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The Apparent "Dual Emitter" Characteristics of $[Ir(bpy)_x(phen)_{3-x}]^{3+}$ for $x = 1, 2$

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The luminescence behavior of the title series, $x = 0$–3, has been examined using 337-nm pulsed N_2 laser excitation, 360-nm Kr^+ cw excitation and pulsed dye laser excitation in the origin region, near 446 nm, for the temperature range 1.5–80 K in 4:1 ethanol/methanol glasses. Strongly nonexponential behavior is observed, invariably, for the mixed ligand ($x = 1$ and 2) species. Direct laser excitation into the origin region leads to the same nonexponential luminescence decays as UV excitation. This is not consistent with the complexes being "dual emitters". The luminescence characteristics are quantitatively accounted for by a simple model in which the $^3\pi$–π^* state on the phen ligand(s) is in thermal equilibrium with a $^3\pi$–π^* state on the bpy at an average 70 cm^{-1} higher in energy. The apparent dual emission arises from the lack of correlation of the individual ligand $^3\pi$–π^* energies which are widely spread relative to the average energy gap, giving rise to species with either phen or bpy $^3\pi$–π^* excited states lowest.

Introduction

Luminescence in coordination compounds almost invariably arises from the lowest excited levels of a system. Fast radiationless and intersystem crossing processes usually ensure an effective thermal equilibrium between any close lying excited states. Over the last 20 years, there have been a number of reports of inorganic complexes having two or more electronic excited states, separated by energies comparable to vibrational or lattice phonon energies, in which the states are largely uncoupled.[1-14] This was used to explain non-exponential decay kinetics,[1,7,10,14] which cannot occur for a single luminophore in thermal equilibrium. The "dual emitter" concept has been instrumental in developing notions of excitation localization within a chromophoric system, and has rather wide acceptance in the inorganic chemistry community.

The most common source of nonexponential decay in a dilute sample is impurities. These can contribute to the overall luminescence although not easily detectable analytically. Most experiments do not distinguish between a "dual emitter" and the presence of more than one emitting species in the sample.

Recently,[15] we reexamined the luminescence characteristics of cis-$[Ir(bpy)_2Cl_2]^+$ (bpy = 2,2′-bipyridine). Although there was sustained evidence for unusual behavior, we discovered, by using variable wavelength excitation at low temperatures, that it was *not* consistent with the original proposal[2-4] of d–d and MLCT states of the complex being separated by 400 cm^{-1}. The level separation was found to be an order of magnitude larger,[15] and the energy transfer dynamics were probably complex. In the $[Ir(bpy)_2Cl_2]^+$ system, the weak, broad, red shifted (d ← d) component of the luminescence was only an extremely small fraction of the majority MLCT emission.

The $[Rh(bpy)_x(phen)_{3-x}]^{3+}$ (phen = 1,10-phenanthroline) $x = 0$–3 series[14] where the luminescence is clearly $^3\pi$–π^* in character, provides, for the $x = 1$ and 2 cases, the most compelling evidence for a "dual emitter". The luminescence origin positions for $[Rh(bpy)_3]^{3+}$ and $[Rh(phen)_3]^{3+}$ are almost indistinguishable in a frozen glass at 77 K, although the emission profiles and lifetimes are quite different. Extremely nonexponential decay for $x = 1$ and 2 was deemed consistent with bpy and phen $^3\pi$–π^* emissions being independent. The fraction of each component of the luminescence followed the stoichiometry. By comparison, the $[Ru(bpy)_x(phen)_{3-x}]^{2+}$ ($x = 0$–3) series showed MLCT emission and no such effects.[14]

The $[Ir(bpy)_x(phen)_{3-x}]^{3+}$ ($x = 0$–3) series has recently been synthesized[16] and has overall luminescence behavior entirely analogous to the rhodium series. The lifetimes of the bpy and phen phosphorescences are greatly reduced, via the increased spin–orbit coupling on iridium(III). In this paper we take advantage of this fact, in that it is possible to excite directly into the $^3\pi$–π^* origins of these systems more easily, because of their increased dipole strength. Furthermore, as the bpy ligand absorbs an order of magnitude more strongly than phen at the $^3\pi$–π^* origin, it is possible to excite dominantly the bpy ligand in the mixed complexes, via pulsed laser excitation. A lack of any phen emission would substantiate the dual emission hypothesis, but any *rise* in the emission arising from phen ligand could quantify the kinetics in the complex.

