

## Excited state properties of bis-tetraazaphenanthrene–Ru(II) diad complexes with a ferrocenyl unit

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### Abstract

The excited state properties of the diad complexes  $\text{Ru}(\text{tap})_2(\text{ppFc})^{2+}$  and  $\text{Ru}(\text{bpy})_2(\text{ppFc})^{2+}$  (tap, 1,4,5,8-tetraazaphenanthrene; bpy, 2,2'-bipyridine), bearing a reducing ferrocenyl (Fc) centre on a derivatized (pyridine)pyrazole (pp) ligand, were compared with those of the corresponding complexes without an Fc unit. For these latter complexes, the existence of intermolecular photoelectron transfer with added ferrocene was clearly demonstrated. However, direct evidence for intramolecular photoelectron transfer in  $\text{Ru}(\text{bpy})_2(\text{ppFc})^{2+}$  and  $\text{Ru}(\text{tap})_2(\text{ppFc})^{2+}$  could not be obtained unambiguously. Although the absence of luminescence in these diad complexes indicated the existence of this intramolecular process, laser flash photolysis did not allow the detection of a reduced complex entity in most experimental conditions. Only flash photolysis of  $\text{Ru}(\text{bpy})_2(\text{ppFc})^{2+}$  in water generated a long-lived intermediate with the characteristic spectral features of the radical anion  $\text{bpy}^{\cdot-}$ . Indirect arguments, such as the formation of a product on illumination of both diad complexes, were in favour of a photoreaction induced by intramolecular electron transfer.

**Keywords:** Photo-electron transfer; Ru complexes; Diad complex; Ferrocenyl diad complex; Flash photolysis

### 1. Introduction

Porphyrins have been widely examined as photosensitizers of electron transfer processes, particularly when they are chemically attached to electron donors and acceptors [1,2] in synthetic molecular structures which mimic the primary processes of photosynthetic reaction centres. Other photosensitizers incorporated into large molecular systems have also been designed, some of which are based on polypyridyl complexes [3–9].

Ferrocene is often used as an efficient electron donor for intermolecular electron transfer, e.g. ferrocenyl (Fc) groups for intramolecular charge transfer in multicomponent systems [10–15]. The ferrocene moiety exhibits a reversible redox behaviour and excellent properties as a reducing agent; however, decomposition problems of the ferricenium species have been reported [16]. In addition to these interesting characteristics as a reducing agent, ferrocene has been shown to behave as an efficient quencher by energy transfer from excited triplets of organic compounds or metallic complexes.

Recent reports [10] have described the synthesis of Ru(II) complexes with 2,2'-bipyridine (bpy) and terpyridyl ligands, covalently linked to Fc units. Although important intramolecular quenching of the metal-to-ligand charge transfer (MLCT) excited triplet states of Ru(II) compounds has been observed, the existence of intramolecular photoelectron transfer has not been demonstrated, in spite of the fact that the electron transfer process is thermodynamically favourable. In these supramolecular systems, the important intramolecular luminescence quenching by Fc groups may also be attributed, as mentioned above, to energy transfer from the complex moiety to the Fc unit, which competes with electron transfer. The triplet energy of ferrocene, evaluated between 1.1 and 1.8 eV [10,16–18], makes the energy transfer from the MLCT triplet excited states of Ru(II) complexes to ferrocene rather favourable. Therefore it is generally difficult to predict whether electron or energy transfer, or both processes, are responsible for the emission quenching.

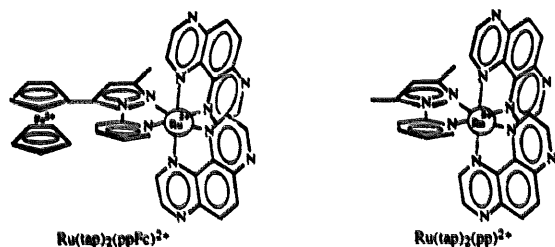
Lee and Wrighton [19] demonstrated, by flash photolysis of Ru(II) complexes in the presence of different ferrocenes, that the increase in the driving force of intermolecular photoelectron transfer favours quite clearly the contribution of electron vs. energy transfer. This has been demonstrated with ferrocenes with increasing reduction powers, i.e. methylated

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ferrocenes, and with excited complexes with enhanced oxidation powers, i.e. when  $\text{Ru}(\text{bpy})_3^{2+}$  is replaced by  $\text{Ru}(\text{bpz})_3^{2+}$  (bpz, 2,2'-bipyrazine).

At the Université Libre de Bruxelles, we have accumulated data on Ru(II) complexes based on oxidizing polyazaaromatic ligands, such as 1,4,5,8-tetraazaphenanthrene (tap) and 1,4,5,9,12-hexaazatriphenylene (hat) [20–22]. We have shown that Ru(II)–tap complexes behave as very efficient oxidants in their  $^3\text{MLCT}$  excited states vs. hydroquinone [21,22], nucleotides [23–25] and DNA [26–28]. On the other hand, the research team in Montpellier has examined the properties of heteroleptic bpy complexes with pyridine-pyrazole ligands derivatized with an Fc group [29,30]. In the present work, we have combined our efforts to design bifunctional complexes (composed of an electron donor and acceptor unit), in which the driving force for intramolecular electron transfer from Fc to the excited complex unit is increased by the high oxidation power of the excited complex moiety containing tap ligands. In this paper, we present the first report on the photophysics of a complex containing tap and 5-ferrocenyl-3-methyl-1-(2'-pyridine)pyrazole (ppFc), i.e.  $\text{Ru}(\text{tap})_2(\text{ppFc})^{2+}$ . Its properties, especially the electron donor–acceptor properties, are compared with those of the corresponding compound without an Fc unit (i.e.  $\text{Ru}(\text{tap})_2(\text{pp})^{2+}$ ), and with those of complexes in which the two tap ligands are substituted by two bpy chelates (with the third ligand corresponding to pp or ppFc).



## 2. Experimental section

### 2.1. Preparation of the complexes

The syntheses of the ligands and complexes ( $\text{Ru}(\text{bpy})_2(\text{pp})^{2+}$  and  $\text{Ru}(\text{bpy})_2(\text{ppFc})^{2+}$ ) were carried out as described previously [29,30].

The precursor  $\text{Ru}(\text{tap})_2\text{Cl}_2$  was synthesized according to a well-known procedure [31].  $\text{Ru}(\text{tap})_2(\text{pp})^{2+}$  and  $\text{Ru}(\text{tap})_2(\text{ppFc})^{2+}$  were prepared by refluxing for 5 h one equivalent of pp or ppFc with one equivalent of  $\text{Ru}(\text{tap})_2\text{Cl}_2$  in a water– $\text{CH}_3\text{OH}$  (1 : 1) solution. The complexes were purified by chromatography on Sephadex SP C25 by elution with aqueous solutions of NaCl ( $1 \times 10^{-2}$  M to  $2.5 \times 10^{-2}$  M), and were precipitated by the addition of a saturated  $\text{NH}_4\text{PF}_6$  aqueous solution; they were characterized by nuclear magnetic resonance (NMR) spectroscopy (250 MHz) in  $\text{CD}_3\text{CN}$ . The assignments of the different peaks in the NMR

spectrum of  $\text{Ru}(\text{tap})_2(\text{ppFc})^{2+}$  were performed on the basis of the corresponding  $^1\text{H}$ – $^1\text{H}$  correlation spectroscopy (COSY) spectrum.

