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Long-Range Electron Transfer Quenching and Recombination in a Rhenium−Pyridiniumylacrylamide Complex

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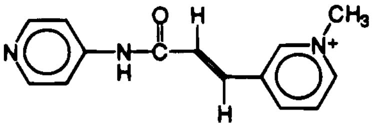
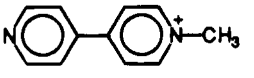
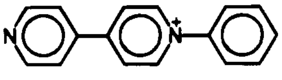
A subject of continuing photochemical interest is photoinduced electron and energy transfer in chromophore−quencher complexes and the development of new acceptor and donor ligands. The ligand pyAm-Mepy$^+$ (*N*-(4-pyridyl)-β-(*N*-methylpyridinium-3-yl)acrylamide) was used previously as an electropolymerizable ligand in the formation of metallopolymeric films.[1] Electrochemical measurements on *cis*-[Ru^{II}(bpy)$_2$(pyAm-Mepy$^+$)$_2$]$^{4+}$ (bpy = 2,2′-bipyridine) revealed an irreversible reduction, characteristic of the *N*-methylpyridinium group, at −1.0 V (vs SCCE) in CH$_3$CN, suggesting that the ligand could function as an electron acceptor. Photophysical measurements have been reported for Re^I complexes of the type [(4,4′-(X$_2$)-bpy)Re^I(CO)$_3$(A)]$^{2+}$, where X is an electron-donating or -withdrawing substituent and A an electron-accepting ligand, such as *N*-methyl-4,4′-bipyridinium (monoquat, MQ$^+$) or *N*-benzyl-4,4′-bipyridinium (benzoquat, BzQ$^+$).[2] These studies have shown that metal-to-ligand charge transfer (MLCT) excitation of [(bpy)Re^I(CO)$_3$(MQ$^+$)]$^{2+}$, for example, leads to rapid formation of the lowest lying MLCT excited state, [(bpy)Re^{II}(CO)$_3$(MQ$^•$)]$^{2+}$ (Scheme 1), in which there is strong electronic coupling between Re^{II} and the MQ$^•$ acceptor ligand. The final state is reached by rapid intramolecular bpy$^{•-}$ → MQ$^+$ electron transfer, k_q in Scheme 1, or by direct excitation, $h\nu'$.[3]

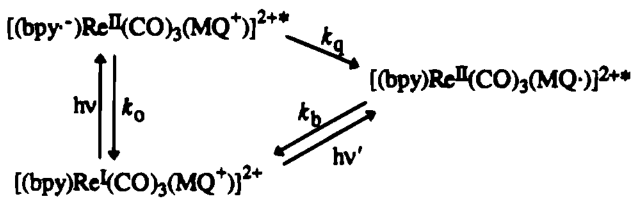

pyAm-Mepy$^+$


(MQ$^+$)


(BzQ$^+$)

The use of the olefin-bridged pyridinium (pyAm-Mepy$^+$) as an electron acceptor provides a contrast in behavior even though the ligand is pyridinium-based. Unlike MQ$^+$ or BzQ$^+$ as acceptor ligands, there is no orbital basis for significant electronic coupling between the pyridinium quencher and the metal. It shares this property with bpy-based pyridinium acceptors such as [bpy−(CH$_2$)$_n$−PQ^{2+}], n = 1 or 2.[4]

Scheme 1



Following Re^I → dmb MLCT excitation of [(dmb)Re^I(CO)$_3$(pyAm-Mepy$^+$)]$^{2+}$ (dmb is 4,4′-dimethyl-2,2′-bipyridine), electron transfer is expected to lead to a Re^{II}−pyridinium radical pair separated by a relatively rigid, eight-atom bridge. In contrast to the case shown in Scheme 1, where return to the ground state occurs by both radiative and nonradiative decay via the MQ$^+$-based MLCT excited state, in [(dmb)Re^{II}(CO)$_3$(pyAm-Mepy$^•$)]$^{2+*}$, return to the ground state occurs by back electron transfer in the inverted region between a weakly coupled, electron-transfer donor−acceptor pair, (pyAm-Mepy$^•$),(Re^{II}).

