

# Nanosecond transient absorption studies of Ru(II) complexes with tris(1-pyrazolyl)methane unit and an intercalating benzo[*i*]dipyrido[3,2-*a*:2',3'-*c*]phenazine (dppn) ligand

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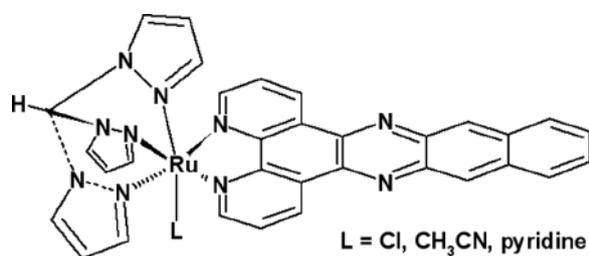
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## Introduction

Transition metal complexes with polypyridine ligands have attracted much attention as DNA intercalators, as they allow the photophysical properties of DNA and the mechanisms involved in its radiative damage to be probed. Much attention has been focused on the dipyrido[3,2-*a*:2',3'-*c*]phenazine (dppz) ligand.<sup>[1]</sup> Recently, the interaction with DNA of metal complexes bearing the more conjugated ligand system, benzo[*i*]dipyrido[3,2-*a*:2',3'-*c*]phenazine (dppn), has been investigated.<sup>[2]</sup>

The present work is a preliminary report on photophysical properties of *achiral* Ru(II) complexes with tris(1-pyrazolyl)methane unit (tmp) and the dppn ligand, [Ru(tmp)(dppn)L], which contain an easily modulated coordination site. The structures of the compounds are presented at Scheme 1.



Scheme 1. Ru(II) compounds studied.

## Results and discussion

The nature and localisation of the lowest excited state in these chromophores, the influence of the co-ligands (L = pyridine vs. CH<sub>3</sub>CN vs. Cl), and that of the environment (water vs. acetonitrile) were evaluated, as there is potential for interplay between several possible excited states in these type of chromophores. Indeed, previous studies on [Ru<sup>II</sup>(dppz)] complexes have established the existence of close-lying excited states of different origin – including intra-ligand  $\pi\pi^*$ , and MLCT(s) states.<sup>[1]</sup>

Compound [Ru(tmp)(dppn)L]	lifetime, $\mu\text{s}$	
	acetonitrile	water
L = CH <sub>3</sub> CN	18 $\pm$ 2	5.3 $\pm$ 0.5
L = py	2.6 $\pm$ 0.3	0.34 $\pm$ 0.05
L = Cl	2.5 $\pm$ 0.3	n/a
[Ru(bpy) <sub>2</sub> dppn](PF <sub>6</sub> ) <sub>2</sub>	6.7 $\pm$ 0.6	–

Table 1. Excited state lifetimes of the Ru(II) complexes investigated in deoxygenated solutions.

The transient absorption spectra on the nanosecond time scale of the [Ru(tmp)(dppn)X]-derivatives as PF<sub>6</sub>-salts have been investigated in CH<sub>3</sub>CN, and as Cl-salts - in water. The lifetimes of their lowest excited state are summarised in Table 1. The related compound, [Ru(bpy)<sub>2</sub>(dppn)](PF<sub>6</sub>)<sub>2</sub>, has also been studied for comparison (Fig. 1). The spectra were recorded under 355 nm excitation, in the range 365 – 800 nm.

Laser excitation of [Ru(bpy)<sub>2</sub>(dppn)](PF<sub>6</sub>)<sub>2</sub> in deoxygenated CH<sub>3</sub>CN (Fig. 1) yields a bleach of the ground state absorbance at 420 nm, and a formation of transient absorption bands at 375 nm, 500 nm (sh), and 530 nm. The 420 nm bleach of the ground state band corresponds to a depopulation of a <sup>1</sup>MLCT transition.

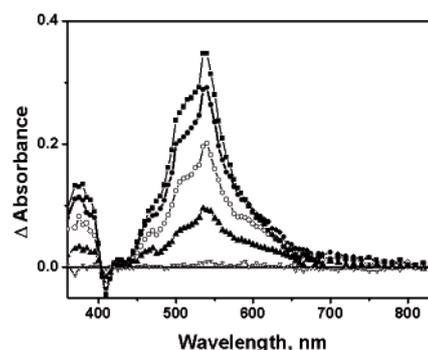
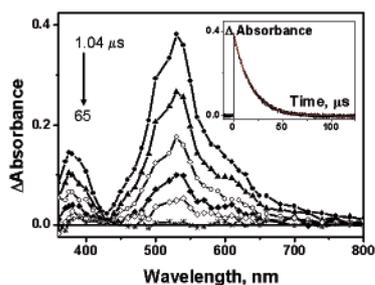


Figure 1. Transient absorption spectra of [Ru(bpy)<sub>2</sub>(dppn)](PF<sub>6</sub>)<sub>2</sub> in deoxygenated CH<sub>3</sub>CN. The spectra are recorded at 1.3, 2.5, 5, 6 and 25 microseconds after the 355 nm laser excitation pulse. The transient bands decay monoexponentially, simultaneously with the restoration of the ground state bleach.

The transient bands decay monoexponentially, simultaneously with the restoration of the ground state bleach, confirming that the transient features originate from the same excited state. The lifetime of the excited state, determined from both transient decay and parent recovery is 6.7 ( $\pm$  0.6)  $\mu\text{s}$ . No emission was observed from [Ru(bpy)<sub>2</sub>(dppn)](PF<sub>6</sub>)<sub>2</sub> in CH<sub>3</sub>CN under our experimental conditions, indicating that the lowest excited state in this complex is a “dark” state.