#### 2.1.1. $\text{Ru}(\text{tap})_2(\text{pp})^{2+}$

Spectral data  $\delta$ : 1.34 (s, 3H, pyrazole 3), 2.86 (s, 3H, pyrazole 5), 6.39 (s, 1H, pyrazole 4), 7.15 (m, 1H, pyridyl 5), 7.52 (d, 1H, pyridyl 6), 7.96 (d, 1H, tap 3, 6), 8.09 (m, 2H, pyridyl 4 and 3), 8.12 (d, 1H, tap 3, 6), 8.30 (d, 1H, tap 3, 6), 8.50 (d, 1H, tap 3, 6), 8.57 (m, 4H, tap 9, 10), 8.79 (d, 1H, tap 2, 7), 8.85 (d, 1H, tap 2, 7), 9.15 (d, 1H, tap 2, 7), 9.19 (d, 1H, tap 2, 7).

#### 2.1.2. $\text{Ru}(\text{tap})_2(\text{ppFc})^{2+}$

Spectral data  $\delta$ : 1.42 (s, 3H, pyrazole), 4.32 (s, 5H, ferrocene), 4.619 (s, 4H, ferrocene), 6.83 (s, 1H, pyrazole 4), 7.23 (d, 1H, pyridyl 3), 7.76 (m, 1H, pyridyl 4), 7.05 (m, 1H, pyridyl 5), 7.46 (d, 1H, pyridyl 6), 7.96 (d, 1H, tap 3, 6), 8.16 (d, 1H, tap 3, 6), 8.36 (d, 1H, tap 3, 6), 8.56 (d, 1H, tap 3, 6), 8.6 (d, 4H, tap 9, 10), 8.83 (d, 1H, tap 2, 7), 8.85 (d, 1H, tap 2, 7), 9.19 (d, 1H, tap 2, 7), 9.27 (d, 1H, tap 2, 7).

## 2.2. Reagents and solvents

Acetonitrile (spectroscopic grade) was used as received for absorption and luminescence spectroscopy and water was purified with a Milli-Q (Millipore) system. Ferrocene was purchased from Sigma and was used without further purification.

## 2.3. Electrochemistry

Cyclic voltammetry was performed with a platinum disc electrode in freshly distilled acetonitrile, with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. The potential of the working electrode, scanned at 200  $\text{mV s}^{-1}$  between  $-2$  V and 2 V, was controlled by a Sirius potentiogalvanostat vs. a saturated calomel electrode (SCE) separated from the solution by a Tacussel bridge; the counter electrode was a platinum wire.

## 2.4. Absorption and luminescence

Absorption spectra were recorded on an HP 8452 A diode array spectrophotometer or a Varian Cary 219 UV–visible spectrophotometer. The molar extinction coefficients of the complexes were determined by ruthenium titration by atomic emission from plasma atomization (spectrometric Spectrospan IV instrument).

Luminescence spectra were obtained with a Shimadzu RF-5001 PC spectrofluorometer equipped with a Hamamatsu R-928 photomultiplier tube, with 420 nm excitation; they were corrected for the photomultiplier response.

Emission quantum yields ( $\phi_{\text{em}}$ ) were determined by integrating the corrected emission spectra over the frequency.

The optical dilute method was used [32]; Ru(bpy)<sub>3</sub><sup>2+</sup> in water under air was chosen as the standard luminophore ( $\phi=0.028$ ) [33]. The oxygen concentration in aqueous solution was calculated according to standard data [34] ( $0.27 \times 10^{-3}$  M in aqueous solution and  $1.9 \times 10^{-3}$  M in acetonitrile at 25 °C).

### 2.5. Laser flash photolysis and luminescence lifetimes

Transient absorbance signals were recorded after pulse excitation of approximately 8–9 ns at 355 nm from a neodymium-YAG laser (Continuum NY 61-10) with a 300 W Xe lamp as monitoring source; the signals were analysed according to a procedure described previously [26]. This laser equipment allows the detection and analysis of transients with lifetimes longer than a few tens of nanoseconds. Emission lifetimes were determined with a modified Applied Photophysics laser kinetic spectrometer equipped with a Hamamatsu R-928 photomultiplier tube and an excitation source at 355 nm.

### 2.6. Photolysis of the complexes under continuous irradiation

Photolysis of the different complexes was carried out in a standard 1 cm<sup>3</sup> quartz cell using visible light excitation from a 2000 W Phillips lamp with an NaNO<sub>2</sub> UV cut-off filter.

## 3. Results

### 3.1. Electrochemistry

The redox potentials in CH<sub>3</sub>CN of the four complexes Ru(tap)<sub>2</sub>(pp)<sup>2+</sup>, Ru(tap)<sub>2</sub>(ppFc)<sup>2+</sup>, Ru(bpy)<sub>2</sub>(pp)<sup>2+</sup> and Ru(bpy)<sub>2</sub>(ppFc)<sup>2+</sup>, measured by cyclic voltammetry, are collected in Table 1. Two reversible reduction waves are observed for the four compounds; they correspond to successive additions of one electron on the first bpy (or tap) and second bpy (or tap) ligands. The pp reduction is not accessible in the potential range investigated. The voltammograms also exhibit one reversible oxidation wave for the mononuclear complexes (without Fc), attributed to the oxidation of the Ru(II) centre. The diad complexes exhibit two oxidation waves. The first is reversible and attributed to the oxidation of the Fc unit; it is shifted anodically (0.14–0.16 V) compared with ferrocene itself (0.50 V vs. saturated sulfate calomel electrode (SSCE); 0.49 V vs. SCE) [35]. The second oxidation wave is irreversible and corresponds to the oxidation of the Ru<sup>2+</sup> centre.

### 3.2. Behaviour in absorption and emission

The absorption data for the four complexes, Fc and ppFc are collected in Table 2. The absorption spectra of

Table 1  
Electrochemical data<sup>a</sup>

Complex	Reduction		Ru <sup>2+</sup> / Ru <sup>3+</sup>	Fe <sup>2+</sup> / Fe <sup>3+</sup>
Ru(bpy) <sub>2</sub> pp <sup>2+</sup>	-1.37 <sup>b</sup>	-1.61 <sup>b</sup>	+1.23 <sup>b</sup>	
Ru(bpy) <sub>2</sub> ppFc <sup>2+</sup>	-1.30	-1.55	+1.45 (irr) <sup>c</sup>	+0.63
Ru(tap) <sub>2</sub> pp <sup>2+</sup>	-0.79	-1.00	+1.74 <sup>b</sup>	
Ru(tap) <sub>2</sub> ppFc <sup>2+</sup>	-0.78	-1.00	+1.85 (irr) <sup>c</sup>	+0.65

<sup>a</sup>The redox potentials were determined by cyclic voltammetry in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte, a platinum electrode and a scan rate of 200 mV s<sup>-1</sup> between -2 V and 2 V; potentials are given in volts vs. SCE; irr, irreversible wave. <sup>b</sup>See Refs. [29,30]. <sup>c</sup>When irreversible, the potential corresponds to the peak potential.