Experimental Methods

Materials. All chemicals were reagent grade and were used as received. Acetonitrile for spectral, electrochemical, and photophysical experiments was Burdick and Jackson spectrograde and was degassed by Ar bubbling for 15 min prior to measurements. The ligand *N*-(4-pyridyl)-β-(*N*-methylpyridinium-3-yl)acrylamide (pyAm-Mepy$^+$) was available from a previous study.[1]

The new complex [(dmb)Re^I(CO)$_3$(pyAm-Mepy$^+$)]$^{2+}$ was prepared as the PF$_6^-$ salt by means of a technique previously described with slight modification.[5] Solid [(dmb)Re^I(CO)$_3$(TFMS)] (83 mg, 0.14 mmol; TFMS = trifluoromethanesulfonato anion) was dissolved in 60 mL of ethanol/water (2:1 v/v) and bubbled with Ar for $^1/_2$ h. The ligand salt [pyAm-Mepy$^+$](PF$_6$) (79.5 mg, 0.2 mmol) was added, and the solution was heated at reflux under Ar in the dark for 3 h and then rotoevaporated until a yellow precipitate appeared. It was filtered off and washed with water. This solid dissolved in 5 mL of CH$_3$CN was adsorbed onto an alumina column (5 × 2.5 cm). Free ligand and unreacted complex were eluted with 1:1 CH$_3$CN/toluene, and the desired 2+ ion was eluted with pure CH$_3$CN. The eluate was rotoevaporated, the residue was dissolved in 5 mL of CH$_3$OH/water (3:1 v/v), and 0.5 g of NH$_4$PF$_6$ in 5 mL of water was added. A precipitate appeared after cooling on ice for $^1/_2$ h; this was collected by filtration, washed with water and ether, and then recrystallized from CH$_3$CN/ether. Yield: 22 mg (15%). The HPLC showed one band. Anal. Calcd for C$_{29}$H$_{26}$N$_5$O$_4$ReP$_2$F$_{12}$·2H$_2$O: C, 34.12; H, 2.96; N, 6.86. Found: C, 34.58; H, 2.63; N, 6.84. IR (KBr): 2029 and 1917 cm^{-1} (ν(CO)). UV−vis (CH$_3$CN), λ_{max} (ϵ): 366 sh (2900), 326 sh (15 000), 304 (25 639), 316 (23 500), 270 nm (27 345 M^{-1} cm^{-1}). ^{1}H NMR (CD$_3$CN): 9.00 (2 H, d), 8.76 (1 H, s), 8.58 (3 H, m), 8.22 (2 H, s), 8.03 (3 H, m), 7.58 (5 H, m), 6.81 (1 H, d), 4.28 (3 H, s), 2.54 (6 H, s), 2.13 ppm (4 H, d).

Measurements. HPLC chromatography was performed on a Perkin-Elmer Series 4 liquid chromatograph with an LC-95 UV−visible spectrophotometer detector set at λ = 300 nm. The column used was an Aquapore CX-300 column (1.0 × 10.0 cm) of poly(DL-Asp)−silica (Brownlee) with a gradient of 0−400 mM KBr in 2:3 (v/v) CH$_3$CN/0.6 mM phosphate buffer (pH 7.2). ^{1}H NMR spectra were recorded on a Bruker AC 200 spectrometer, and all shifts are referenced to TMS.

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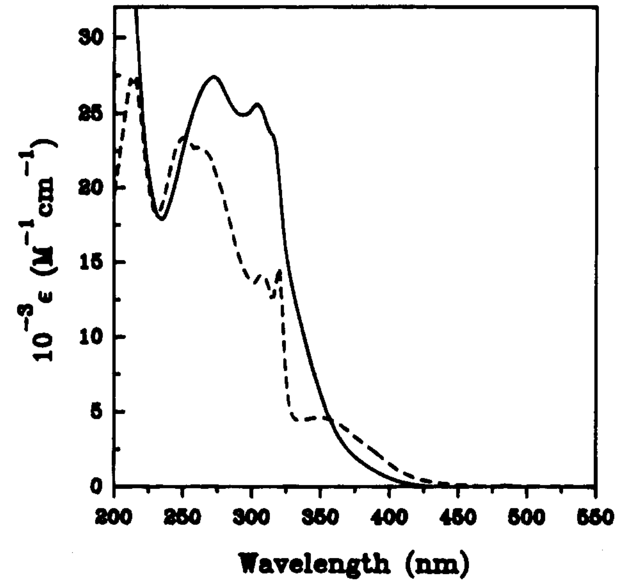


Figure 1. UV–visible absorption spectra of $[(dmb)Re^{I}(CO)_3(pyAm\text{-}Mepy^+)]^{2+}$ (solid line) and $[(dmb)Re^{I}(CO)_3(4\text{-}Etpy)]^+$ in CH_3CN at 22 °C.