Experimental Section

The title series were prepared as previously described.[16] Both the trifluoromethanesulfonate (triflate) salt and the PF_6^- salts were used without significant differences in the luminescence properties, as measured in 4:1 ethanol/methanol glass. We were able to identify a persistent type of impurity in these systems as being the alkoxy derivatives, which are intermediates in the synthesis.[17] These are difficult to remove entirely, but show MLCT luminescence with characteristic short lifetimes and red-shifted luminescence spectra.

Spectra were collected on a computer-controlled apparatus, built around a Oxford Instruments SM4 cryomagnet, a Spex 0.75 m 1704 monochromator, and a Tektronix 2439 digital oscilloscope. Further details are provided in a number of recent papers.[15,18-21]

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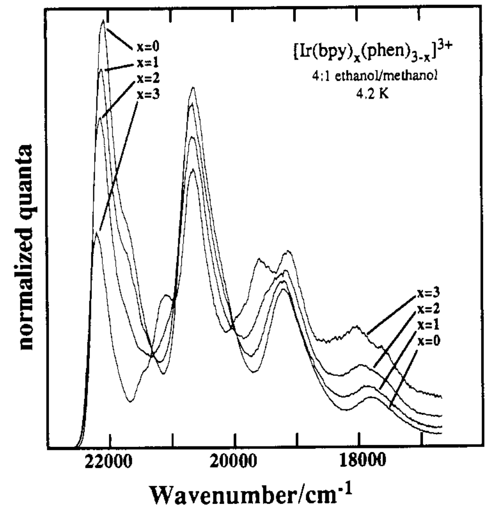

Figure 1. Corrected luminescence spectra of the series $[Ir(bpy)_x(phen)_{3-x}]^{3+}$ (x = 0–3) taken in ≈10^{-4} M 4:1 ethanol/methanol at 4.2 K using 10 mW of 360-nm Kr^+ ion laser excitation.

Table I. $[Ir(bpy)_x(phen)_{3-x}]^{3+}$ Luminescence Properties in 4:1 Ethanol/Methanol

	$x = 3$	$x = 2$	$x = 1$	$x = 0$
ν_{max} (4.2 K)[a]	22 160	22 110	22 090	22 070
Γ (cm^{-1})	370	370	370	370
% bpy				
4.2 K[b]	100	50[d]	20[d]	0
77 K	100	81[d]	50[d]	0
τ (μs) at 5 T				
1.5 K[c]	54	55, 751[e]	50, 840[e]	809†
4.2 K	54	50, 721[e]	57, 788[e]	816†
20 K	49	51, 870[e]	51, 872[e]	907†
40 K	47	51, 854[e]	51, 851[e]	954
60 K	46	56, 760[e]	55, 757[e]	
80 K	45	87, 622[e]	60, 453[e]	950

[a] ±10 cm^{-1}. [b] ±1%. [c] x = 0 and 3; lifetimes ±3 μs except values marked with a † were some degree of nonexponentiality remained at 5 T. [d] These values are also calculated for ΔE = 70 cm^{-1} and Γ = 220 cm^{-1}; see text. [e] Dual exponential fitted lifetimes; these (pairs of values) are correlated in the fitting procedure and are affected by residual nonthermalization. They are of qualitative significance only.