Ru(tap)<sub>2</sub>(pp)<sup>2+</sup> and Ru(tap)<sub>2</sub>(ppFc)<sup>2+</sup> in water are shown in Fig. 1.

Photolysis at room temperature of Ru(bpy)<sub>2</sub>(pp)<sup>2+</sup> in CH<sub>3</sub>CN leads to rapid absorption changes as a function of the illumination time (Fig. 2(A)), which indicates photodecomposition (the photolysis of Ru(ppFc)<sub>3</sub><sup>2+</sup> in CH<sub>3</sub>CN leads to the loss of one ppFc ligand, replaced by two CH<sub>3</sub>CN molecules, with transformations of the absorption spectrum similar to those in Fig. 2) [30]. When illuminated in water (Fig. 3(A)), in the same conditions, Ru(bpy)<sub>2</sub>(pp)<sup>2+</sup> also reveals the existence of photodegradation (changes in absorption as in Fig. 3(A) are typical of the loss of a bidentate ligand, with substitution by at least one Cl<sup>-</sup> ion (and one

Table 2  
Spectroscopic data:  $\lambda_{\max}$  (nm) ( $\epsilon \times 10^{-4}$  (M<sup>-1</sup> cm<sup>-1</sup>))<sup>a</sup>

Complex	Abs/H <sub>2</sub> O	Abs/CH <sub>3</sub> CN	Em/H <sub>2</sub> O	Em/CH <sub>3</sub> CN
Ru(bpy) <sub>2</sub> pp <sup>2+</sup>	244 (2.85)	246	628 <sup>d</sup>	616 <sup>d</sup>
	284 (5.8)	282		
	364 (0.77)	366		
	410 (0.87)	408		
	450 (0.96)	448		
Ru(bpy) <sub>2</sub> ppFc <sup>2+</sup>	244 (3.22)		- <sup>d</sup>	- <sup>d</sup>
	282 (6.2)	286		
	410 (1.18)	410		
	450 (1.12)	450		
Ru(tap) <sub>2</sub> pp <sup>2+</sup>	228 (4.15)	228	670	650
	274 (5.84)	274		
	388 (0.96)	390		
	462 (1.15)	458		
Ru(tap) <sub>2</sub> ppFc <sup>2+</sup>	230 (4.79)		- <sup>d</sup>	- <sup>d</sup>
	276 (5.77)	274		
	398 (1.54)	400		
	460 (1.44)	458		
Fc		442 (0.009) <sup>h</sup>	-	-
ppFc		450 (0.026) <sup>c</sup>	-	-

<sup>a</sup>Absorption (Abs) and uncorrected emission (Em). <sup>b</sup>See Ref. [10]. <sup>c</sup>See Ref. [29]. <sup>d</sup>Changes in luminescence intensity were observed on irradiation, indicating decomposition, as concluded from the absorption data. The initial luminescence intensity of Ru(bpy)<sub>2</sub>(pp)<sup>2+</sup> decreases with illumination in water or CH<sub>3</sub>CN, in contrast with that of Ru(tap)<sub>2</sub>(pp)<sup>2+</sup> which remains constant (no decomposition). Ru(bpy)<sub>2</sub>(ppFc)<sup>2+</sup> remains non-luminescent, even after irradiation. Ru(tap)<sub>2</sub>(ppFc)<sup>2+</sup>, which does not luminesce at the beginning of irradiation, exhibits an increased emission, reaching a plateau value as a function of the irradiation time in water and CH<sub>3</sub>CN.

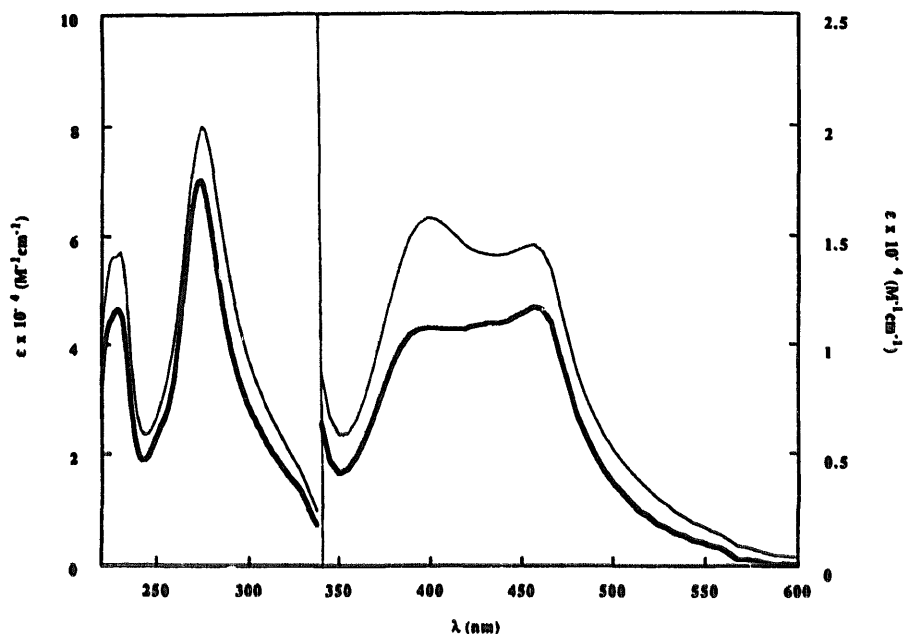


Fig. 1. Absorption spectra of  $\text{Ru}(\text{tap})_2(\text{pp})^{2+}$  (thick line) and  $\text{Ru}(\text{tap})_2(\text{ppFc})^{2+}$  (thin line) in water at room temperature.

