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Journal of Photochemistry and Photobiology A: Chemistry 163 (2004) 381–388

Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Mononuclear and binuclear ruthenium(II) heteroleptic complexes based on 1,10-phenanthroline ligands

Part I: synthesis, spectroscopic and photophysical study

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Received 15 September 2003; received in revised form 5 January 2004; accepted 8 January 2004

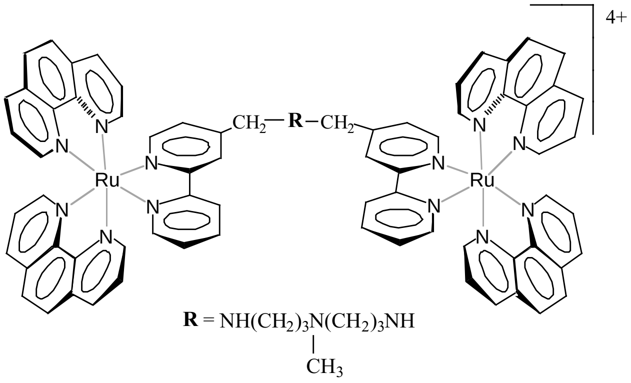
Abstract

A series of mononuclear and binuclear ruthenium(II) heteroleptic complexes as potential sensitizers for DNA photocleavage has been synthesized and characterized. This series based on 1,10-phenanthroline (phen) ligands is of the type $[\mathrm{Ru}_x(\mathrm{phen})_{2x}(\mathrm{L})]^{2x+}$ ($x = 1$ or 2). L is dmbpy (dmbpy = 4, 4′-dimethyl-2,2′-bipyridine) or a bridging ligand of bis-bpy type linked by a polymethylene or polyamine chain (see Scheme 1). The spectroscopic and photophysical properties determined in Tris buffer and ethanol as well as the redox potentials are not affected by the complex nuclearity. Therefore, the two metallic sites of the binuclear complexes are not electronically coupled neither in the ground state nor in the excited state. The results also show that the luminescence properties of the complexes in Tris buffer solution are sensitive to the presence of amine functions in the linker chain. In particular, the ^{3}MLCT excited state is better stabilized in the case of the binuclear complex including three amine groups. Improvement of binding with the possibility of a double-interaction of these systems with DNA is discussed.

Keywords: Photophysics; Binuclear ruthenium(II) complexes; Polyamine/polymethylene chain

1. Introduction

The interaction of polypyridyl complexes with DNA has been extensively studied in the last few years [1–8]. The complex $[\mathrm{Ru(phen)_3}]^{2+}$ (phen = 1, 10-phenanthroline) [5–8] shows two modes of binding: surface binding and “partial intercalation” between the base pairs of DNA. Another interesting property of these Ru(II) complexes, in particular $[\mathrm{Ru(phen)_3}]^{2+}$ and $[\mathrm{Ru(bpy)_3}]^{2+}$ (bpy = 2, 2′-bipyridine), is their ability to photosensitize the DNA cleavage, despite the weak affinity of $[\mathrm{Ru(bpy)_3}]^{2+}$ for the DNA helix. Most of the studies on binding of metal complexes to DNA have investigated mononuclear complexes [9,10]. Our approach consists of examining systems having two independent photosensitive metallic sites covalently linked by a sufficiently long bridge in order to give rise to double-interaction with DNA and to increase the efficiency of DNA cleavage (each metallic center could induce one break on very close positions and lead to double-strand breaks). Recently, this new approach has also been considered by others [11–13].



$$\mathbf{R} = \mathrm{NH(CH_2)_3\underset{\displaystyle CH_3}{\underset{|}{N}}(CH_2)_3NH}$$

Scheme 1.

