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Absorption and Luminescence Spectroelectrochemical Characterization of a Highly Luminescent Rhenium(II) Complex

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Luminescent transition metal complexes have been the focus of considerable research efforts over the past two decades. Alterations in the molecular design allow the tuning of the excited state in order to achieve optimum chemical and excited-state properties. As a result, excited states of luminescent transition metal complexes have been exploited for numerous applications such as (i) photocatalysts in energy conversion schemes,[1] (ii) precursors for the development of supramolecular photocatalysts,[2] (iii) molecular probes for biomolecules,[3] and (iv) the development of luminescence-based analytical sensors.[4]

Traditionally, investigations of the photophysical properties of transition metal complexes have been directly dependent on the ability to synthesize and purify a complex in the desired oxidation state. We have recently developed a versatile long optical path spectroelectrochemical cell for use in conjunction with luminescence spectroscopy.[5] The cell permits in situ generation and photophysical investigations of synthetically inaccessible oxidation states, provided the target oxidation state is electrochemically accessible from the parent complex and stable in solution. In this communication we report the absorption and luminescence spectroelectrochemical characterization of the Re(II/I) redox couple of $[Re(dmpe)_3]^+$ in acetonitrile solution, where dmpe denotes 1,2-bis(dimethylphosphino)ethane. Electrogenerated $[Re(dmpe)_3]^{2+}$ is found to be highly emissive in fluid solution. The emission is described as a rare example of room temperature luminescence in solution from a transition metal complex with a ligand-to-metal charge-transfer (LMCT) excited state.[6]

$[Re(dmpe)_3]^+$ is an air-stable white complex, which can be synthesized as the PF_6^- or the $CF_3SO_3^-$ salt by a literature method.[7] Cyclic voltammetry of a 1 mM solution of $[Re(dmpe)_3]^+$ in 0.1 M $(n\text{-Bu})_4NPF_6/CH_3CN$ at a platinum disk electrode was performed in a conventional electrochemical cell at 100 mV/s. $E^{\circ\prime}$ is +0.330 V versus the Ag/AgCl reference electrode with $\Delta E_p = 60$ mV and $i_{pa}/i_{pc} = 1.02$. The electrochemical response of the Re(II/I) redox couple fulfills the standard criteria for a diffusion-controlled reversible one-electron oxidation[8] and is consistent with electrochemical measurements of $[Re(dmpe)_3]^+$ in dimethylformamide.[9] The cyclic voltammogram of a similar solution in the luminescence spectroelectrochemical cell gives $E^{\circ\prime}$, ΔE_p, and i_{pa}/i_{pc} values of +0.320 V, 200 mV, and 1.00, respectively. The larger value for ΔE_p is inherent to the electrode geometry and configuration used in the spectroelectrochemical cell.[5]

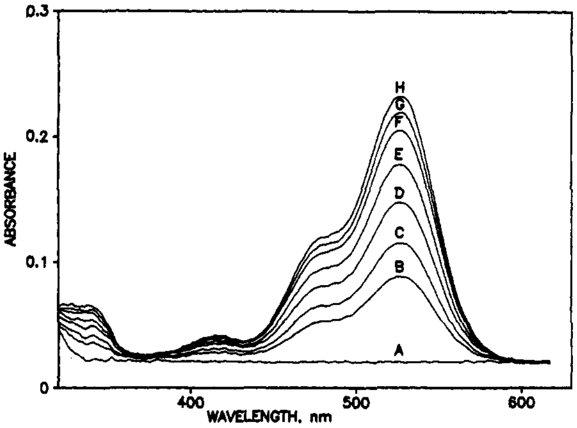

Figure 1. Spectra recorded during an absorption spectropotentiostatic experiment of 0.14 mM $[Re(dmpe)_3]^+$ in 0.1 M $(n\text{-Bu})_4NPF_6/CH_3CN$ in the luminescence spectroelectrochemical cell in the absorption mode. Applied potentials in volts vs Ag/AgCl are as follows: (A) −0.131; (B) +0.316; (C) +0.329; (D) +0.344; (E) +0.361; (F) +0.384; (G) +0.406; (H) + 0.531.