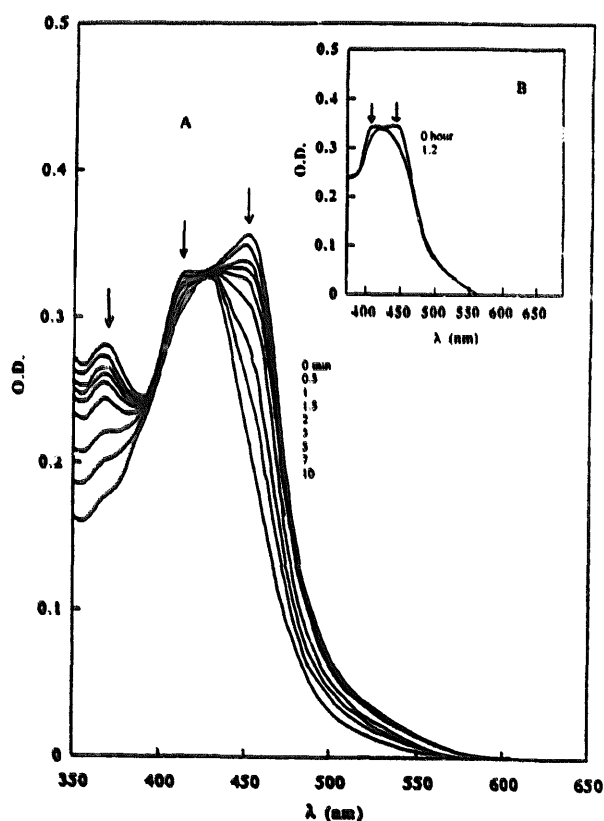


Fig. 2. (A) Photolysis of  $\text{Ru}(\text{bpy})_2(\text{pp})^{2+}(\text{PF}_6^-)_2$  in  $\text{CH}_3\text{CN}$  under Ar at room temperature. (B) Photolysis of  $\text{Ru}(\text{bpy})_2(\text{ppFc})^{2+}(\text{PF}_6^-)_2$  in  $\text{CH}_3\text{CN}$  under Ar at room temperature.

$\text{H}_2\text{O}$ ) responsible for the bathochromic shift) [36]. The attachment of the Fc unit to  $\text{Ru}(\text{bpy})_2\text{pp}^{2+}$  clearly diminishes the rate of photodecomposition in  $\text{CH}_3\text{CN}$  (Fig. 2(B)) and water (Fig. 3(B)); the illumination times required to observe absorption changes are indeed much longer in the presence of the Fc group.

In contrast, irradiation of  $\text{Ru}(\text{tap})_2(\text{pp})^{2+}$  in  $\text{CH}_3\text{CN}$  or water, in the same conditions as above, does not lead to any modification of the starting absorption, and thus no photodecomposition is detected. However, the addition of an Fc unit induces weak variations of the MLCT absorption band of  $\text{Ru}(\text{tap})_2(\text{ppFc})^{2+}$  on illumination (not shown) in water

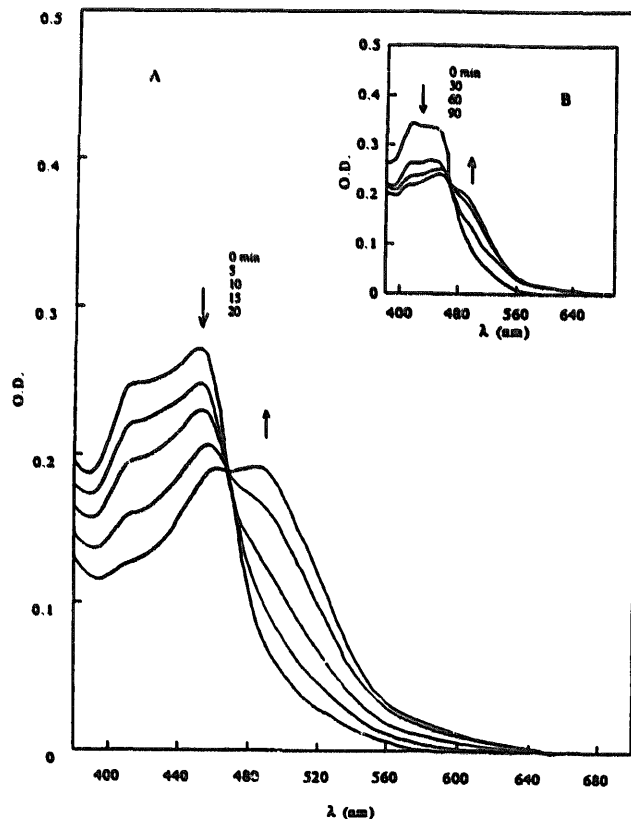


Fig. 3. (A) Photolysis of  $\text{Ru}(\text{bpy})_2(\text{pp})^{2+}(\text{Cl}^-)_2$  in  $\text{H}_2\text{O}$  under Ar at room temperature. (B) Photolysis of  $\text{Ru}(\text{bpy})_2(\text{ppFc})^{2+}(\text{Cl}^-)_2$  in  $\text{H}_2\text{O}$  under Ar at room temperature.

or CH<sub>3</sub>CN. These features indicate that the Fc group induces photoreactivity in this diad complex.

The emission spectra originating from the <sup>3</sup>MLCT excited states were recorded at room temperature in aqueous and acetonitrile solutions. The emission maxima are given in Table 2. Without Fc, the luminescence of the tap complex is bathochromic relative to the bpy compound, and as usually observed with most Ru(II) complexes [37], there is a slight red shift from CH<sub>3</sub>CN to water. No emission is detected for the Fc derivatized complexes.

Under pulsed excitation, without the Fc unit, the luminescence decays according to a single exponential. The corresponding luminescence lifetimes are given in Table 3, together with the values for the reference compounds. The emission lifetimes are longer for Ru(tap)<sub>2</sub>(pp)<sup>2+</sup> than for Ru(bpy)<sub>2</sub>(pp)<sup>2+</sup> in CH<sub>3</sub>CN and water. Moreover, Ru(tap)<sub>2</sub>(pp)<sup>2+</sup> has a longer emission lifetime in CH<sub>3</sub>CN than in water, whereas Ru(bpy)<sub>2</sub>(pp)<sup>2+</sup> exhibits a shorter luminescence lifetime in CH<sub>3</sub>CN than in water. The quenching rate constants of the excited complexes by O<sub>2</sub>, calculated from the emission lifetimes, are also given in Table 3.

The quantum yields of luminescence in water and in CH<sub>3</sub>CN are given in Table 4, together with the values for the reference compounds. The quantum yields are strikingly small for the complexes with the pp ligand relative to the values for the reference compounds. As for the luminescence lifetimes, for Ru(tap)<sub>2</sub>(pp)<sup>2+</sup>,  $\phi_{em}$  is higher in CH<sub>3</sub>CN than in water, whereas the opposite is observed for Ru(bpy)<sub>2</sub>(pp)<sup>2+</sup>.

### 3.3. Laser flash photolysis

Laser flash photolysis was carried out in order to determine the contribution of the electron transfer process to the total luminescence quenching. The reduced complexes that should be formed can be easily detected, as the corresponding transient absorption spectra with bpy and tap ligands have been fully characterized [21,22]. Laser flash photolysis experiments were first performed with the mononuclear complexes, i.e. without the Fc group, and then with the diad complexes for comparison.

Table 3  
Emission lifetimes and quenching rate constants by oxygen

Complex	$\tau$ (ns)				$k_q \times 10^{-9}$ (M <sup>-1</sup> s <sup>-1</sup> )	
	H <sub>2</sub> O/air	H <sub>2</sub> O/Ar	CH <sub>3</sub> CN/air	CH <sub>3</sub> CN/Ar	H <sub>2</sub> O	CH <sub>3</sub> CN
Ru(bpy) <sub>2</sub> (pp) <sup>2+</sup>	118	140	79	120	5	2.3
Ru(tap) <sub>2</sub> (pp) <sup>2+</sup>	176	183	450 <sup>a</sup>	936	0.8	0.6
Ru(tap) <sub>2</sub> (bpy) <sup>2+</sup>	–	778 [20]	–	2134 [20]	–	–
Ru(bpy) <sub>3</sub> <sup>3+</sup>	–	630 [20]	–	855 [20]	–	–

Estimated error in luminescence lifetimes: 3%–5%.