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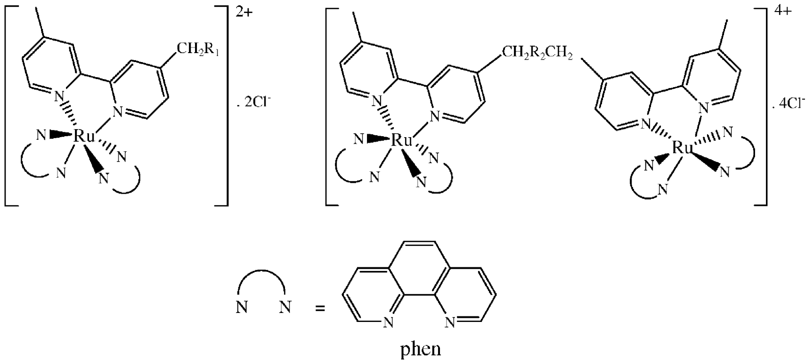
doi:10.1016/j.jphotochem.2004.01.007



Complex	R_1	R_2
$[Ru(phen)_2(4,4'\text{-}dmbpy)]^{2+}$	H	-----------
$[Ru(phen)_2(bpyC10)]^{2+}$	$(CH_2)_8CH_3$	-----------
$[Ru_2(phen)_4(bpy_2C10)]^{4+}$	------------	$(CH_2)_8$
$[Ru(phen)_2(bpyC8N)]^{2+}$	$NH(CH_2)_6CH_3$	-----------
$[Ru_2(phen)_4(bpy_2C10N2)]^{4+}$	------------	$NH(CH_2)_8NH$
$[Ru_2(phen)_4(bpy_2C8N3Me)]^{4+}$	------------	$NH(CH_2)_3\underset{\overset{\vert}{CH_3}}{N}(CH_3)_3NH$

Fig. 1. Molecular structure of the mononuclear and binuclear ruthenium complexes.

We had previously examined a series of bipyridine complexes of the type $[Ru_x(bpy)_{2x}(L)]^{2x+}$ ($x = 1$ or 2) [14] where L was dmbpy (dmbpy = 4, 4′-dimethyl-2,2′-bypyridine) or a linked bis-bpy by a polycarbon or polyamine chain (see Fig. 1). The two metal sites were connected either by a polymethylene bridge or by a chain including two or three amine functions in order to increase the affinity of binding of such compounds for DNA by electrostatic interaction. The structure of the amino bridges is similar to that of natural polyamines [15] like spermidine known for their affinities for DNA [16]. As $[Ru(phen)_3]^{2+}$ has a better affinity for DNA than $[Ru(bpy)_3]^{2+}$ [9], we have developed a new series of analogous complexes of the type $[Ru_x(phen)_{2x}(L)]^{2x+}$ ($x = 1$ or 2) similar to the bpy series (Fig. 1). The complexes $[Ru(phen)_2(dmbpy)]^{2+}$, $[Ru(phen)_3]^{2+}$ and $[Ru(bpy)_3]^{2+}$ were taken as references.

In this report, steady-state spectroscopy and emission lifetime measurements and, in some cases, laser flash photolysis techniques have been used to evaluate the importance of the nature of the coordinating ligand. The photophysical properties of these complexes, at room or at low temperature, have been carried out, combined with electrochemical data. These investigations show a similarity between the mono- and binuclear complexes indicating that there is no interaction between the metallic sites of the binuclear complexes. However, some photophysical changes are observed when the polymethylene chain was substituted with the polyamine linkers.

2. Materials and methods

2.1. Synthesis

Preparation of the complexes of the phenanthrolyl series was similar to that of the complexes of the bipyridyl series previously reported [14], with 3 days of reflux and addition of phosphate buffer [17]. As an example, the synthesis of $[Ru(phen)_2(bpyC10)]^{2+}$ (for abbreviations, see Fig. 1) is described: to 0.25 mM of $Ru(phen)_2Cl_2$ in 15 ml of 95% ethanol were added 0.25 mM of ligand and 1.15 ml of 0.2 M phosphate buffer. After reflux for 3 days under argon, the solvent was evaporated and the crude product was chromatographed twice on LH20 Sephadex, using 95% ethanol as the eluent. The complex was eluted first and was recovered pure as an orange-brown compound. The same procedure was followed for the binuclear complexes using only half the amount of ligand. All compounds gave satisfactory elemental analyses, ^1H NMR (Table 1), and UV-Vis spectra. Plasma desorption mass spectra of the complexes were obtained using a time-of-flight mass spectrometer fitted with a ^{252}Cf source and have been already reported [18].

