

# Evidence for the presence of dual emission in a ruthenium(II) polypyridyl mixed ligand complex

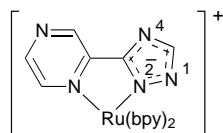
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The complex  $[\text{Ru}(\text{bpy})_2(\text{pztr})]^+ \mathbf{1}$  [bpy = 2,2'-bipyridyl, Hpztr = 3-(pyrazin-2-yl)-1,2,4-triazole] exhibits two emission maxima in fluid solution [ethanol–methanol (4:1)] over the temperature range 120–260 K; from fluorometric studies two well resolved emission maxima are observed at 590 and 700 nm, accompanied by two different lifetimes; the observations suggest the presence of two emitting states in this compound, one bpy and one pyrazine based.

The photophysical properties of ruthenium(II) polypyridyl complexes make them attractive building blocks for supra-molecular assemblies and as a result several thousands of homo- and hetero-leptic compounds have been reported in the literature.<sup>1</sup> It is generally accepted that emission in ruthenium polypyridyl complexes originates from a triplet metal-to-ligand charge-transfer (<sup>3</sup>MLCT) state.<sup>1</sup> In the case of a mixed ligand complex this excited state can in principle be located on any of the ligands. Many detailed studies have therefore been carried out to determine the location of the emitting state in such compounds. From theoretical considerations one would predict that emission will occur from the lowest triplet state only<sup>2</sup> and indeed this is observed in almost all cases. In rigid media a number of dual emissions have been documented.<sup>3</sup> However, in solution such reports are rare,<sup>4</sup> and to our knowledge no clear-cut cases have been reported in solution for ruthenium polypyridyl type compounds.

In this contribution, we wish to present direct evidence for dual emission in solution over a wide temperature range for the mononuclear mixed ligand ruthenium(II) polypyridyl complex  $[\text{Ru}(\text{bpy})_2(\text{pztr})]\text{PF}_6$ ,  $\mathbf{1}$  [bpy = 2,2'-bipyridyl, Hpztr = 3-(pyrazin-2-yl)-1,2,4-triazole].



The compound under investigation was synthesised as described previously.<sup>5</sup> The  $N^2$  and  $N^4$  isomers were separated by semi-preparative HPLC and characterized by <sup>1</sup>H NMR spectroscopy, analytical diode array HPLC, and elemental analysis. These techniques confirm that the purity of  $\mathbf{1}$  is >99%. In this study only the  $N^2$  isomer, shown above, was investigated.

Earlier work on these compounds has shown that isomerisation, photoinduced or otherwise, of the deprotonated  $N^2$  and  $N^4$  isomers does not occur,<sup>5c,d</sup> while  $\text{p}K_a$  values obtained for the ground state and excited state for the  $N^2$  isomer are between 3.5 and 4 and as a result, protonation of  $\mathbf{1}$  under the experimental conditions discussed here is unlikely.<sup>5a</sup>

One can therefore be confident that in the experiments carried out in this contribution only one species will be present. It is furthermore important to note that  $\text{p}K_a$  values, electrochemical experiments and resonance Raman data have shown that bpy and pyrazine based excited states are similar in energy. In  $\mathbf{1}$  the bpy state is lower in energy, while in the complex containing a protonated triazole the emitting state is pyrazine based.<sup>5b,d</sup>

Finally, emission and absorption maxima of  $\mathbf{1}$  in its protonated and deprotonated states are very similar.<sup>5a</sup>

