand is reasonable.

The observed photosubstitution quantum yield for $[Re(CO)_4(dmb)]^+$, represented by eq 5, was examined in the presence of TMB, which quenches the excited state according to eq 7. The observed photosubstitution quantum yield decreased linearly as the concentration of TMB increased. This evidence is in accord with Figure 7A; namely, the quenching and photosubstitution processes occur from a common origin, which in this case is the ³LC state. Interception of the energy from this state by TMB diminishes the intersystem-crossing quantum efficiency and lowers the photosubstitution quantum yield.

Ground-State and Excited-State Behavior. The only ground-state redox activity in the +2.0 to −2.0 V vs SSCE range was in the reduction region. The first reduction for the complexes was associated with addition of an electron to the π^* energy level of the heterocyclic ligand (eq 3). The reductions followed the order $[Re(CO)_4(bpm)]^+$ (−0.87 V) > $[Re(CO)_4(phen)]^+$ (−1.20 V) > $[Re(CO)_4(bpy)]^+$ (−1.22 V) > $[Re(CO)_4(dmb)]^+$ (−1.30 V). This

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[31] Balzani, V.; Carassiti, V. *Photochemistry of Coordination Compounds*; Academic Press: New York, 1970.

ordering followed the same trend as the reduction potentials of the free ligands: bpm (−1.80 V) > phen (−2.04 V) > bpy (−2.18 V) > dmb (−2.24 V).[32] A plot of $E_{1/2}[[\mathrm{Re(CO)_4(L\text{-}L)}]^{+/0}]$ vs $E_{1/2}[(\mathrm{L\text{-}L})^{0/-}]$ was linear. The slope of the line was near 1 (0.94 ± 0.19) and had a correlation coefficient of 0.93.

The first prominent high-energy feature of the emission manifold places the emitting state approximately 2.5 eV above the ground state in the tetracarbonyl complexes. This is approximately 0.3–0.5 eV higher in energy than found in rhenium tricarbonyl complexes[4,7,13] and on a par with emission energies found in certain iridium, platinum, and rhodium complexes.[33] The higher energy emitting states provide additional driving force for effecting electron-transfer events. The potentials ranged from 1.49 to 1.55 V for the $[\mathrm{Re(CO)_4(L\text{-}L)}]^{+*/0}$ redox couples. An attempt was made to use this driving force for reductive quenching of $[\mathrm{Re(bpm)(CO)_4}]^+$ by $\mathrm{Cl^-}$ in order to generate $\mathrm{Cl_2}$. Excited-state quenching occurred. Unfortunately, $\mathrm{Cl_2}$ was not observed as the product, presumably due to rapid back electron transfer within the solvent cage. Alternatively, one might argue that if Cl atoms were generated, they would rapidly abstract a proton from the solvent to form HCl.

Photosubstitution. One unique feature of the tetracarbonyl complexes is that photolysis of a highly luminescing complex results in a product that has greater luminescence intensity than the parent. This observation contradicts the energy gap law,[34] where k_{nr}, the nonradiative decay rate constant, increases as the energy gap between the excited state and ground state decreases. One possible explanation is that the two excited states, the one for the parent and the one for the product, differ in spin multiplicity and, therefore, display different excited-state properties. Another explanation, consistent with the lack of the dependence of the emission quantum yield on the energy gap, is the presence of more than one decay channel from higher energy excited states. Examination of transient absorption spectra and delay emission techniques are currently being employed to seek an answer to this question.

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(33) Watts, R. J. *Comments Inorg. Chem.* **1991**, *11*, 303.

(34) (a) Caspar, J. V.; Kober, E. M.; Sullivan, B. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 630. (b) Kober, E. M.; Caspar, J. V.; Lumpkin, R. S.; Meyer, T. J. *J. Phys. Chem.* **1986**, *90*, 3722. (c) Caspar, J. V.; Sullivan, B. P.; Meyer, T. J. *Chem. Phys. Lett.* **1982**, *91*, 91. (d) Lumpkin, R. S.; Meyer, T. J. *J. Phys. Chem.* **1986**, *90*, 5307.