those presented here. Other surfaces such as membranes can be explored. Applications to assays that involve enzyme labels (e.g., immunoassays and DNA probe assays) and to biosensors are anticipated.

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Interligand and Charge-Transfer Emission from $[Ru(bpy)(HDPA)_2]^{2+}$: A Dual Emitting Ru(II) Complex

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Tris-chelated complexes with bidentate α,α'-diimine ligands such as bipyridine and phenanthroline have been shown to have single ligand localized emitting states.[1,2] Therefore, in mixed-ligand complexes a dual emission might be expected since localized states involving each type of ligand would exist. Such a result occurs for the $[Rh(bpy)_n(phen)_{3-n}]^{2+}$ (n = 1, 2) complexes where a π-π^* emission is observed from both a coordinated bpy and a coordinated phen.[3] This type of mulitple luminescence is termed "spatially isolated" since the emissions are from spatially distinct regions of the molecule.[4] A second type of dual emission is found for $[Ir(phen)_2Cl_2]^+$ where both a d-d* and a d-π^* emission occur.[5] Since these emitting states have different orbital origins, this type of phenomena is termed "distinct orbital".[4] Even though photoselection data for $[Ru(bpy)_3]^{2+}$ indicates a single ligand emission,[1,2] no dual luminescence could be characterized for the $[Ru(bpy)_n(phen)_{3-n}]^{2+}$ (n = 1, 2) ions[6] due to the fact that the MLCT emissions from the two chromophores have virtually identical energies, contours, and lifetimes, thus precluding energy or time resolution. Other Ru(II) mixed-ligand complexes[7,8] obey Kasha's rule[4] with relaxation occurring from the higher energy chromophore to the lower energy radiative chromophore. In Ru(II) complexes involving the nonplanar ligand HDPA (2,2'-dipyridylamine) which has an amine function ~0.2 nm from the π system of an adjacent ligand,[9] the electrochemistry[10] is different from $[Ru(bpy)_3]^{2+}$, the former species being easier to oxidize but more difficult to reduce. Spectroscopy of Ru complexes with an HDPA ligand[11] has shown an emission close in energy to the emission observed for $[Ru(bpy)_3]^{2+}$, inferring mixed-ligand complexes of HDPA and bpy might have a detectable dual luminescence. We now wish to report the first dual emission for a Ru(II) complex, since to date no bona fide Ru(II) dual emission has been reported.[12-14]

Table I. Low-Temperature (77 K) Lifetimes Measured at the Emission Maxima

complex	solvent	$\bar{\nu}$, cm^{-1}	77 K, us[a]
$[Ru(bpy)(HDPA)_2]^{2+}$	H_2O	14 800	2.54 ± 0.09
	ETOH	16 400	13.3 ± 0.5
	ETOH	14 900	5.04 ± 0.3
$[Ru(bpy)_2(HDPA)]^{2+}$	H_2O	15 500	2.91 ± 0.08
	ETOH	16 400	4.60 ± 0.11
$[Ru(bpy)_3]^{2+}$	H_2O	16 900	3.67 ± 0.14
	ETOH	17 300	5.94 ± 0.29

[a] Errors are the calculated 95% confidence limits.

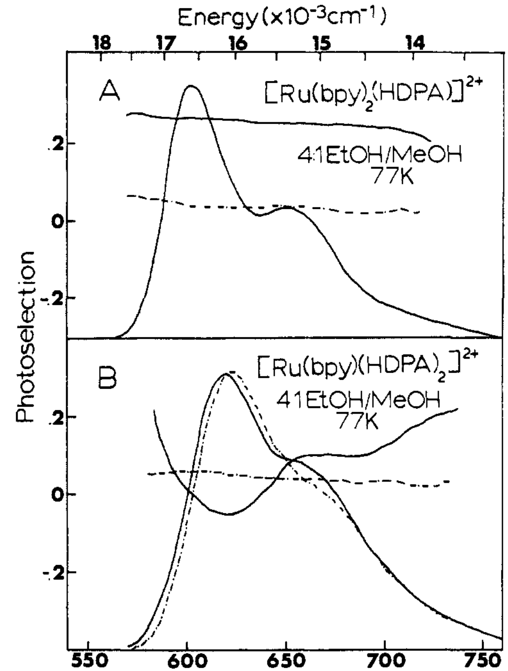

Figure 1. Emission photoselection (77 K) (350 (---) and 460 nm (—) excitation) plotted across the 77 K emission spectrum in 4:1 EtOH/MeOH for (A) $[Ru(bpy)_2(HDPA)]^{2+}$ and (B) $[Ru(bpy)(HDPA)_2]^{2+}$.