Chemical analyses were carried out by Oneida Research Services, Whitesboro, NY. IR spectra were recorded as KBr disks on a Mattson Galaxy Series FTIR 5000 instrument. UV–visible spectra were recorded on a HP8451A diode-array spectrophotometer. Cyclic voltammograms were obtained on a PAR potentiostat/galvanostat in an H-type cell, with Pt as working and auxiliary electrodes and Ag/AgCl as a reference electrode. The potential of this electrode was +310 mV vs SSCE. Emission spectra were obtained with a SPEX Fluorolog F212 photon-counting spectrofluorimeter and were corrected for detector sensitivity. Transient absorption and lifetime measurements were conducted on the nanosecond time scale with a laser system previously described.[2d]

Results

The UV–visible spectrum of the ligand ($pyAm\text{-}Mepy^+$) in CH_3CN features prominent absorption bands at 316 and 236 nm. The absorption of the ligand overlaps with the Re → dmb MLCT band (λ_{max} = 350 nm) in the 330–360 nm region in $[(dmb)Re^{I}(CO)_3(pyAm\text{-}Mepy^+)]^{2+}$, Figure 1, and typical $\pi \rightarrow \pi^*$ bands are observed at λ = 320–240 nm. The electron-withdrawing effect of the $-Am\text{-}Mepy^+$ substituent relative to $-Et$ in 4-Etpy shifts the Re → dmb band slightly to higher energy. There is no evidence for an additional low-energy band attributable to Re → $pyAm\text{-}Mepy^+$ charge transfer. In cyclic voltammograms recorded in CH_3CN (or in very dry THF) an irreversible wave appeared at $E_{p,c} = -1.04$ V (vs SCE), corresponding to the reduction of $pyAm\text{-}Mepy^+$. Pyridinyl radicals, once formed, are known to polymerize in solution.[6] In the voltammogram there was also a reversible wave at $E_{1/2} = -1.30$ V (vs SCE) for the $dmb^{0/-}$ couple and a quasi-reversible wave, at $E_{1/2}$ = 1.67 V (vs SCE) for the $Re^{II/I}$ couple. These assignments are reasonable based on the properties of related complexes.[7]

The complex $[(dmb)Re^{I}(CO)_3(pyAm\text{-}Mepy^+)]^{2+}$ luminesces at 22 °C in CH_3CN with λ_{max} = 575 nm, Φ_{em} = 0.004, and a lifetime τ = 18 ns. When compared with the model, $[(dmb)Re^{I}(CO)_3(4\text{-}Etpy)]^+$ (4-Etpy = 4-ethylpyridine) (λ_{max} = 581 nm, Φ_{em} = 0.035, τ = 282 ns),[7b] it appears that the initial $Re^{II}(dmb^{\bullet -})$ excited state is largely quenched by electron transfer to the more easily reduced $pyAm\text{-}Mepy^+$ ligand. No new, low-energy emission attributable to $[(dmb)Re^{II}(CO)_3(pyAm\text{-}Mepy^{\bullet}\text{-})]^{2+}$ was detected.

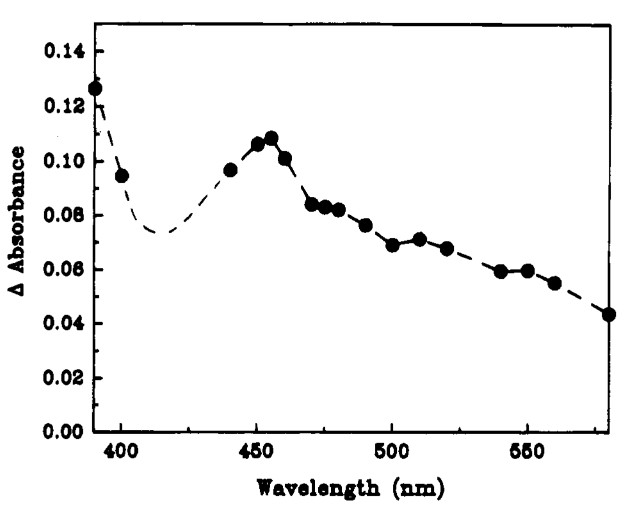


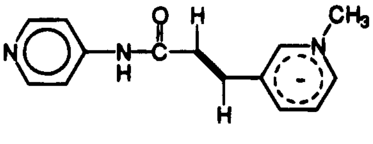
Figure 2. Transient absorption difference spectrum of $[(dmb)Re^{I}(CO)_3(pyAm\text{-}Mepy^+)]^{2+}$ (~2 × 10^{-4} M) in CH_3CN at 22 °C acquired 20 ns after laser excitation with a 420-nm, 4-ns laser pulse (1.2 mJ/pulse).

Transient absorption experiments on $[(dmb)Re^{I}(CO)_3(pyAm\text{-}Mepy^+)]^{2+}$ in CH_3CN detected the formation of an intermediate following laser-flash excitation with a 420-nm, 4-ns pulse. The new transient absorption feature appeared at λ_{max} = 455 nm (Figure 2). It formed during the laser pulse and decayed with $\tau_{22 °C}$ = 39 ns ($k_b = 2.6 \times 10^7$ s^{-1}).

