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ARTICLE in JOURNAL OF THE AMERICAN CHEMICAL SOCIETY · JANUARY 2003

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Isotope Effects on the Picosecond Time-Resolved Emission Spectroscopy of Tris(2,2'-bipyridine)ruthenium (II)

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Because of their favorable photophysical properties, ruthenium(II) polypyridine complexes are playing a key role in the development of multicomponent (supramolecular) systems capable of performing useful photo- or redox-triggered functions such as charge¹ and information storage.² These compounds emit from a long-lived triplet metal-to-ligand charge-transfer state (³MLCT) that is populated from higher-energy excited states. The photophysical behavior of the emitting triplet state is well understood,^{1–6} but much less is known about the events that lead to its formation. The observation that, in nanocrystalline TiO₂ solar cells modified with monolayers of a ruthenium complex, the electron injection from the excited dye into the TiO₂ is subpicosecond has led to a sharp increase in the interest in the parameters that control the formation of the triplet state. Issues of interest are the lifetime of the lowest singlet state/s and the efficiency of the intersystem crossing (ISC) process that leads to population of the triplet state.

In the present report, picosecond time-resolved luminescence (ps-trl) spectroscopy⁷ has been employed for the first time to study the early processes, which occur after excitation of [Ru([H₈]-bpy)₃]²⁺ (**1a**) and [Ru([H₁₆]-ph₂phen)]²⁺ (**2a**) and their deuterated analogues [Ru([D₈]-bpy)₃]²⁺ (**1b**) and [Ru([D₁₄]-ph₂phen)]²⁺ (**2b**) (where bpy = 2,2'-bipyridine, ph₂phen = 4,7-diphenyl-1,10-phenanthroline). Recently, studies into the short time scale behavior of **1a** have been carried out by McCusker and co-workers⁸ and by Bhasikuttan et al.⁹ using transient absorption and fluorescence upconversion spectroscopy, respectively.

For both **1a** and **2a**, an emission signal with maximum near 520 nm decays within the instrument time of the excitation pulse (3 ps) to the long-lived ³MLCT emission (λ_{max} 610 nm) (Figure 1a).¹⁰ In sharp contrast, for the perdeuterated complex **1b** the emission at 520 nm persists for times beyond 200 ps (Figure 1b and S1). A comparison of Figure 1a and Figure 1b shows clearly that deuteration results in a dramatic increase in the lifetime of the 520-nm emission. Although the number of data points available precludes the accurate fitting of the decays, which are clearly nonexponential, estimates of emission lifetimes can still be made. For **1a** the emission signal decays in less than 3 ps, whereas for **1b**, a fast process with a time constant of some 15 ps is followed by a slower process ($\tau > 200$ ps). Similar results were obtained for their respective hexafluorophosphate salts in acetonitrile. For **2a** a similar emission was observed with a lifetime of less than 3 ps, and as for **1b**, the lifetime of the longer component observed for the 520-nm emission of **2b** persisted beyond 200 ps. Extensive studies of free ligand and the corresponding Fe(II) and Os(II)

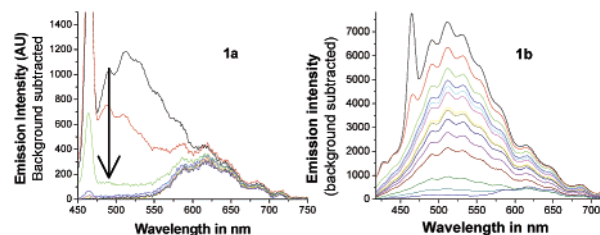


Figure 1. Time-resolved emission spectra of (a) **1a** in H₂O at 0, 2, 4, 6, 8, 10, 15, and 20 ps. (b) **1b** in H₂O at 0, 2, 4, 6, 8, 10, 15, 20, 30, 50, 100, 500, 1500, and 3000 ps. $\lambda_{\text{exc}} = 400$ nm. Raman band of water at ~ 475 nm indicates the temporal response function of the detection system (~ 4 ps).

complexes, both perprotio and perdeuterio, eliminate the possibility that the observations are the result of impurities or experimental artifacts.

On the basis of earlier studies, the increase in the lifetime of the emission signal upon deuteration is found to be quite unexpected. Recently, Bhasikuttan et al.⁹ reported a very weak emission from **1a** at 520 nm using fluorescence upconversion spectroscopy. Their results were interpreted in terms of fast ISC from ¹MLCT states to a vibrationally hot, emissive ³MLCT state, followed by vibrational cooling of the latter on a time scale of 600 fs to 1 ps. An increase in emission lifetime from less than 3 ps to over 200 ps upon deuteration does not seem to support this hypothesis.