The results from an absorption spectropotentiostatic experiment in 0.1 M $(n\text{-Bu})_4NPF_6/CH_3CN$ in the luminescence spectroelectrochemical cell are shown in Figure 1. Each spectrum was recorded at the applied potential after equilibrium conditions were established in the cell. In this instance, a 20-min equilibration time was determined to be sufficient by independent chronoabsorptometry measurements. $[Re(dmpe)_3]^+$ shows no absorptions in the visible region (spectrum A); two absorptions are observed in the UV at 220 and 252 nm. After oxidation to Re(II), the two UV peaks coalesce into a single peak at 232 nm,[10] and new absorption bands grow in the visible region at 340 nm (430 M^{-1} cm^{-1}), 418 (205), 482 (990), and 530 (2110) (Figure 1, spectrum H). A Nernst plot[11] of the data at 530 nm from Figure 1 yields $E^{\circ\prime} = +0.335$ V vs Ag/AgCl and $n = 1.0$.

The absorption maxima observed in the spectroelectrochemistry experiments are in agreement with the UV–visible data in acetonitrile previously reported by Deutsch and co-workers.[7,12] The UV absorption bands in both oxidation states of the complex are assigned to dmpe intraligand bands. This assignment is based on the insensitivity of the UV absorption maxima to the nature of the metal center in analogous $[M(dmpe)_3]^{2+/+}$ (M = Tc, Re)[7,12,13] complexes and the fact that the free ligand exhibits an absorption maximum at 204 nm in deoxygenated acetonitrile solution. UV absorption of the related tertiary phosphine, $P(Me)_3$, has been observed at 201 nm and attributed to an n to σ^* transition.[14] The intraligand transition is best described as $\sigma_b \rightarrow \sigma^*$ in the Re complex. The lowest energy absorption band for

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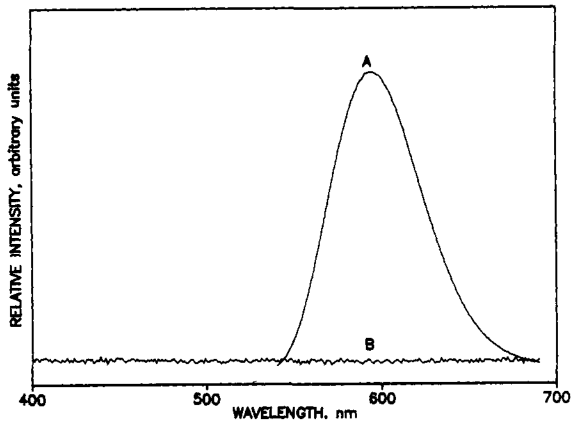

Figure 2. Uncorrected emission spectra of 0.14 mM (A) $[Re(dmpe)_3]^{2+}$ (λ_{ex} = 530 nm) and (B) $[Re(dmpe)_3]^+$ (λ_{ex} = 220 nm) in 0.1 M (n-Bu)$_4NPF_6/CH_3CN$ in the luminescence spectroelectrochemical cell.

$[Re(dmpe)_3]^{2+}$ is tentatively assigned as a LMCT transition. In contrast to the UV absorptions, the visible absorption maxima of $[Re(dmpe)_3]^{2+}$ are shifted to higher energies relative to $[Tc(dmpe)_3]^{2+}$; the lowest energy absorption maximum for $[Tc(dmpe)_3]^{2+}$ is 569 nm (810 M^{-1} cm^{-1}).[13] Consistent with this observation is the fact that electrochemical measurements for the $[M(dmpe)_3]^{2+/+}$ complexes indicate that the Re(II) complex is harder to reduce by 80 mV.[7] Cariatti et al.[15] have reported LMCT transitions at wavelengths greater than 400 nm for Re(II), Re(III), and Re(IV) phosphine complexes, which they have assigned as $\sigma(P) \rightarrow d\pi(Re)$ in nature. By analogy and considering the relatively high molar absorptivity of $[Re(dmpe)_3]^{2+}$, the lowest energy absorption(s) in $[Re(dmpe)_3]^{2+}$ may also involve a LMCT transition from $\sigma(P)$ to $d\pi(Re)$. If octahedral symmetry is assumed for $[Re(dmpe)_3]^{2+}$, the d electrons in the low-spin configuration will occupy the t_{2g} orbitals. In the case of d^5 Re(II), the t_{2g} and e_g levels can serve as the terminus for charge transfer, whereas for low-spin d^6 Re(I) a transition to the e_g level is required. The lack of low-energy transition(s) in the spectrum of $[Re(dmpe)_3]^+$ supports the involvement of the $d\pi(t_{2g})$ level in the low-energy transition(s) of the Re(II) complex.