- $[Ru(phen)_2(bpyC10)]^{2+}$—Anal. calculated for $C_{45}H_{46}N_6RuCl_2{\cdot}7H_2O$: C, 55.30 (calc. 55.78); H, 6.06 (calc. 6.20); N, 8.76 (calc. 8.68).
- $[Ru(phen)_2(bpyC8N)]^{2+}$—Anal. calculated for $C_{43}H_{43}N_7RuCl_2{\cdot}4H_2O$: C, 57.10 (calc. 57.23); H, 5.15 (calc. 5.65); N, 18.38 (calc. 18.87).

Table 1
Chemical shifts of ^{1}H NMR and yields (%) of the ruthenium complexes

Complex	^{1}H NMR chemical shifts	Yield (%)
$[\mathrm{Ru(phen)_2(bpyC10)}]^{2+}$	0.92 (m, 3H), 1.41 (m, 14H), 1.76 (m, 2H), 2.65 (s, 3H), 2.91 (t, $J = 5$ Hz, 2H), 7.30 (m, 2H), 7.63 (dd, $J = 7$ and 4 Hz, 2H), 7.74 (dd, $J = 7$ and 4 Hz, 2H), 7.97 (dd, $J = 7$ and 4 Hz, 2H), 8.06 (m, 2H), 8.39 (m, 6H), 8.71 (dd, $J = 5$ and 1 Hz, 3H), 8.76 (s, 1H), 8.82 (dd, $J = 6$ and 1 Hz, 2H)	52
$[\mathrm{Ru(phen)_2(bpy_2C8N)}]^{2+}$	0.92 (m, 3H), 1.34 (m, 10H), 1.71 (m, 2H), 2.62 (s, 3H), 2.94 (t, $J = 5$ Hz, 2H), 4.24 (s, 2H), 7.27 (d, $J = 6$ Hz, 2H), 7.45 (d, $J = 6$ Hz, 1H), 7.59 (d, $J = 6$ Hz, 1H), 7.70 (m, 2H), 7.77 (d, $J = 6$ Hz, 1H), 7.92 (m, 2H), 8.02 (m, 2H), 8.35 (m, 6H), 8.69 (m, 3H), 8.78 (d, $J = 8$ Hz, 2H), 8.92 (s, 1H)	62
$[\mathrm{Ru_2(phen)_4(bpy_2C10)}]^{4+}$	1.37 (m, 12H), 1.74 (m, 4H), 2.62 (s, 6H), 2.87 (t, $J = 8$ Hz, 4H), 7.28 (m, 4H), 7.60 (d, $J =7$ Hz, 2H), 7.63 (d, $J = 7$ Hz, 2H), 7.67 (d, $J = 5$ Hz, 2H), 7.71 (d, $J = 5$ Hz, 2H), 7.91 (d, $J =8$ Hz, 2H), 7.95 (d, $J =8$ Hz, 2H), 8.02 (m, 4H), 8.34 (m, 12H), 8.68 (d, $J = 7$ Hz, 8H), 8.78 (d, $J = 8$ Hz, 4H)	55
$[\mathrm{Ru_2(phen)_4(bpy_2C10N2)}]^{4+}$	1.37 (m, 8H), 1.62 (m, 4H), 2.58 (s, 6H), 2.72 (t, $J = 7$ Hz, 4H), 4.06 (s, 4H), 7.26 (d, $J = 6$ Hz, 4H), 7.41 (d, $J = 6$ Hz, 2H), 7.59 (d, $J = 6$ Hz, 2H), 7.71 (m, 4H), 7.91 (dd, $J = 6$ Hz and 1 Hz, 2H), 7.95 (dd, $J = 7$ and 1 Hz, 2H), 8.03 (m, 4H), 8.35 (m, 12H), 8.69 (dd, $J = 8$ Hz and 1 Hz, 6H), 8.80 (dd, $J = 8$ and 1 Hz, 4H), 8.86 (s, 2H)	64
$[\mathrm{Ru_2(phen)_4(bpy_2C8N3Me)}]^{4+}$	1.86 (m, 4H), 2.47 (s, 3H), 2.62 (s, 6H), 2.72 (t, $J = 7$ Hz, 8H), 4.03 (s, 4H), 7.27 (d, $J = 6$ Hz, 4H), 7.42 (dd, $J = 6$ and 1 Hz, 2H), 7.60 (d, $J = 6$ Hz, 2H), 7.71 (m, 4H), 7.95 (m, 4H), 8.04 (m, 4H), 8.37 (m, 12H), 8.70 (dd, $J = 8$ and 1 Hz, 6H), 8.80 (dd, $J = 8$ and 1 Hz, 4H), 8.84 (s, 2H)	19