<sup>a</sup>It should be noted that, after exhaustive photolysis of Ru(tap)<sub>2</sub>(ppFc)<sup>2+</sup>, pulsed excitation of the irradiated solution produces a single exponential decay with a lifetime of 450 ns in CH<sub>3</sub>CN under air, which is equal to the luminescence lifetime of Ru(tap)<sub>2</sub>(pp)<sup>2+</sup>.

Table 4  
Emission quantum yields<sup>a</sup>:  $\phi_{em} \times 10^3$

Complex	H <sub>2</sub> O/air	H <sub>2</sub> O/Ar	CH <sub>3</sub> CN/ air	CH <sub>3</sub> CN/Ar
Ru(bpy) <sub>2</sub> (pp) <sup>2+</sup>	4.3	5	3	5
Ru(tap) <sub>2</sub> (pp) <sup>2+</sup>	3.4	3.5	7	15
Ru(tap) <sub>2</sub> (bpy) <sup>2+</sup>	–	40 [20]	–	174 [20]
Ru(bpy) <sub>3</sub> <sup>3+</sup>	28 [33]	42 [38]	12 [39]	62 [40]

<sup>a</sup>Quantum yields of emission (see Section 2) were determined relative to Ru(bpy)<sub>3</sub><sup>3+</sup> at room temperature in aqueous solution. For the Fc derivatives, no reliable luminescence can be detected.

#### 3.3.1. Mononuclear complexes alone

The transient absorption spectra in argon-purged aqueous solution, obtained after the laser pulse, for Ru(bpy)<sub>2</sub>(pp)<sup>2+</sup> (Fig. 4(A)) and Ru(tap)<sub>2</sub>(pp)<sup>2+</sup> (not shown) exhibit a depletion in the 400–470 nm region and a positive absorption at 350–370 nm and 500–540 nm. Kinetic analysis of the absorption decay and recovery (Fig. 4(B)) indicates that the processes are monomolecular with lifetimes corresponding to the luminescence lifetimes of the complexes in aqueous solution, i.e. 140 ns (Fig. 4(B)) for Ru(bpy)<sub>2</sub>(pp)<sup>2+</sup> and 180 ns for Ru(tap)<sub>2</sub>(pp)<sup>2+</sup>. When the laser flash photolysis experiments were performed in argon-purged CH<sub>3</sub>CN, the same type of transient absorption was detected (not shown), with lifetimes corresponding to the luminescence lifetimes in CH<sub>3</sub>CN (Table 3). These kinetic data clearly indicate that the transient absorptions without an Fc unit correspond to those of the <sup>3</sup>MLCT states (triplet–triplet absorption).

#### 3.3.2. Mononuclear complexes with added ferrocene

Intermolecular quenching of the two excited monometallic complexes (without Fc) by ferrocene has been examined in order to test ultimately the existence of intramolecular quenching by electron transfer in the Fc derivatized complexes. Because of the weak solubility of ferrocene in water, the quenching rate constant could not be obtained for this solvent and was determined only in CH<sub>3</sub>CN. Stern–Volmer plots of the luminescence intensities and lifetimes are linear over a large range of quencher concentration and lead to identical quenching rate constants:  $1.35 \times 10^{10}$  and  $9.7 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup> for Ru(tap)<sub>2</sub>(pp)<sup>2+</sup> and Ru(bpy)<sub>2</sub>(pp)<sup>2+</sup> respec-

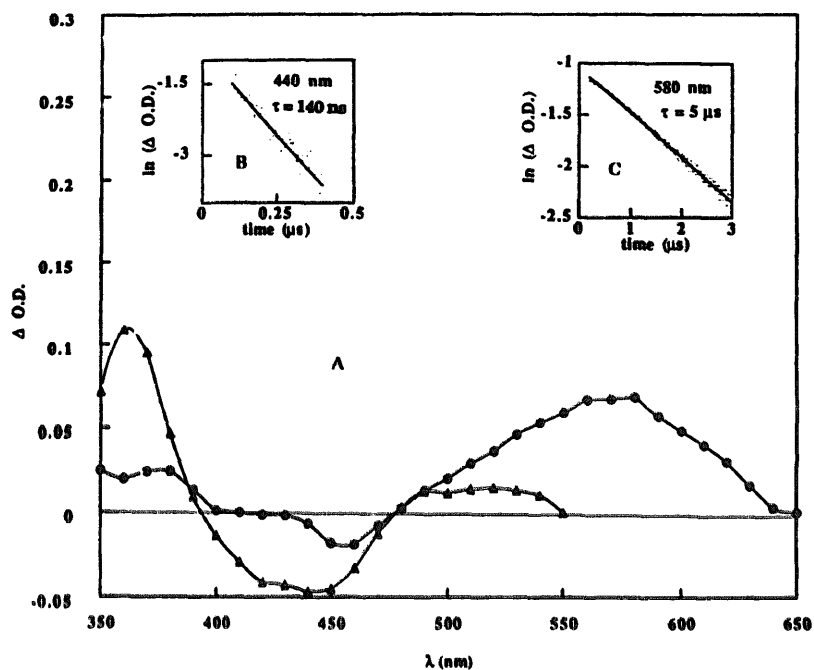


Fig. 4. (A) Transient differential absorption spectra for  $\text{Ru}(\text{bpy})_2(\text{pp})^{2+}$  ( $\blacktriangle$ ) and  $\text{Ru}(\text{bpy})_2(\text{ppFc})^{2+}$  ( $\bullet$ ) in water under Ar after the laser pulse. (B) First-order kinetic analysis of transient absorption of  $\text{Ru}(\text{bpy})_2(\text{pp})^{2+}$  at 440 nm in  $\text{H}_2\text{O}$  under Ar ( $\tau = 140$  ns). (C) First-order kinetic analysis of transient absorption of  $\text{Ru}(\text{bpy})_2(\text{ppFc})^{2+}$  at 580 nm in  $\text{H}_2\text{O}$  under Ar ( $\tau = 5$   $\mu\text{s}$ ).

tively. When ferrocene (1 mM) is added to an acetonitrile solution of  $\text{Ru}(\text{bpy})_2(\text{pp})^{2+}$  (50% quenching), no transient is observed. When the ferrocene concentration is increased to  $10^{-2}$  M (92% luminescence quenching), a positive transient absorption is detected in the 490–550 nm region (not shown), which decays on a time scale of approximately 50  $\mu\text{s}$  according to a bimolecular process. These data indicate that this new transient originates from the quenching of the