The representative transient absorption spectra for [Ru(tmp)(dppn)(CH<sub>3</sub>CN)](PF<sub>6</sub>)<sub>2</sub> obtained in degassed CH<sub>3</sub>CN are shown at Fig. 2. Upon excitation with 355 nm laser light, the new, transient absorption bands are formed, at the same energies as for [Ru(bpy)<sub>2</sub>(dppn)](PF<sub>6</sub>)<sub>2</sub>: 375,



**Figure 2.** Transient absorption spectra of  $[\text{Ru}(\text{tmp})(\text{dppn})\text{CH}_3\text{CN}](\text{PF}_6)_2$  in  $\text{CH}_3\text{CN}$  under 355 nm excitation, collected 1.04, 7, 15, 25, 35 and 65  $\mu\text{s}$  after the laser pulse. The insert shows a kinetic trace at 530 nm; the red line represents a monoexponential fit to the data.

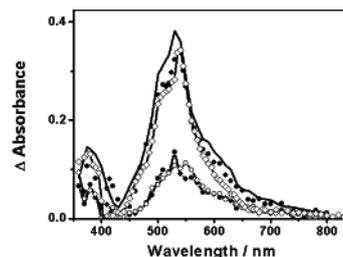
500 (sh) and 530 nm. The spectrum decays simultaneously, confirming that all the spectral features observed correspond to the same excited state. The decay follows first order law (Fig. 2, insert) with the corresponding lifetime of 18  $\mu\text{s}$ . No emission has been detected from the sample; a dip in the spectra is observed at ca. 430 nm which coincides with the position of the ground state lowest absorption band for this complex.

The  $\text{CH}_3\text{CN}$ - and py derivatives studied, both in water and acetonitrile, show virtually identical features in the transient absorption spectra, which are also identical to that of  $[\text{Ru}(\text{bpy})_2(\text{dppn})]^{2+}$  (Fig. 3). This observation indicates unambiguously the nature of the lowest excited state in these chromophores is the same.

However, the lifetime of this excited state is clearly dependent on the co-ligand, and the solvent. The L = py derivative in both  $\text{CH}_3\text{CN}$  and water exhibits a much shorter lifetime than the MeCN derivative. Replacing acetonitrile with water as a solvent also leads to a substantial decrease in the lifetime for both L =  $\text{CH}_3\text{CN}$  and L = py derivatives.

These observations can be rationalised in terms of an equilibrium between two excited states that are close in energy. The similarity of the transient absorption spectra of all the chromophores studied points to the  $\pi\pi^*$  nature of the excited state observed in these measurements. Furthermore, the long lifetimes detected are indicative of a triplet excited state, as could be anticipated for a complex containing a heavy atom. The change in the lifetime observed as a function of the solvent and of the ligand field of the co-ligand could be explained by a presence of an energetically close, short-lived  ${}^3\text{MLCT}$  excited state. The decrease in energy of the  ${}^3\text{MLCT}$  excited state in water if compared to acetonitrile would decrease the energy gap between  ${}^3\text{MLCT}$  and  ${}^3\pi\pi^*$  states, increase the quenching rate constant and lead to an observed decrease in the lifetime of the  ${}^3\pi\pi^*$  state. Likewise, a replacement of L = acetonitrile with a co-ligand of a weaker ligand field, L = pyridine, would decrease the energy gap between the  ${}^3\text{MLCT}$  and the  ${}^3\pi\pi^*$  excited states, facilitating quenching of the  ${}^3\pi\pi^*$  state and consequently decreasing its lifetime (Table 1).

Preliminary TD-DFT calculations into electronic structure of the Ru(II) chromophores studied are in accord with this hypothesis, and suggest that the  ${}^3\text{MLCT}$  state involved is of  $\{\text{Ru} \rightarrow \pi^*$  (phenazine) $\}$  origin.



**Figure 3.** An overlap of the transient absorption spectra of the  $[\text{Ru}(\text{tmp})(\text{dppn})\text{L}]$  derivatives, obtained after 355 nm excitation:

- $[\text{Ru}(\text{tmp})(\text{dppn})\text{CH}_3\text{CN}](\text{PF}_6)_2$  (solid line) in  $\text{CH}_3\text{CN}$ ;
- $[\text{Ru}(\text{tmp})(\text{dppn})\text{py}](\text{PF}_6)_2$  (■) in  $\text{CH}_3\text{CN}$ ;
- $[\text{Ru}(\text{bpy})_2(\text{dppn})](\text{PF}_6)_2$  in acetonitrile (-◇-);
- $[\text{Ru-dppn-CH}_3\text{CN}]\text{Cl}_2$  in water (-●-);
- $[\text{Ru-dppn-py}]\text{Cl}_2$  in water (○).

The spectra are scaled for clarity.

### Experimental details

Ru(II) complexes were prepared as described previously.<sup>[2]</sup> Nanosecond flash photolysis studies for transient absorption measurements were performed on solutions of the samples dissolved in degassed water or dry, degassed by three freeze-pump-thaw cycles acetonitrile. The home-built set-up comprised a Spectra-Physics Nd:YAG laser, 9 ns pulse width (laser loan pool). The typical laser energy used in the experiments was 1 – 3 mJ. A steady-state Xe lamp (Hamamatsu L 2273) was used as a probe source. The detection system includes a Hamamatsu R928 PMT, and a Tektronix 3032B oscilloscope, interfaced with a standard PC. The pump and probe beams were arranged in a collinear geometry.

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