Chemical shifts were measured in CD_3OD, relative to the resonance of the solvent which occurs at 3.34 ppm from $SiMe_4$.

- $[\mathrm{Ru_2(phen)_4(bpy_2C10)}]^{4+}$—Anal. calculated for $C_{80}H_{70}N_{12}Ru_2Cl_4{\cdot}8H_2O$: C, 56.73 (calc. 56.90); H, 5.35 (calc. 5.09); N, 9.62 (calc. 9.96).
- $[\mathrm{Ru_2(phen)_4(bpy_2C10N2)}]^{4+}$—Anal. calculated for $C_{80}H_{72}N_{14}Ru_2Cl_4{\cdot}10H_2O$: C, 54.40 (calc. 54.79); H, 5.21 (calc. 5.25); N, 11.06 (calc. 11.19).
- $[\mathrm{Ru_2(phen)_4(bpy_2C8N3Me)}]^{4+}$—Anal. calculated for $C_{79}H_{71}N_{15}Ru_2Cl_4{\cdot}10H_2O$: C, 53.35 (calc. 53.53); H, 5.27 (calc. 5.14); N, 12.22 (calc. 11.86).

2.2. Spectroscopic methods

Electronic absorption spectra were recorded on a Perkin Elmer Lambda 9 spectrophotometer. The experiments were carried out in tris(hydroxymethyl)aminomethane (Tris) 10 mM, pH 7.4 buffer or ethanol solutions. The corrected emission and excitation spectra were obtained with a Jobin Yvon JY9CI spectrofluorimeter or on a Jobin Yvon Spex Fluorolog FL111 spectrofluorimeter. Emission quantum yields of the complexes were determined relative to an aqueous solution of $[\mathrm{Ru(bpy)_3}]^{2+}$ (Strem Chemicals) using $\phi_{\mathrm{em}} = 0.042$ [19] at room temperature. Emission and luminescence excitation spectra were carried out at 77 K using cylindrical cells. For spectroscopic measurements, the optical density of the deoxygenated solutions was adjusted to 0.1 at the excitation wavelength of 450 nm.

The laser flash photolysis spectrometers used for these investigations have been described in detail elsewhere [20]. The excitation source is an excimer laser (Lambda Physik EMG100, 308 nm pulses of 10 ns duration and 150 mJ energy). For measurements of emission lifetimes, we used solutions with optical densities close to 0.8 at 308 nm. Solutions were deoxygenated by bubbling with argon.

2.3. Cyclic voltammetry

Cyclic voltammograms were recorded in acetonitrile with a Wenking system (model 81 potentiostat) using vitreous carbon (Solea Tacussel EDI 101T) as the working electrode, and a platinum wire of 1 mm diameter as a counter-electrode. Acetonitrile (spectrophotometric grade, 99.5%; Aldrich) was used as solvent and tetrabutylammonium tetrafluoroborate 0.1 M (99%; Janssen) as supporting electrolyte. These chemicals were used as received. Potentials were measured with respect to the saturated calomel electrode (SCE).

3. Results

3.1. Synthesis

The different bridging ligands L and the substituted dmbpy were prepared as already described [14]. The synthesis of the complexes of the phenanthroline series is much slower (3 days) than for the bipyridine series and needed addition of a small quantity of phosphate buffer as observed by Nakamaru [17]. The structures of all compounds were confirmed by ^{1}H NMR (Table 1), microanalysis and molecular weight determination by plasma desorption mass spectrometry [18]. Additional PDMS data concerning the environment around the metal demonstrate unambiguously the nature of the ligands chelating the metal [18]. Microanalyses show that the complexes crystallize with few water molecules, as it is often the case for complexes. Some attempts to eliminate them by lyophilisation led to products with only partial loss of water molecules (30% less). Moreover, it must be pointed out that the different diastereoisomers ($\Lambda\Delta$, Δ^2 and its enantiomer Λ^2) have not been separated and that the results discussed in this paper correspond to their statistic mixtures.