$^3\text{MLCT}$  excited state by ferrocene. When ferrocene (1 mM) is added to an acetonitrile solution of  $\text{Ru}(\text{tap})_2(\text{pp})^{2+}$  (93% luminescence quenching), a transient absorption (Fig. 5(A)) is also observed and decays at 550 nm in approximately 50  $\mu\text{s}$  (Fig. 5(B)) according to a bimolecular process. This again demonstrates that the transient originates from the quenching of the  $^3\text{MLCT}$  excited state. For comparable percentages of luminescence quenching by ferrocene, the

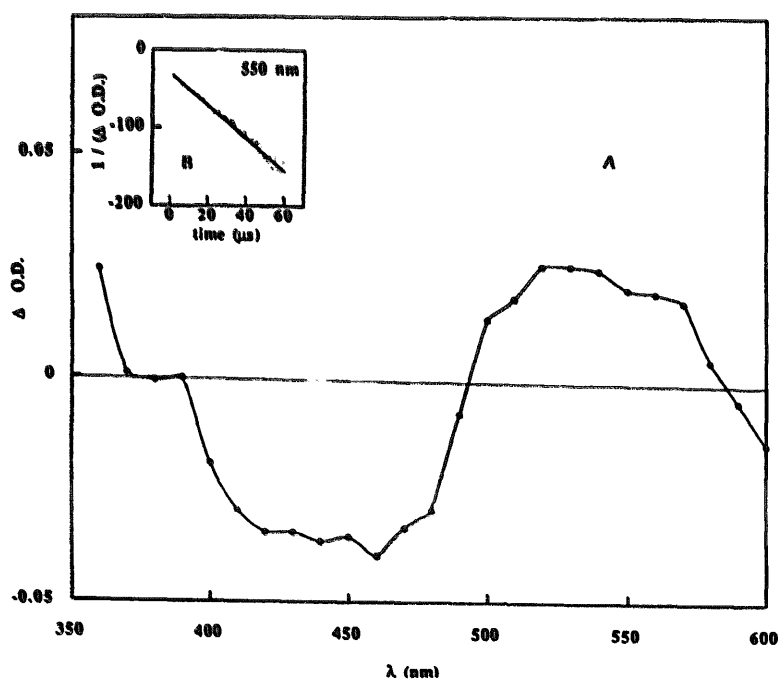


Fig. 5. (A) Transient differential absorption of  $\text{Ru}(\text{tap})_2(\text{pp})^{2+}$  ( $5 \times 10^{-5}$  M) and ferrocene (1 mM) in  $\text{CH}_3\text{CN}$  under Ar after the laser pulse. (B) Corresponding second-order kinetic analysis of absorption at 550 nm.

intensity of the transient is approximately five times larger with  $\text{Ru}(\text{tap})_2(\text{pp})^{2+}$  than with  $\text{Ru}(\text{bpy})_2(\text{pp})^{2+}$ .

### 3.3.3. The diad complexes

Laser flash photolysis of the Ru(II) complexes bearing an Fc unit, in acetonitrile, does not produce any detectable transient absorption after the laser pulse. In aqueous solution, although  $\text{Ru}(\text{tap})_2(\text{ppFc})^{2+}$  does not produce any detectable transient species,  $\text{Ru}(\text{bpy})_2(\text{ppFc})^{2+}$  exhibits an important transient absorption (Fig. 4) after the laser pulse. Analysis at 580 nm indicates that the decay corresponds to a first-order process, with a lifetime of approximately 5  $\mu\text{s}$  (Fig. 4(C)). It is clear that this transient does not correspond to the  $^3\text{MLCT}$  absorption, but to an intermediate originating from intramolecular luminescence quenching.

## 4. Discussion

### 4.1. Electrochemistry

The electrochemical data clearly show the effect of the  $\pi$ -accepting properties of the tap ligand relative to the bpy ligand [20] on the reduction (more than 0.5 V difference) and oxidation (0.51 V anodic shift) potentials of  $\text{Ru}(\text{tap})_2(\text{pp})^{2+}$  relative to  $\text{Ru}(\text{bpy})_2(\text{pp})^{2+}$ . Moreover, for both complexes, the addition of the Fc unit makes the oxidation wave of the  $\text{Ru}^{2+}$  centre into  $\text{Ru}^{3+}$  irreversible. This indicates that heterogeneous electron transfer is followed by a fast chemical reaction. In this case, and for certain boundary conditions on the chemical reaction rate constant, the anodic peak potential  $E_{\text{pa}}$  is anodically [41] shifted relative to the redox oxidation potential  $E_{\text{ox}}$ . Thus the shift of the oxidation wave with the introduction of the Fc unit is caused by a chemical reaction (such as decomposition) which follows the Ru(II) to Ru(III) oxidation. The diad complexes, in their completely oxidized forms, decompose within the time scale of cyclic voltammetry. The generated Ru(III) oxidizes, probably irreversibly, the ferrocenium unit, which explains the absence of Ru(III) ion to be reduced on the reverse scan.

### 4.2. Absorption and luminescence

The effect of the attachment of the pp moiety on the absorption spectrum of ferrocene (Table 2) is much weaker than that of the 4'-aryl-terpyridine fragment studied previously by other researchers [10]. These workers attributed the effects of this fragment to a charge transfer transition from ferrocene to the  $\pi^*$  terpyridine ligand orbital. On the basis of the above data on the free ligand ppFc, the increase in  $\epsilon$  of the MLCT band of  $\text{Ru}(\text{tap})_2\text{ppFc}^{2+}$  relative to  $\text{Ru}(\text{tap})_2\text{pp}^{2+}$  (Fig. 1) cannot be attributed solely to the additional absorption of the ppFc unit. The increase in intensity of the MLCT Ru–tap transition, more importantly in the 400 nm than in the 450 nm region, is probably caused by the underlying presence of the MLCT Ru–ppFc band. The latter shifts bathochromically

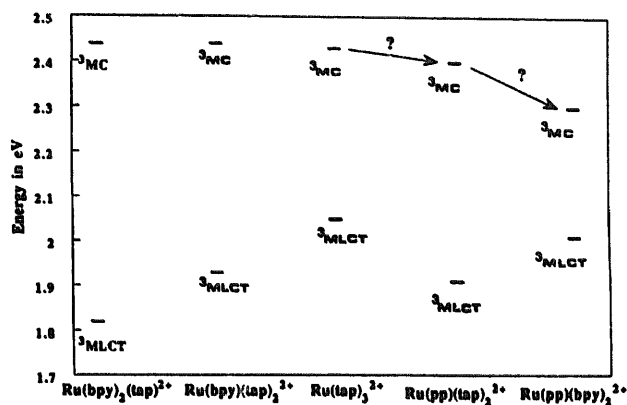


Fig. 6. Energetic diagram of the  $^3\text{MLCT}$  and  $^3\text{MC}$  states for  $\text{Ru}(\text{bpy})_2(\text{tap})^{2+}$ ,  $\text{Ru}(\text{bpy})(\text{tap})_2^{2+}$  and  $\text{Ru}(\text{tap})_3^{2+}$  (from [20]) and  $\text{Ru}(\text{tap})_2(\text{pp})^{2+}$  and  $\text{Ru}(\text{bpy})_2(\text{pp})^{2+}$  from this work in  $\text{CH}_3\text{CN}$ .