Comparative uncorrected emission spectra for the Re(I) and Re(II) complexes are shown in Figure 2. Excitation of a deoxygenated acetonitrile solution of $[Re(dmpe)_3]^+$ at 220 or 252 nm yields no detectable emission in a standard luminescence cell or in the luminescence spectroelectrochemical cell (Figure 2B). However after oxidation at +0.53 V in the luminescence spectroelectrochemical cell and excitation into the lowest energy absorption band at 530 nm, $[Re(dmpe)_3]^{2+}$ is luminescent with an uncorrected emission maximum at 593 nm (Figure 2A); the corrected emission maximum is 600 nm. The emission band is observed to overlap the lowest energy absorption with a Stokes shift of 2200 cm^{-1}. The corrected excitation spectrum is shown in Figure 3 and parallels the Re(II) visible absorption spectrum. An additional excitation band is observed at 277 nm, which is not observed in the absorption spectrum presumably because the 277-nm band is masked by the more intense 232-nm absorption.

$[Re(dmpe)_3]^{2+}$ is highly emissive in acetonitrile solution with a quantum efficiency (ϕ) 50% greater than that of the MLCT emission of $[Ru(bpy)_3]^{2+}$, where bpy is 2,2′-bipyridine. The quantum efficiency was measured[16] in the luminescence spectroelectrochemical cell to be 0.066 (±0.008) and 0.064 (±0.007) by comparison to standard solutions of $[Ru(bpy)_3]^{2+}$ in water and fluorescein in 0.1 M NaOH, respectively.[17] In conjunction with the excited-state lifetime (τ), which was determined to be 16 ns,[19] an estimate of the radiative rate constant from the ratio

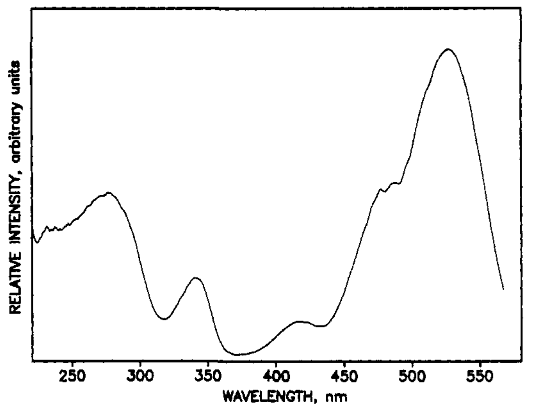

Figure 3. Corrected excitation spectrum of 0.14 mM $[Re(dmpe)_3]^{2+}$ in 0.1 M (n-Bu)$_4NPF_6/CH_3CN$ in the luminescence spectroelectrochemical cell: λ_{em} = 593 nm.

ϕ/τ is 4×10^6 s^{-1}. The relatively large radiative rate constant with a short excited-state lifetime is consistent with a spin-allowed emission. As a result of these observations and the fact that the emission maximum is independent of the excitation wavelength, the emission most probably originates from the lowest energy LMCT state. An approximation of the radiative rate constant can also be obtained from the spectral features of the lowest energy absorption band and eq 1,

$$k = \tau^{-1} \approx (3 \times 10^{-9})\epsilon_{\max}\bar{\nu}^2\Delta\bar{\nu} \qquad (1)$$

where $\bar{\nu}$ is the maximum wavelength of the absorption band in cm^{-1} and $\Delta\bar{\nu}$ is the width of the band at half-height in cm^{-1}.[20] In support of the LMCT assignment, a comparable rate constant of 5×10^6 s^{-1} is estimated with $\bar{\nu}$ = 18 868 cm^{-1} (530 nm) and $\Delta\bar{\nu}$ = 2200 cm^{-1}. Emission from either an intraligand or ligand field excited state is considered unlikely. In the first case, the energy of the lowest energy absorption band and the maximum emission wavelength are clearly out of the range expected for phosphine-based absorption and emission.[21] Although proximate d–d states may promote deactivation of the excited state, ligand field emission from the lowest energy excited state of a low-spin d^5 metal complex would be spin forbidden and require a longer lifetime than is observed for $[Re(dmpe)_3]^{2+}$.

Luminescence from LMCT excited states of transition metal complexes is rare with the few examples having the d^0, d^5, or d^{10} electron configurations.[6,22,23] Examples of emissive LMCT d^5 systems are limited to $[Ru(CN)_6]^{3-}$ at 77 K,[23] which is analogous to $[Re(dmpe)_3]^{2+}$ in that it is a complex of a reducible metal and an oxidizable strong field π-acid ligand, and $(\eta^5\text{-}C_5Me_5)_2Re$,[6d] which exhibits a weak room temperature emission at 605 nm in toluene. $[Re(dmpe)_3]^{2+}$ is a novel example of a d^5 complex that is highly luminescent in fluid solution.

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