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# Temperature dependence of dual emission in ruthenium(II) complexes containing 3,3'-bi-1,2,4-triazine derivatives

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## ABSTRACT

Three new ruthenium(II) polypyridyl complexes with highly  $\pi$ -deficient ligands,  $[Ru(bpy)_2(btm)]^{2+}(1)$ ,  $[Ru(bpy)_2(btb)]^{2+}(2)$  and  $[Ru(bpy)_2(btp)]^{2+}(3)$  (bpy=2,2'-bipyridine, btm=3,3'-bis(5,6-dimethyl-1,2,4-triazine, btb=3,3'-bis(5,6-diphenyl-1,2,4-triazine, btp=3,3'-bis(phenanthro[9,10-e][1,2,4]triazine) were synthesized and characterized. Electrochemical data together with molecular calculations show that the first redox process in these complexes is not bpy based. Complexes **1**, **2** and **3** display luminescence in ethanol/methanol (4/1, V/V) at 80 K, and all three complexes exhibit a temperature switch from single (150 K) to dual (80 K) emission behavior.

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Tremendous interest has been attracted to ruthenium(II) polypyridyl complexes because of their potentials in molecular electronic devices [1], as DNA structural probes or new therapeutic agents [2], and as photosensitizers in the conversion of solar energy to chemical or electrical energy [3]. Over the past decade quite a large amount of data has been accumulated on the changes in the electrochemical and photophysical properties of Ru(II) complexes. Although nearly all Ru (II) heteroleptic complexes abide by Kasha's rule [4] and exhibit a single emissive excited-state, a few Ru(II) complexes have been recently found to possess two simultaneously emissive excited states [5–10].

To observe dual emission from an individual molecule, the molecule must exhibit two excited electronic states. However, it is difficult to achieve because the excited states usually involve occupation of orbitals extending over the entire molecule and space at very modest energy separations. One possible approach for obtaining dual emission in Ru(II) complexes is the coexistence of <sup>3</sup>MLCT (metal-to-ligand charge transfer) with <sup>3</sup>IL (intraligand) or <sup>3</sup>ILCT (intraligand charge transfer) states [6,7]. Another viable way is to separate the two excited electronic states by the energy barrier and prevents interconversion of populations. Vos et al. reported the dual emission of complex  $[Ru(bpy)_2(pztr)]^+$  (Hpztr = 3-(pyrazin-2-yl)-1,2,4-triazole] in fluid solution [ethanol-methanol (4:1)] over the temperature range 120-260 K [5]. Recently, dual emission was observed from a family of heteroleptic Ru(II) complexes containing substituted 1,10-phenanthroline ligands with extended conjugation at room temperature in fluid solution [8]. Herein we present three new ruthenium(II) diimine complexes with highly  $\pi$ -deficient ligands. The dual emission behaviors of Ru(II) complexes are investigated in solution over a wide temperature range.

The synthesis of Ru(II) complexes  $[Ru(bpy)_2(btm)]^{2+}$  (1),  $[Ru(bpy)_2(btb)]^{2+}$  (2), and  $[Ru(bpy)_2(btp)]^{2+}$ (3) (bpy = 2,2'-bipyridine, btm = 3,3'-bis(5,6-dimethyl-1,2,4-triazine, btb = 3,3'-bis(5,6-diphenyl-1,2,4-triazine, btp = 3,3'-bis(phenanthro[9,10-e][1,2,4] triazine) were achieved as shown in Scheme 1. The ligands were synthesized on the basis of the method for the 1,2,4-triazine ring preparation established by Case [11]. The Ru(II) complexes were obtained in satisfactory yields (42–68%) by direct reaction of ligands with appropriate mole ratios of the precursor complex *cis*-Ru(bpy)\_2Cl<sub>2</sub> in ethylene glycol. The product was purified by column chromatography and characterized by NMR, ES–MS and elemental analyses. (Caution! Perchlorate salts of metal complexes are potentially explosive and should be handled in small quantity with care).

The electrochemical behaviors of the complexes have been studied in CH<sub>3</sub>CN by cyclic voltammetry (Fig. S1). The oxidation of the Ru(II) complexes shifts to more positive potential (1.43–1.53 V) in comparison with that of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> (1.28 V) [12]. Extended-Hückel calculation results show that the lowest unoccupied molecular orbital (LUMO) energy of btm (-10.33 eV), btb (-10.25 eV) and btp (-10.53 eV) are lower than that of bpy (-9.76 eV) (Fig. S2). Therefore, the better  $\pi^*$  acceptor character of btm, btb and btp stabilizes the ruthenium-based HOMO, rendering the oxidation of the metal more difficult. For complex **1**, the first reduction, which is usually controlled by the ligand having the most stable lowest unoccupied molecular orbital (LUMO), is assigned to a reduction centered on the ligand btm. However, the situation in complexes **2** and **3** is different from that of complex **1**. The LUMO and LUMO + 1 on btb (or btp) are similar except that the LUMO + 1 is 0.05 eV higher in

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Scheme 1. Synthetic routes to the ligands and Ru(II) complexes.

energy, and the LUMO + 1 orbitals of btb and btp are also significantly lower in energy than the LUMO orbital of bpy. So the first and second reductions of **2** (or **3**) are assigned to the LUMO and LUMO + 1 of btb (or btp), and the third reduction involves the bpy ligand.