[29] relative to the MLCT Ru–pyridine transition which appears at 350 nm [31].

The luminescence of the two monometallic complexes is quenched by oxygen, as observed for most Ru(II) complexes. In water and  $\text{CH}_3\text{CN}$ , the quenching rate constant is lower for  $\text{Ru}(\text{tap})_2(\text{pp})^{2+}$  than for  $\text{Ru}(\text{bpy})_2(\text{pp})^{2+}$ . The effect of the ligand has been attributed, for other complexes, to the existence of quenching by electron transfer from the excited complex to oxygen, which is higher for the more reducing complexes, i.e. the bpy compounds relative to the tap compounds [42].

The fact that the luminescence of the tap complex is red shifted relative to that of the bpy compound is in accord with the electrochemical data. Indeed, as shown by the shifts of the oxidation and reduction potentials from  $\text{Ru}(\text{bpy})_2(\text{pp})^{2+}$  to  $\text{Ru}(\text{tap})_2(\text{pp})^{2+}$  in Table 1, the metallic-type  $d\pi$  orbital and the ligand-centred  $\pi^*$  orbital are both stabilized, but the stabilization of the tap  $\pi^*$  orbital is more important, leading to a bathochromic shift when two bpy ligands are replaced by two tap ligands.

The excited state behaviour (lifetimes and photodecomposition) can be rationalized on the basis of Fig. 6, where the energy levels of the excited  $^3\text{MLCT}$  and  $^3\text{MC}$  (MC, metal-centred) states in  $\text{CH}_3\text{CN}$  are plotted for a series of tap complexes ( $\text{Ru}(\text{bpy})_2\text{tap}^{2+}$ ,  $\text{Ru}(\text{bpy})(\text{tap})_2^{2+}$  and  $\text{Ru}(\text{tap})_3^{2+}$ ) according to literature data [20,37]. By comparison with this series,  $\text{Ru}(\text{tap})_2(\text{pp})^{2+}$  behaves in a similar fashion to  $\text{Ru}(\text{bpy})(\text{tap})_2^{2+}$  (and as most Ru(II) complexes), i.e. it exhibits a shorter luminescence lifetime in water than in  $\text{CH}_3\text{CN}$  due to efficient energy transfer to the OH vibrators of water [38] and negligible photodecomposition. This ‘classical behaviour’ is, however, not observed with  $\text{Ru}(\text{bpy})_2(\text{pp})^{2+}$  (shorter emission lifetime in  $\text{CH}_3\text{CN}$  than in water and photodecomposition) which behaves like  $\text{Ru}(\text{tap})_3^{2+}$ . For the latter complex, it was shown [20] that, due to its smaller energy difference  $^3\text{MLCT} - ^3\text{MC}$  (Fig. 6), thermal activation from  $^3\text{MLCT}$  to  $^3\text{MC}$  is rather efficient. Therefore its luminescence lifetime is controlled by the rate constant of thermal activation  $k_{\text{MC}}$  ( $\tau \approx 1/(k_r + k_{\text{nr}} + k_{\text{MC}})$  with  $k_{\text{MC}} \gg k_r + k_{\text{nr}}$ ) [20], which gives rise to important pho-

todecomposition. (The situation is not as clear in water because, in this solvent, the rate constant of radiationless deactivation from the  $^3\text{MLCT}$  state to the ground state ( $k_{nr}$ ) increases due to energy transfer to the OH vibrators, which leads to less control by  $k_{MC}$ .) Thus, as the observed behaviour for excited  $\text{Ru}(\text{bpy})_2(\text{pp})^{2+}$  is similar to that of excited  $\text{Ru}(\text{tap})_2^{3+}$  (concerning trends in emission lifetimes and photodecomposition), we assume that the photophysics of  $\text{Ru}(\text{bpy})_2(\text{pp})^{2+}$  is also similar to that of  $\text{Ru}(\text{tap})_2^{3+}$ . In the energy level diagram of Fig. 6, this will mean that, for  $\text{Ru}(\text{bpy})_2(\text{pp})^{2+}$ , the energy difference  $^3\text{MLCT} - ^3\text{MC}$  should be equal to or smaller than that for  $\text{Ru}(\text{tap})_2^{3+}$ : this implies a drop of the  $^3\text{MC}$  energy of  $\text{Ru}(\text{bpy})_2(\text{pp})^{2+}$  (Fig. 6) due to distortion introduced by the ligand (pp) containing a five-membered ring [43,44].

The values of  $\phi_{em}$  for the pp complexes in Table 4 reflect the trends in the luminescence lifetimes, although only crudely. These values are strikingly smaller than those for the standard complexes  $\text{Ru}(\text{bpy})_3^{3+}$  and  $\text{Ru}(\text{tap})_2(\text{bpy})^{2+}$ . This is particularly strange since the luminescence lifetime of  $\text{Ru}(\text{tap})_2(\text{pp})^{2+}$  (936 ns) is approximately the same as that of  $\text{Ru}(\text{bpy})_3^{3+}$  (855 ns) in  $\text{CH}_3\text{CN}$  under argon, despite the fact that  $\phi_{em}$  of  $\text{Ru}(\text{tap})_2(\text{pp})^{2+}$  is approximately four times smaller than that of  $\text{Ru}(\text{bpy})_3^{3+}$ . These observations suggest that the quantum yield of intersystem crossing is not equal to unity for the pp complexes. Such a lower  $\phi_{ISC}$  value has already been measured for complexes exhibiting a high degree of distortion, such as  $\text{Ru}(\text{pytda})_3^{3+}$  (pytda, 5-(2'-pyridyl)-1,2,4-thiadiazole) containing a five-membered heterocyclic moiety [43,44].

#### 4.3. Presence of a photoelectron transfer process

##### 4.3.1. Intermolecular

The laser flash photolysis of  $\text{Ru}(\text{bpy})_2(\text{pp})^{2+}$  and  $\text{Ru}(\text{tap})_2(\text{pp})^{2+}$  in the presence of ferrocene in  $\text{CH}_3\text{CN}$  demonstrates clearly the appearance of intermolecular electron transfer from ferrocene to the excited complex. Thus, in the presence of ferrocene, the absorption at 500 nm decays according to a bimolecular process during a few tens of microseconds due to back electron transfer. In accord with this, the absorption in the 500–590 nm region corresponds to the  $\pi-\pi^*$  transitions typical of the radical anions  $\text{bpy}^{\cdot-}$  [45,46] and  $\text{tap}^{\cdot-}$  [21,22], characteristic of the reduced complexes  $[\text{Ru}(\text{bpy})(\text{bpy}^{\cdot-})(\text{pp})]^+$  and  $[\text{Ru}(\text{tap})(\text{tap}^{\cdot-})(\text{pp})]^+$  respectively.