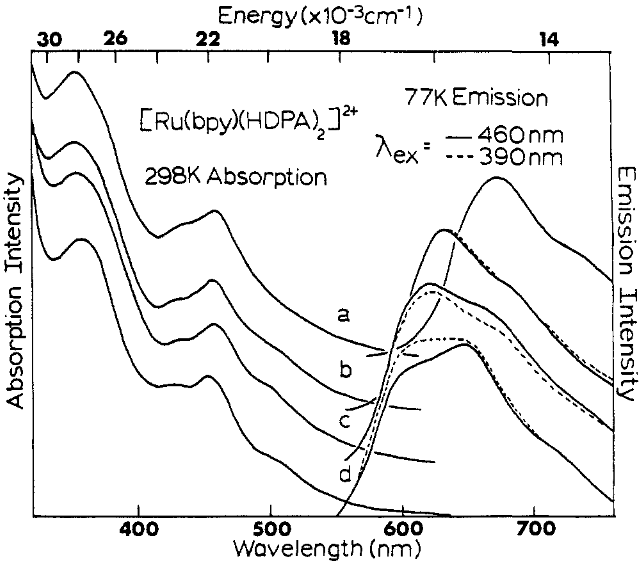

Figure 2. Room temperature absorption and the 77 K emission spectra (460 and 390 nm excitation) for $[Ru(bpy)(HDPA)_2]^{2+}$ in the solvents (a) H_2O, (b) MeOH, (c) EtOH, and (d) 2-PrOH. The intensity scales are offset for clarity.

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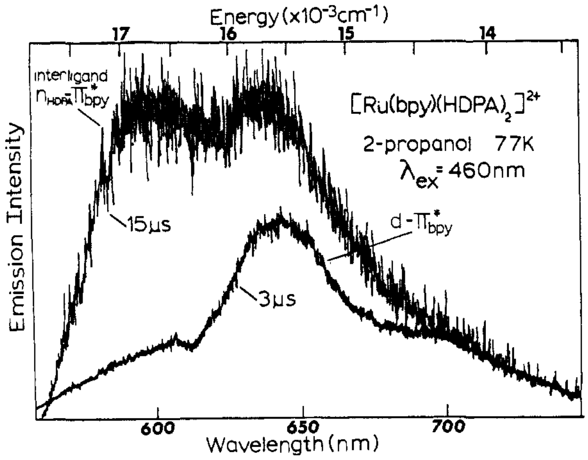

Figure 3. Time-resolved emission spectra obtained at 3 and 15 μs after the laser pulse for $[Ru(bpy)(HDPA)_2]^{2+}$ in 2-PrOH at 77 K. Assignments of the emission are given (see text).

The $[Ru(bpy)_2(HDPA)]^{2+}$ complex exhibits absorption bands characteristic of the HDPA and bpy unit; however, the emission band position and structure as well as the emission lifetime (Table I) and emission photoselection (Figure 1) indicate that this emission is an MLCT emission involving only the bpy ligand. In contrast $[Ru(bpy)(HDPA)_2]^{2+}$ has a new low-energy absorption band and two emissions depending upon the excitation wavelength and solvent (Figure 2). Subsequently, lifetimes were measured as a function of emitting wavelength (Table I) and time-resolved spectra were obtained (Figure 3). Excitation spectra and emission photoselection spectra (Figure 1) were measured and found to be consistent with the results in Figures 2 and 3 and Table I, indicating a higher energy, longer lived (13 μs) emission and a lower energy, shorter lived (5.0 μs) emission.

The broad emission band measured at room temperature can be time resolved to show the presence of two bands, a higher energy emission with $\tau = 1.05 \pm 0.04$ μs and a lower energy with $\tau = 0.33 \pm 0.02$ μs.