The absorption spectrum of Ru(II) complexes is characterized by intense  $\pi$ - $\pi$ \* ligand transitions in the UV and metal-to-ligand charge transfer (MLCT) transition in the visible region (Fig. S3). The bands between 230 and 380 nm, especially the absorption bands near 348 nm are attributed to intraligand (IL)  $\pi$ - $\pi$ \* transitions, by comparison with the spectra of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> [12]. The lowest energy bands at 400–500 nm are assigned to metal-ligand charge transfer (MLCT) transition. Two distinct MLCT bands might be expected for the



**Fig. 1.** Emission spectra of complexes **1** (dash line), **2** (dot line), **3** (dash dot line) and  $[Ru(bpy)_3]^{2+}$  (solid line) at 80 K in 4:1 EtOH/MeOH.

three complexes. However, as a result of the broad nature of the bands and their relatively small wavelength separation, a broad MLCT band with shoulder peak is observed in the spectra of these complexes.

The emission signals of three complexes are too weak to measure at room temperature. Their emission spectra are recorded in ethanolmethanol (4:1) rigid matrix at 80 K (Fig. 1). Emission decays of all complexes are biexponential. The emission band maxima and excitedstate lifetime ( $\tau$ ) obtained are collected in Table 1. For complex **1**, the spectrum obtained at 80 K is resolved into two marked distinct bands; one, as expected, at 596 nm, and an additional feature at 663 nm. Normal curve fitting procedures yield lifetime of 4570 and 3670 ns with ratios of 60 and 40%, respectively. Excitation spectra obtained at both emission maxima are sufficiently similar to suggest that both emissions are base on MLCT emissions. The excitation spectrum of the 596 nm emission shows an absorption maximum at 458 nm, while for the 663 nm band a maximum is observed at 485 nm. On increasing the temperature to 150 K, the contribution from the lower energy component decreases, and the spectrum obtained is a single emission being observed at 608 nm (Fig. 2). Similar observations are noticed for complexes 2 and 3 (Figs. S4 and S5).

 Table 1

 Luminescence data for the ruthenium(II) complexes<sup>a</sup>.

Complex	150 K	80 K			
	$\lambda_{max}$ , nm	$\lambda_{max1}$ , nm	au, µs	$\lambda_{max2}$ , nm	<i>τ</i> , μs
[Ru(bpy) <sub>3</sub> ] <sup>2+</sup> 1 2 3	600 608 605 602	580 596 578 579	4.37 4.57 4.27 4.37	663 688 667	3.67 4.81 5.42

<sup>a</sup> Matrix, EtOH/MeOH = 4:1.



**Fig. 2.** (a) Temperature-dependent emission spectra of complex **1** in ethanol/methanol (4:1, v/v). Spectra were recorded from 80 to 300 K at intervals of 10 K. The arrow shows the intensity changes on decreasing the temperature. (b) Temperature-dependent luminescent decay rates of complex **1** in ethanol/methanol (4:1, v/v).

The simplest explanation for our data is that there are two MLCT excited states localized on different ligands of certain Ru(II) complexes, with the short-wavelength component being essentially bipyridine-based, while the long-wavelength component is localized predominantly on the more conjugated 3,3'-bi-1,2,4-triazine derivatives ligand. For the three complexes at room temperature, after excitation to the <sup>1</sup>MLCT level, efficient intersystem crossing to the lowest, strongly coupled bi-1,2,4-triazine based triplet state is observed, and the main decay pathways are deactivation of the bi-1,2,4-triazine based triplet state via the triplet metal-centered (<sup>1</sup>MC) state by tunnelling and on non-radiative processes. Therefore, the emission signals obtained for the three compounds at room temperature are very weak, analogously to the other rutheniumtriazine complexes. Over the temperature range 150–220 K, a single emission with maxima around 600 nm was observed, indicated that the excited-state is the bpy based more than the bi-triazine based. Below 150 K, the solvent turned into rigid glassy matrix, and barrier crossing would be slowed on such a condition, and as a consequence strongly coupled bpy based and bi-1,2,4-triazine based triplet states are observed.

In summary, we have shown that three Ru(II) complexes with highly  $\pi$ -deficient ligands can exhibit a temperature switch from single (150 K) to dual (80 K) emission behavior. The present results should be of value in further understanding the photophysical properties of Ru(II) polypyridyl complexes, as well as offer valuable approach for tuning excited-state energies in Ru(II) polypyridyl complexes. Further investigations involving temperature dependence of dual emission in Ru(II) complexes containing different ligands are in progress.

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2010.05.019.

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