As shown in Fig. 7, such a photoelectron transfer process is exergonic for the bpy and tap complexes. However, the driving force is much higher for the tap (0.63 eV exergonicity) than for the bpy (0.15 eV exergonicity) complex. As in both cases the energy transfer to ferrocene can compete with electron transfer, the participation of electron transfer to the total luminescence quenching should increase for the tap relative to the bpy compound. This is reflected by the larger amount of reduced complex produced after the laser pulse

for  $\text{Ru}(\text{tap})_2(\text{pp})^{2+}$  than for  $\text{Ru}(\text{bpy})_2(\text{pp})^{2+}$  for the same percentage of quenching by ferrocene.

##### 4.3.2. Intramolecular

The occurrence of intermolecular electron transfer furnishes an argument in favour of intramolecular electron transfer in the diad complexes  $\text{Ru}(\text{tap})_2(\text{ppFc})^{2+}$  and  $\text{Ru}(\text{bpy})_2(\text{ppFc})^{2+}$ .

However, after excitation by the laser pulse,  $\text{Ru}(\text{tap})_2(\text{ppFc})^{2+}$  in  $\text{CH}_3\text{CN}$  or water does not produce any observable transient originating from intramolecular luminescence quenching. Fast intramolecular back electron transfer (according to the characteristics of the flash photolysis described in Section 2, the recombination should take place in times shorter than a few tens of nanoseconds) thus prevents the observation of a transient reduced complex unit, as also concluded by other workers for other diads with Fc [10–15]. However, in the present case, there should be a leak reaction to this back electron transfer in order to explain the photodecomposition of  $\text{Ru}(\text{tap})_2(\text{ppFc})^{2+}$  (as observed by changes in the absorption spectrum and by the occurrence of luminescence as a function of the irradiation time). The fact that, after a sufficiently long illumination,  $\text{Ru}(\text{tap})_2(\text{ppFc})^{2+}$  produces one species with a luminescence lifetime which corresponds to that of  $\text{Ru}(\text{tap})_2(\text{pp})^{2+}$  (see Table 2 and Table 3) suggests that the Fc unit has been inactivated. This may originate from the production of oxidized Fc, which decomposes, as does oxidized ferrocene in aqueous solution and in most organic solvents [16,47]. Intramolecular luminescence quenching by energy transfer, which is of course also possible as discussed above, should not lead a priori to such destruction of the Fc group after a certain irradiation time.

For  $\text{Ru}(\text{bpy})_2(\text{ppFc})^{2+}$ , although no transient absorption is observed by laser flash photolysis in  $\text{CH}_3\text{CN}$ , comparison of the experiments under continuous irradiation, with and without the Fc unit (Fig. 2(A) and Fig. 2(B)), indicates that the presence of Fc quenches the photodecomposition of  $\text{Ru}(\text{bpy})_2(\text{pp})^{2+}$ . This decrease in photodecomposition may thus originate from quenching by electron transfer, although quenching by energy transfer cannot be completely excluded. When the laser flash photolysis of  $\text{Ru}(\text{bpy})_2(\text{ppFc})^{2+}$  is carried out in aqueous solution, transient absorption in the 500 nm region, i.e. with the spectroscopic characteristics of  $\text{bpy}^{\cdot-}$ , with a lifetime of approximately 5  $\mu\text{s}$ , is observed. This is indicative of intramolecular electron transfer. The observation of such reduced species with  $\text{Ru}(\text{bpy})_2(\text{ppFc})^{2+}$  and not with  $\text{Ru}(\text{tap})_2(\text{ppFc})^{2+}$  may originate from the higher exergonicity of back electron transfer with the bpy than with the tap compound, which would correspond to the Marcus inverted region and thus would lead to a slower recombination rate. However, an important solvent effect on the exergonicity and thus on the rate of back electron transfer must also play a role, as the transient is not detected for  $\text{Ru}(\text{bpy})_2(\text{ppFc})^{2+}$  in  $\text{CH}_3\text{CN}$ . It may also be argued that, as the lifetime of the reduced transient for



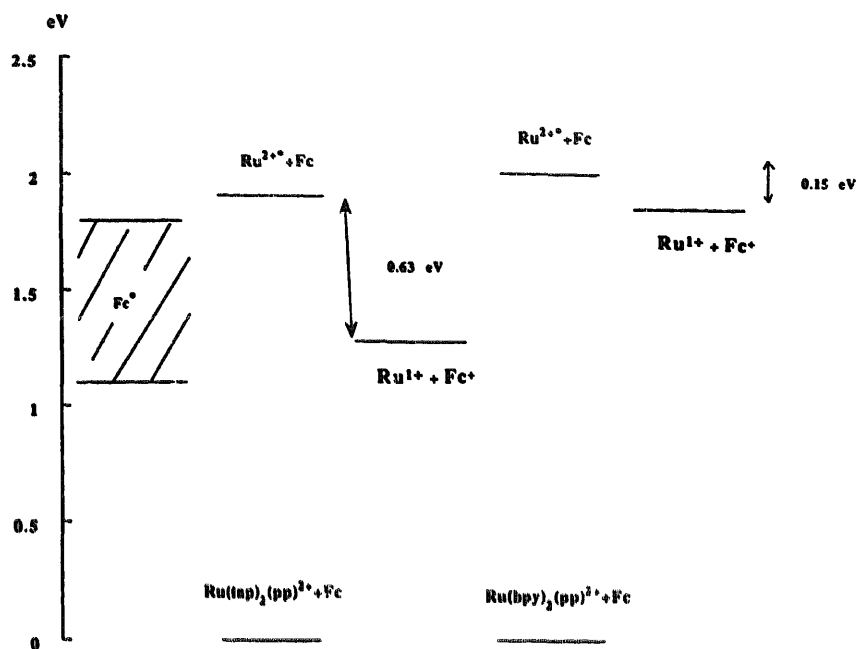


Fig. 7. Energy level diagram for photoelectron transfer from ferrocene to Ru(tap)<sub>2</sub>(pp)<sup>2+</sup>\* and Ru(bpy)<sub>2</sub>(pp)<sup>2+</sup>\*.

Ru(bpy)<sub>2</sub>(pnFc)<sup>2+</sup> in water is 5 μs, the intermediate will no longer correspond to an intact, but to a partially decomposed, complex. Indeed, due to intramolecular electron transfer on bpy, and because of some distortion in the complex, one coordination bond may break, which will lead to an intermediate in which back electron transfer will be slower than inside the intact diad. Again the solvent, i.e. water vs. CH<sub>3</sub>CN, should also play a role in this process.

## 5. Conclusions

This study shows that, for Ru(bpy)<sub>2</sub>(pp)<sup>2+</sup> and Ru(tap)<sub>2</sub>(pp)<sup>2+</sup>, intermolecular photoelectron transfer with ferrocene is favoured when bpy is replaced by tap. The different excited state behaviour in the absence of reducing agent can be explained on the basis of photophysical data available for other tap complexes. Concerning the intramolecular photoelectron transfer in Ru(bpy)<sub>2</sub>(ppFc)<sup>2+</sup> and Ru(tap)<sub>2</sub>(ppFc)<sup>2+</sup>, no clearcut conclusions can be drawn; however, indirect arguments, such as the photoinduced reactivities, are in favour of the intramolecular process.

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