The effect of deuteration on photophysical processes has been considered by Siebrand and others.^{11–14} Deuteration reduces the energy of the C–H vibrational modes (as well as ring breathing and other modes). If it is assumed that the effect of deuteration on ground- and excited-state vibrational modes is approximately the same then only minor changes in emission energy (within the experimental error) are expected and, indeed, observed. The rate of vibrational relaxation of excited states is related to the ability of the solvent to dissipate the excess vibrational energy. Deuteration of the ligands would be expected to perturb this process. However, in most solvents and especially in hydrogen-bonding solvents, deuteration should not substantially affect the rate of vibrational cooling, and thus no significant increase in emission lifetime on that account should be observed.¹⁵

In ruthenium complexes the geometric distortion between the ¹MLCT and the ³MLCT states is small ($S < 1$),¹⁶ and the interaction between the states is best described in the weak-coupling limit, in which, nonradiative transitions such as ISC rely on high-energy vibrational modes such as O–H and C–H. Hence, for weakly coupled systems (i.e., nested states) the theory predicts a significant deuteration effect on the rate of IC/ISC, as is observed here. For example, for the complex [Pt(μ -P₂O₅H₂)₄]^{4–} a nonradiative pathway ascribed to weak coupling between ³A_{2u} and ¹A_{2u} states with high-energy vibrational acceptor modes of the solvent has been

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reported.¹⁷ For this system deuteration was shown to reduce the ISC rate and thereby enhance the fluorescence lifetime.

The marked influence of deuteration on the decay rate of the 520-nm emission from **1a** suggests that this emission may be assigned, tentatively, as ¹MLCT in origin rather than being from vibrationally hot triplet states. It is important to note in this respect that Yersin and co-workers in an earlier publication reported a shoulder on the triplet emission, which they attributed as a singlet emission.¹⁸ The emission data reported in this contribution support that observation.

Preliminary investigations of **1a** and **1b** by picosecond time-resolved resonance Raman (ps-TR³) spectroscopy show that for **1a** the grow-in of the ³MLCT state, indicated by the prominent 1506-cm⁻¹ feature in Figure S2, occurs within the cross-correlation time of the laser pulse.¹⁹ For **1b** the grow-in of the ³MLCT state (1472 cm⁻¹ in Figure S3) occurs over 10–20 ps.^{19,20} In addition however, there is evidence of decay on the same 10–20 ps time scale of a distinct feature (marked by an asterisk in Figure S3).²¹ Beyond 20 ps no further changes were observed. The measured decay of the **1b** ¹MLCT state derived from the TR³ data (10–20 ps) corresponds to the shorter component observed in the ps-trl studies. However the longer-lived component observed in the ps-trl studies ($\tau > 200$ ps) is not easily identified in the TR³ data.

The ps-TR³ spectroscopy of the present systems is currently being explored further to elucidate the nature of the processes observed and will be reported in a later contribution. It should be noted, however, that any model proposed to explain our observations must involve the possibility of a second electronic [singlet] state, which is strongly affected by deuteration of the molecule. This state is not immediately observable in the TR³ data available, but given that the population of this state is likely to be less than 10% compared with the population of the ³MLCT state then it is unlikely to be observed. Furthermore, even if ISC to the ³MLCT excited state from the excited-state responsible for the 520-nm emission does occur, the low levels generated via this mechanism would not be observable in TR³ spectra.

The observations reported here may have important consequences for the design of supramolecular systems. Although, at this stage, a completely satisfactory picture describing the processes responsible is not available, some worthwhile points can be made. First, the effects reported here may have significant implications in regard to the engagement of excited states, other than the lowest ³MLCT manifold, in photochemical processes in interfacial supramolecular systems involving Ru polypyridyl complexes, such as injection of electrons in nanocrystalline TiO₂. Second, it appears that deuteration may influence the efficiency of ISC between excited states. The observation of emission from excited states above the lowest ³MLCT state confirms that the efficiency of ISC is less than unity, although possibly not appreciably less. Since our findings suggest that energy transfer from the upper states (presumably singlet) to the lowest ³MLCT state may be controllable, new approaches to the design of supramolecular systems driven by photonics can be considered. We believe this interesting observation warrants reporting at this stage but recognize further work is required to fully understand the novel photophysics.

Acknowledgment. This work is supported by the EPSRC (GR/M45696), including access to the laser facility at RAL. W.R.B. and J.G.V. thank Enterprise Ireland for financial support.

Supporting Information Available: Experimental methods and preparations, luminescence decay curve for **1b** (S1), and time-resolved

excited-state resonance Raman spectra of **1a** (S2) and **1b** (S3) (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>

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JA0289346