Results

Steady-State Luminescence and Excitation Spectra. The luminescence spectra of the series x = 0–3 were measured at 4.2 and 77 K using 360-nm UV Kr^+ laser excitation. After correction for instrumental response, these were normalized to the same area (i.e. to the same number of quanta emitted from each complex). Figure 1 shows the data at 4.2 K. The additivity of the spectra is immediately indicated by the appearance of two isoquantal points near 21 300 and 20 000 cm^{-1}. The 4.2 K spectra show slightly sharper features than at 77 K and a gradual shift to lower energy from x = 3 to x = 0 is evident (Table I). The overall shift in the series is less than 100 cm^{-1}.

Luminescence spectra of the x = 1 and 2 systems can be accurately synthesized by linear combinations of the x = 3 and x = 0 spectra. Figure 2 shows the least-squares fit of the x = 1 case at 4.2 K. Small systematic (≈10 cm^{-1}) shifts are seen, most evident as the differential form of the residuals. This indicates that there is an increase in average energy of a bpy (or phen) ligand in the x = 2 or 1 complex compared to the tris bpy (or phen) complex. Similar fits are seen at 77 K. This analysis allows a rather accurate determination of the bpy and phen contributions to the total luminescence and these are given in Table I. The phen contribution is significantly larger at lower temperatures.

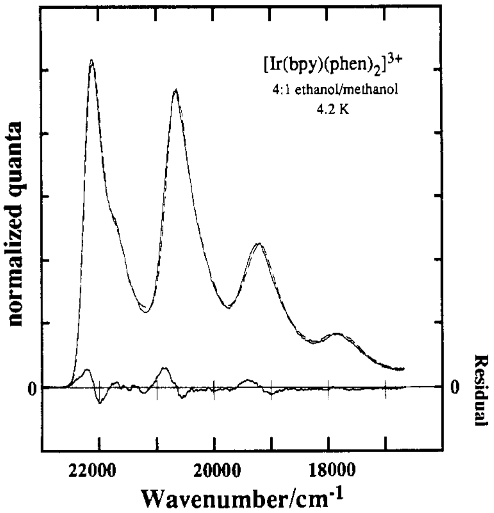

Figure 2. Least-squares fit (- - -) of the x = 1 spectrum of Figure 1 (—) with 21% of x = 0 and 79% of x = 3. The bottom trace shows the residual.

Excitation spectra for the x = 3, 2, and 1 complexes showed a feature near 22 300 cm^{-1} of comparable width to the $^3\pi$–π^* origin on the bpy observed in luminescence. This feature was less pronounced in the x = 1 material and not visible in the x = 0 complexes. The origin absorption of the phen is relatively weak and lies on the tail of stronger higher lying absorptions.

The Stokes shift (≈200 cm^{-1}) observed between maxima in absorption and luminescence of the bpy is due to dominant intensity being in the phonon wing rather than in the zero phonon line. This phenomenon has been quantified using resonant luminescence line narrowing (FLN) experiments in the x = 3 and x = 0 complexes.[22]

Decay Profiles. Luminescence decay profiles were measured using ≈3-ns pulsed excitation at 337 nm into the $^1\pi$–π^* region or excitation at the $^3\pi$–π^* origin near 446 nm (22 300 cm^{-1}). None of the systems showed single exponential decay curves of the precision shown by MLCT type emitters such as $[Ru(bpy)_3]^{2+}$ in the same environment.[23-26] Decays of the x = 3 and x = 0 (homoligated) complexes are quite nonexponential at 4 K, but less so at 77 K. This is due to the lack of thermal equilibrium between the $^3\pi$–π^* sub-levels which are typically split by ≈0.1 cm^{-1} (the zero field splittings or ZFS's). Each triplet sublevel may in general have quite different decay rates, which are in turn faster than the spin–lattice relaxation rates. They are not thermalized.

Taking the observed decay profiles of x = 3 and x = 0 at 1.5 K, it was possible to fit the decay profiles of the x = 2 and 1 materials quite well as a linear combination of the parent (x = 3 and x = 0) decays, in a manner analogous to the fitting of the total luminescence, shown in Figure 2. The fraction of each component agreed, to within experimental accuracy, with the bpy/phen intensity ratio deduced from the steady state experiments.