Since a small amount of luminescent impurity[14] can result in erroneous identification of a dual emission, the following precautions have been taken: (1) Repeated recrystallization and chromatographic separations have been used and the emission has been monitored as a function of the number of repurifications. (2) The samples have been prepared in the dark and light and irradiated for long periods, and no difference in the emission or absorption bands could be determined in any case. (3) The $[Ru(phen)(HDPA)_2]^{2+}$ analogue has been synthesized, and a dual emission is also obtained for it. $[Ru(bpy)_2(HDPA)]^{2+}$ would be the most likely impurity since its emission is coincident with the higher energy emission band of $[Ru(bpy)(HDPA)_2]^{2+}$, but the lifetime of the emissions from the two complexes are 4.6 and 13 μs, respectively. Therefore, $[Ru(bpy)_2(HDPA)]^{2+}$ can be eliminated as an impurity in $[Ru(bpy)(HDPA)_2]^{2+}$. The 13-μs emission has also been shown to disappear in H_2O leaving only a single emission band which was found to be excitation wavelength independent verifying the purity of the $[Ru(bpy)(HDPA)_2]^{2+}$ complex. Moreover, the absorption spectra and emission spectra of the dual emitter have been measured as a function of concentration (10^{-4}–10^{-6} M) and no change is noted, consequently dimer emission can be excluded.

A criterion for dual emission that the zero point energies of the two emitting excited states are near degenerate is apparently met in the $n = 1$ complex, yet the two emission bands can be resolved, thereby implying that the two excited-state manifolds are displaced by different amounts. In addition, the different contours for the two emissions and the difference in the lifetime enable ready resolution of the two emission bands. For the $n = 2$ compound, the single emission implies that the separation between the lowest energy levels must be sufficient to allow nonradiative relaxation to the lowest lying state consistent with Kasha's rule.

The short-lived, lower energy emission in $[Ru(bpy)(HDPA)_2]^{2+}$ and the single emission observed in $[Ru(bpy)_2(HDPA)]^{2+}$ are characteristic of the Ru–bpy chromophore and permit identification of these emissions as from a Ru–bpy MLCT state.

A key to the assignment of the second emission in the $n = 1$ species is the occurrence of the new absorption band at 19 600 cm^{-1}. Careful examination of the absorption spectrum of $[Ru(bpy)_2(HDPA)]^{2+}$ indicates that this band does occur but with lower intensity than in $[Ru(bpy)(HDPA)_2]^{2+}$, therefore it is nearly covered by the more intense MLCT (Ru–bpy) band. This band does not occur in either of the parent compounds; in fact, it is only visible in complexes in which an HDPA and a bpy ligand are present. Upon examination of spectroscopic properties of $[Ru(bpy)(py)_4](ClO_4)_2$ where no bridging amine is present, the unusual absorption and emission bands are not observed. Moreover, this absorption blue shifts as the hydrogen bonding ability of the solvent is increased (Figure 2), a characteristic of n–π* transitions in organic chromophores.[15] Indeed, this absorption band disappears in H_2O, likely due to hydrogen bonding to the amine lone pair, and now only a single emission band is observed. Consequently, this emission is assigned as an *interligand* n–π* transition involving the nonbonding electrons of the amine nitrogen on HDPA and the π* orbital of the adjacent bpy ligand.

Further data and details on these and related systems are to be published.

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Gas-Phase Reactions. 55.[1] O=C=C=C=S: Synthesis and PE Spectrum

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3-Thioxo-1,2-propadien-1-one (O=C=C=C=S), a five-atomic linear molecule, is of considerable interest to both astronomers[2-4] and spectroscopists:[5] Recently, the novel interstellar molecule O=C=C=C has been discovered in the cold dark cloud Taurus TMC 1,[3] which is rich in carbon chain compounds such as HC_nN (n = 1, 3, 5, 7, 9).[2] It could well be a precursor of O=C=C=C=S,[5a] which according to previous evidence occurs most likely in other interstellar molecular clouds.[4] The need to provide precise spectroscopic data, measured on earth, for an unequivocal assignment in space coincides with the interest of spectroscopists to know more about OC_3S, which in contrast to

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