Discussion

The observation of $Re^{II}(dmb^{\bullet -})$ quenching in $[(dmb^{\bullet -})Re^{II}(CO)_3(pyAm\text{-}Mepy^+)]^{2+*}$ and the appearance of a new intermediate with λ_{max} = 455 nm by transient absorption spectroscopy indicate that MLCT excitation to form $[(dmb^{\bullet -})Re^{II}(CQ)_3(pyAm\text{-}Mepy^+)]^{2+}$ is followed by intramolecular electron transfer to give $[(dmb)Re^{II}(CO)_3(pyAm\text{-}Mepy^{\bullet})]^{2+}$, Scheme 2. It is possible to estimate k_q from $k_q = (1/\tau - 1/\tau_0)$,[8] where τ is the lifetime of the emitting state in the chromophore–quencher complex (18 ns) and τ_0 the lifetime of the model, $[(dmb^{\bullet -})Re^{II}(CO)_3(4\text{-}Etpy])^{+*}$ (282 ns),[7b] from which $k_q \sim 5.2 \times 10^7$ s^{-1}. This value and $k_0 = 1/\tau_0$ are cited in Scheme 2.

The lifetime of the transient observed following laser flash photolysis monitored at 550 nm is 39 ns ($k_b = 2.6 \times 10^7$ s^{-1}), Figure 3. The new transient absorption feature associated with its formation is consistent with a $\pi \rightarrow \pi^*$ absorption of the *N*-methylpyridinium-3-yl radical,



This assignment is reinforced by comparison with spectra of related radicals obtained by pulse radiolysis, such as the *N*-methylnicotinamide radical, which absorbs at λ_{max} = 445 nm in aqueous solutions.[9]

The estimated rate constant for quenching, k_q, is comparable to k_b for back electron transfer, and the two processes should be kinetically coupled. This is evident in the 390–400 nm region, where both the $Re^{II}(dmb^{\bullet -})$ and $Re^{II}(pyAm\text{-}Mepy^{\bullet})$ states

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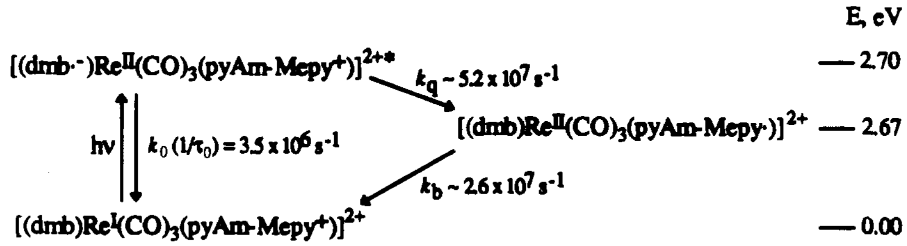
Scheme 2



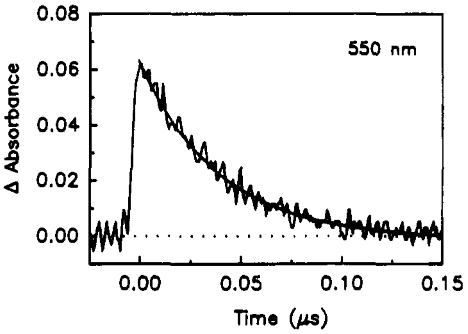


Figure 3. Kinetic decay trace for $[(dmb)Re^I(CO)_3(pyAm\text{-}Mepy^+)]^{2+}$ ($\sim 2 \times 10^{-4}$ M) in CH_3CN at 22 °C acquired at 550 nm after laser excitation with a 420-nm, 4-ns laser pulse (1.2 mJ/pulse).

absorb appreciably. All of the kinetic decay traces (from which the transient absorption spectrum shown in Figure 2 was extracted) were subjected to a more detailed global analysis,[10] the results of which were consistent with the magnitudes of k_q and k_b reported in Scheme 2.

We conclude that pyAm-Mepy$^+$ is an efficient quencher of the MLCT excited state in $[(dmb^{\bullet-})Re^{II}(CO)_3(pyAm\text{-}Mepy^+)]^{2+}$, even at a separation distance of ~14 Å and a driving force of ≤ 0.1 eV. The back electron transfer reaction, k_b in Scheme 2, falls deeply in the inverted region with $\Delta G° \cong -\Delta E_{1/2} = [E_{1/2}(Re^{II/I}) - E_{p,c}(pyAm\text{-}Mepy^{+/0})] = -2.67$ eV from the electrochemical measurements.

From the fundamental point of view, the back electron transfer reaction is an interesting case since it involves a metal-based redox couple at which only low-frequency metal–ligand vibrations at the metal should be appreciably coupled to the electron transfer.[11] The ring stretching modes at pyAm-Mepy$^+$ are expected to dominate the role of energy acceptor. We are currently extending the series by varying the substituents at bpy in order to investigate the effect of $\Delta G°$ on k_b.

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