When a strong magnetic field is applied and the Zeeman splittings of the spin triplet states of the ligands are larger than ≈1 cm^{-1}, then a far greater degree of thermal equilibrium is established between the triplet components even at 1.5 K and a nearly exponential decay profile results. Table I indicates that the thermalization is not complete below about 40 K, leading to an (apparent) increase in the lifetime of the x = 0 material with warming. This gradual achievement of thermal equilibrium with increasing field is evidenced by both Zeeman FLN measure-

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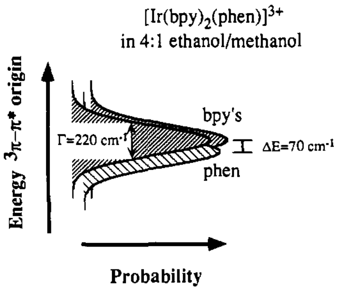

Figure 3. Schematic diagram of the statistical model for $x = 2$.

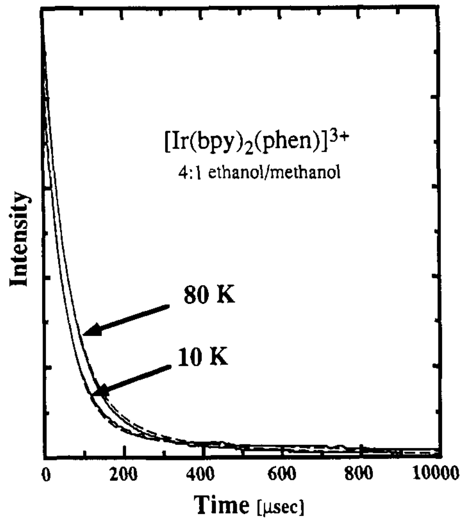

Figure 4. Decay profiles (- - -) of the $x = 2$ system in an applied field of 5 T at the indicated temperatures. These were measured at the first isoquantal point near 21 300 cm^{-1} (Figure 1). Solid lines are calculated using the model with values of $\Delta E = 70$ cm^{-1} and $\Gamma = 220$ cm^{-1} determined from fitting the steady-state luminescence spectra.

ments[22,27,28] and broad-band MCPL measurements. In the former, side features appear separated by $g\beta B$ with the appropriate intensities. In the latter, linear (MCPL), magnetic field dependence and approximately reciprocal absolute temperature dependence ($1/T$) appropriate to a C type term are achieved.

In an applied field of 5 T, the $x = 3$ and $x = 0$ complexes did show greatly improved exponentiality of decay profiles. The decay curves of the mixed complexes were still strongly nonexponential and could be fitted to a biexponential with the lifetimes shown in Table I. The two rates were virtually identical to those of the homoligated complexes at 1.5 K, but become distinctly intermediate at higher temperatures (Table I, Figure 4). The overall luminescence of the complexes did not change in a magnetic field of 5 T.

Excitation into the $^3\pi-\pi^*$ origin region in an applied field of 5 T gave decay profiles almost identical to those excited in the $^1\pi-\pi^*$ region, except for fast components that could be definitely attributed to known impurities. The impurities were identified by tuning the dye laser in and out of the origin region and by measuring time-resolved spectra. The impurity feature was most prominent in the $x = 0$ complex as absorption for the phen is low.

With low energy excitation in the $x = 3$ complex, in the absence of an applied magnetic field, there is a pronounced fast component of the nonexponential decay. The triplet component with the highest dipole strength is populated directly under resonant excitation and emits without thermal equilibration into the other triplet levels, which have longer radiative lifetimes.