Selected temperature dependent luminescence spectra for  $\mathbf{1}$  [ethanol–methanol (4:1), containing 1% diethylamine or ammonia to assure deprotonation of the triazole ring] are shown in Fig. 1. At 90 K, the spectrum obtained [Fig. 1(a)] is typical for compounds of this type with a single emission being observed at 617 nm. After laser excitation at 355 nm the luminescence decays according to a single exponential with a lifetime of 3200 ns (all lifetimes  $\pm 10\%$ ). On increasing the temperature to 145 K, [Fig. 1(b)] the emission spectrum of  $\mathbf{1}$  is resolved into two distinct bands; one, as expected, at 710 nm and an additional feature at 590 nm. The luminescent signal obtained at this temperature monitored at 650 nm cannot be fitted as a single exponential. Normal curve fitting procedures yield lifetimes of 2400 and 800 ns with ratios of 60 and 40%, respectively. Measurements monitored out at 700 and 590 nm yield single exponential decays and identify the long lifetime as belonging to the 700 nm signal. At higher temperatures the contribution from the higher energy component decreases. The temperature dependence of the emission decay for the two signals is therefore different. Excitation spectra obtained at both emission maxima are sufficiently similar to suggest that both emissions are based on MLCT emissions. The excitation spectrum of the 590 nm emission shows an absorption maximum at 440 nm, while for the 700 nm band a maximum is observed at 465 nm.

In cases where a dual emission is observed, the contribution from impurities is always a concern. However, we do not believe that the data above can be attributed to the presence of an impurity. First of all, the lifetimes and intensities observed for the two emission components (see above) suggest that the concentration of an impurity would have to be high and this is not observed. Also, the same results were obtained for various samples of  $\mathbf{1}$ . Finally, when the triazole is protonated a normal single exponential behavior is obtained over the entire temperature range [77 K (2200 ns), 175 K (800 ns) and room temperature (230 ns)].

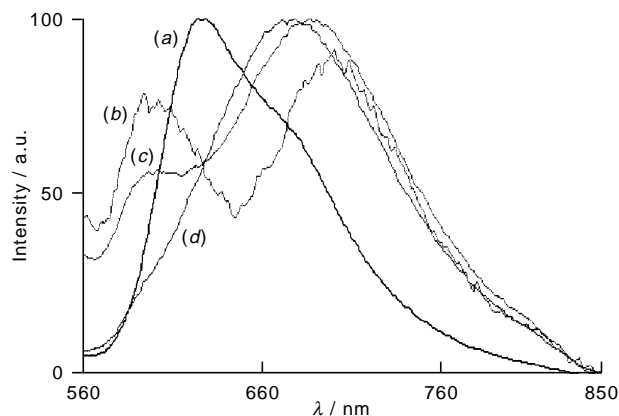


Fig. 1 Temperature dependent luminescent spectra of  $\mathbf{1}$  in ethanol–methanol (4:1) and 1% diethylamine, at (a) 90, (b) 145, (c) 220 and (d) 298 K

On the basis of these considerations we are confident that the results obtained are best explained by the presence in the title compound of two weakly coupled emitting states. As pointed out above, earlier work has shown that bpy and pyrazine based MLCT states are similar in energy. For example, the energy separation between these two emitting states of  $2400\text{ cm}^{-1}$  which at 145 K is consistent with the electrochemistry of this complex which shows a potential difference of 0.33 eV between the first two bpy and pyrazine based reductive steps of **1**. We therefore propose, based on our earlier results,<sup>5</sup> that the highest energy emitting state observed between 120 and 260 K, is pyrazine based. After excitation to the <sup>1</sup>MLCT level, efficient intersystem crossing to the lowest, strongly coupled bpy based triplet state is observed. Up to 260 K it is the lowest energy manifold of the bpy triplet that is populated. Population of the pyrazine based triplet state can in this model only occur by thermal means. The lower energy components of this manifold are weakly coupled to a pyrazine state, and population of the pyrazine state occurs thermally between *ca.* 120 and 260 K. Above this temperature the upper, fourth <sup>3</sup>MLCT of the bpy triplet manifold is thermally populated,<sup>6</sup> such population is observed in the temperature dependent luminescent lifetimes of related<sup>5c</sup> complexes, where population of this state was observed to occur from around 240 K. This upper state, which contains more singlet character, is not coupled to the pyrazine, and therefore a single emission primarily based on the fourth <sup>3</sup>MLCT is observed. Further investigations are at present in progress to further develop this picture.

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## Notes and References

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