

simple model would suggest. However, application of both theories is consistent with a ground-state dipole pointed toward the ortho-metalated C atoms and an excited-state dipole pointed toward the chelating ligand.

Modification of the McRae theory to take into account solvent shifts of emission as well as absorption according to eq 3 leads to estimates of a transition dipole substantially smaller than that taken from absorption data alone. This result is consistent with a substantial reduction of the excited-state dipole moment in the

emitting levels relative to the levels responsible for absorption in the range 400-430 nm. The reduction may be due to different electron distributions on the chelate ligand in the absorbing and emitting states as well as some contribution to the emission from an MLCT state associated with the ortho-metalated ligand.

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Resolution and Analysis of the Components in Dual Emission of Mixed-Chelate/Ortho-Metalate Complexes of Iridium(III)

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Spectral resolutions of the two components in dual emissions of four mixed-chelate/ortho-metalated complexes of Ir(III) are reported. Resolution of the component emissions from samples of the complexes $\text{Ir}(\text{bzq})_2(\text{bpy})^+$ and $\text{Ir}(\text{bzq})_2(\text{phen})^+$ (bzq = benzo[*h*]quinoline, bpy = 2,2'-bipyridine, phen = 1,10-phenanthroline) in rigid glasses at 77 K has been achieved by time-resolved emission spectroscopy. In each case the lower energy emission component is assigned to a metal-to-ligand charge-transfer excited state associated with the chelating ligand and the higher energy component to a MLCT excited state associated with the ortho-metalating bzq ligand. Components in the dual emissions of $\text{Ir}(\text{ppy})_2(\text{bpy})^+$ and $\text{Ir}(\text{ppy})_2(\text{phen})^+$ (ppy = 2-phenylpyridine) are too similar in their lifetimes to permit full resolution of the two emissions by time-resolved emission spectroscopy when both components are populated by 337-nm excitation. However, dye laser excitation of these complexes in their lowest energy absorption bands (≈ 485 nm) results in emission from a single, low-energy component which is assigned to the MLCT excited state associated with bpy or phen . Subtraction of this component from the spectrum excited at 337 nm provides an intensity profile for the higher energy component that is assigned to the MLCT excited state associated with ppy . In all four cases the emission spectra in ambient-temperature fluid solutions display a single lifetime, and emission from the MLCT excited state of the chelate ligand predominates.

Introduction

A wide variety of coordination complexes of the second- and third-row transition metals are now known to display dual emissions from thermally nonequilibrated excited states in rigid media.¹⁻³⁰ Recently, several organometallic Ir(III) species

containing coordinating ligands such as 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen) in combination with ortho-metalating ligands such as 2-phenylpyridine (ppy) and benzo[*h*]quinoline (bzq) were also reported³¹⁻³⁴ to display dual emissions in rigid media; however, structurally analogous Rh(III) complexes were found to display only a single emission.³³⁻⁴⁰ This unanticipated

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