Analysis and Discussion

Factors Influencing Decay Profiles. With resonant excitation into the $^3\pi-\pi^*$ origin region, in the absence of a magnetic field, the triplet sublevel with the strongest absorption (and thus fastest radiative decay) will be excited preferentially. When there is a lack of thermal equilibrium, a shortening of decay times is observed. In a strong magnetic field, the original triplet sublevels, quantized in spatial coordinates, are mixed so as to diagonalize the Zeeman operator. An average dipole strength among the thermally equilibrated Zeeman levels results upon orientational averaging, giving rise to a single exponential decay profile which is slower than the fastest component of the nonthermalized triplet components.

With UV excitation into the $^1\pi-\pi^*$ excited state region, following fast vibrational relaxation and intersystem crossing, population of the ZFS levels is achieved on a different basis, not necessarily favoring those levels with the highest dipole strength to the ground state.

The application of a strong magnetic field largely avoids the complications associated with non equilibrated ZFS's. The field does not influence the overall luminescence profiles of the $x = 2$ and 1 systems. This is evidence that the relative quantum efficiencies (ϕ's) of the bpy and phen emissions do not change, at least relatively, in a magnetic field.

The greatly improved exponentiality of the decays of the $x = 3$ and $x = 0$ species in a field allows us to directly compare, more easily, the lifetimes as a function of temperature. The changes seen (Table I) are small and are taken as due to the variation of ϕ's with temperature. The apparent change for the $x = 0$ material is due to a small degree of residual nonthermalization below 40 K. At the lowest temperatures the ϕ's are assumed to be close to 1, by analogy with previous studies of this class of complex.[26]

Statistical Simulation. The observation of relatively strong phen emission in the $x = 2$ and 1 complexes with resonant excitation is difficult to reconcile with the proposal of zero coupling between the $^3\pi-\pi^*$ states on the bpy and phen ligands, which appear to be resonant to within $\approx$100 cm^{-1}. If bpy and phen emit independently, then dominant bpy absorption in the origin region must lead to dominant bpy emission.

One can interpret the data quite simply using a model in which the $^3\pi-\pi^*$ excitations of the phen and bpy ligands have a large inhomogeneous spread, compared to the average energy difference between bpy and phen excitations. If the energies of the lowest excited states of the bpy and phen ligands are not correlated, a significant proportion of the species in the glass can have the ligand which is on average higher in energy, lower in energy. Figure 3 schematically depicts the proposed situation for the $x = 2$ complex. The region of overlap is where there is some probability that a bpy can have a lower energy than a phen. This approach was suggested by our recent observations, using laser spectroscopy, that correlations of electronic energy levels in coordination compounds in amorphous environments are often very poor.[28,30]

We assume the spread of the energies of the lowest excited state of the ligands L_a, L_b and L_c to be Gaussian with a full width at half-height Γ. We take L_a and L_b to be the two like ligands, which are at an average energy ΔE with respect to L_c. $G_S(E,\Gamma)$ is a function that randomly generates an energy with a Gaussian distribution about E with width Γ. A set of independent energies E_a, E_b, and E_c can then be generated and scaled relative to the average excitation energy of the unique ligand L_c, which is set to zero.

$$E_a = G_S(\Delta E,\Gamma), E_b = G_S(\Delta E,\Gamma), E_c = G_S(0,\Gamma) \quad (1)$$

We use the observed rates for the homoligated complexes, determined in the presence of a strong magnetic field, to avoid ZFS-induced nonexponentialities. These provide values of $k_a = k_b$ and k_c, the decay rates for the two like and one unlike ligand-

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(s). We assume thermal equilibrium between the three levels and calculate a rate k_{sim}

$$k_{sim} = \frac{\{k_a(e^{(-E_a/kT)} + e^{(-E_b/kT)}) + k_c e^{(-E_c/kT)}\}}{\{e^{(-E_a/kT)}\}} \qquad (2)$$

We can also calculate the fraction of emission due to the two like ligands F_{a+b} if we assume that the nonradiative rates are small (ϕ's ≈ 1).

$$F_{a+b} = \frac{k_a(e^{(-E_a/kT)} + e^{(-E_b/kT)})}{\{k_a(e^{(-E_a/kT)} + e^{(-E_b/kT)}) + k_c e^{(-E_c/kT)}\}} \qquad (3)$$

If we then perform the simulation n times, the overall decay profile will be given by the normalized sum over all the simulations

$$I(t) = \sum k_{sim} e^{(-k_{sim}t)} \qquad (4)$$

and the average fraction of emission by the like ligands, $\bar{F}_{a+b}$, by

$$\bar{F}_{a+b} = \sum F_{a+b}/n \qquad (5)$$

We found that adequate convergence is obtained after 500–1000 simulations.

The situation at low temperatures is particularly simple. $\bar{F}_{a+b}$ is determined by the ratio of ΔE to Γ, i.e., the overlap. (In the limit of a small ΔE the value must converge to $^2/_2$.) At low temperatures, the decay profile will be purely biexponential with rates k_a and k_c. In the high temperature limit the decay becomes exponential with a rate $(2k_a + k_c)/3$. At intermediate temperatures the decay is the sum of many different exponentials but often the decay profile can be fitted to a biexponential form with decay rates intermediate to k_a and k_c reflecting the contribution of a range of k_{sim}'s as the increased temperature probes the ΔE region.

A value of $\Delta E/\Gamma = 0.45$ reproduced the observed bpy/phen intensity ratio at 4.2 K for both $x = 2$ and $x = 1$. The 77 K values were then well accounted for by a $\Delta E = 70$ cm^{-1} and $\Gamma = 220$ cm^{-1}.

Decay profiles for intermediate temperatures can be generated quite readily and an indication of the correspondence between observed and calculated profiles is given in Figure 4 and Table I. Figure 4 provides a comparison of experimental and calculated decay curves for the $x = 1$ case at two temperatures. The calculated decay profiles are determined using eq 4 and no further parameterization is required. The same values for ΔE and Γ were used for the $x = 2$ and $x = 1$ systems, and good overall correspondence between experimental and calculated decays is seen at temperatures up to 80 K.

If we assume that the ground states of the ligands have a similar (noncorrelated) width of Γ, then the emission (or absorption) profile will have a width of $2^{1/2}\Gamma$. The width calculated (310 cm^{-1}) from the fitted value of Γ is slightly less than the observed width of 370 cm^{-1} (Table I), but there may be other contributions to the broadening.

Conclusion

The apparent "dual emission" characteristics of the $x = 2$ and 1 systems are well accounted for by an independent spread of ligand-centered luminescent state energies. The analysis is consistent with the observed line widths in solution and small shifts in the peak maxima. The analysis is also consistent with the idea that an excitation resides primarily on a single ligand at low temperatures, as any effective degeneracy between states on adjacent ligands is rarely achieved, because of the lack of correlation between energies in the system. In $x = 2$ and 1 systems, there is a frequent occurrence of individual complex ions in solution where the average order of states is reversed.

At elevated temperatures, phonon-assisted energy back-transfer from the lowest energy ligand to the higher energy ligand, at a rate fast compared to the excited state lifetime, may occur. It may be possible to directly observe this rate by the Lorentzian broadening of resonantly narrowed luminescence.

The influence on emission spectra of the inhomogeneous environment present in glassy solutions is well known. Castelli and Forster[31] discussed the influence of microenvironmental heterogeneity on the nature of the emission of $[Cr(CN)_6]^{3-}$ in rigid solutions following earlier studies on aromatic systems.[32] A series of studies on chromium(III) polypyridine complexes[33,34] have shown, for example, that [*cis*-$Cr(phen)_2F_2]^+$ in DMF/H_2O glass at 77 K shows emission from species with ^2E emitting states or $^2T_1$ emitting states.

Our study has been able to quantify both the spread and overlap of the bpy and phen luminophore excited-state energies for the series under examination with a simple statistical model.

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