Table 2
Absorption data for the ruthenium complexes in Tris and ethanol at room temperature (errors of ±15% for the extinction coefficients ε)

Complex	λ_{max} (nm) (ε (10^4 l mol^{-1} cm^{-1}))					
	Tris			Ethanol		
$[Ru(bpy)_3]^{2+}$	453 (1.46)	286 (8.87)	243 (2.91)	450 (1.26)	287 (7.58)	244 (2.28)
$[Ru(phen)_3]^{2+}$	447 (1.43)	262 (8.57)	223 (6.64)	446 (1.16)	263 (7.18)	223 (5.34)
$[Ru(phen)_2(dmbpy)]^{2+}$	451 (1.06)	281 (3.01)	263 (5.80)	449 (1.14)	282 (3.20)	265 (6.13)
$[Ru(phen)_2(bpyC10)]^{2+}$	450 (1.59)	282 (4.18)	263 (7.70)	449 (1.41)	282 (3.75)	264 (7.15)
$[Ru(phen)_2(bpyC8N)]^{2+}$	452 (1.22)	286 (2.81)	263 (6.14)	449 (1.39)	283 (3.33)	265 (6.88)
$[Ru_2(phen)_4(bpy_2C10)]^{4+}$	450 (2.67)	283 (6.79)	263 (11.70)	449 (2.62)	283 (6.94)	265 (10.30)
$[Ru_2(phen)_4(bpy_2C10N2)]^{4+}$	451 (2.23)	286 (5.19)	263 (10.73)	450 (3.02)	282 (7.43)	265 (11.99)
$[Ru_2(phen)_4(bpy_2C8N3Me)]^{4+}$	452 (3.08)	285 (6.93)	262 (14.81)	451 (3.17)	283 (7.39)	265 (12.70)

3.2. Ground-state absorption

We have carried out the experiments in Tris buffer, which is mostly used for the studies implying DNA. The further studies of the complexes in the presence of DNA [21] are done in this medium. We have also chosen ethanol in order to compare the spectroscopic and photophysical properties of the complexes at room temperature and at low temperature (77 K). Absorption maxima and molar extinction coefficients ε for the various Ru(II) complexes of the series based on phen ligands are presented in Table 2 with those of $[Ru(bpy)_3]^{2+}$, $[Ru(phen)_3]^{2+}$ and $[Ru(phen)_2(dmbpy)]^{2+}$.

The complexes of the mixed-ligand present a MLCT absorption band in the visible region at about 450 nm and $\pi \rightarrow \pi^*$ transitions centered on the ligands in the UV range [22]. Table 2 shows that the absorption at 286 nm is associated with the bipyridine whereas the absorption band at 263 nm is associated with the phenanthroline ligand. These results confirm those obtained by Baggott et al. [23] on mixed-ligand complexes of the type $[Ru(phen)_x(bpy)_{3-x}(L)]^{2+}$ ($x = 0, 3$) and are also in agreement with Nakamaru's study [17]. The excitation of the luminescence spectra is similar to the absorption spectra (Fig. 2).

Absorption data of the mononuclear and dinuclear complexes are very similar to those of the reference complex $[Ru(phen)_2(dmbpy)]^{2+}$ and do not show any side-chain effect.

3.3. Emission properties

The emission spectra of the various complexes, at room temperature, in Tris buffer and in ethanol, present a broad band similar to that of $[Ru(phen)_2(dmbpy)]^{2+}$. Emission spectrum of $[Ru(phen)_2(bpyC8N)]^{2+}$ is given as example (Fig. 2(2)). The binuclear complexes display emission maxima very similar to their corresponding mononuclear analogues. We observe that, in Tris buffer, the emission maximum of the complexes having a polymethylene bridge is located at 603 nm, whereas it is found at 615 nm for the complexes including an amine chain (Table 3).

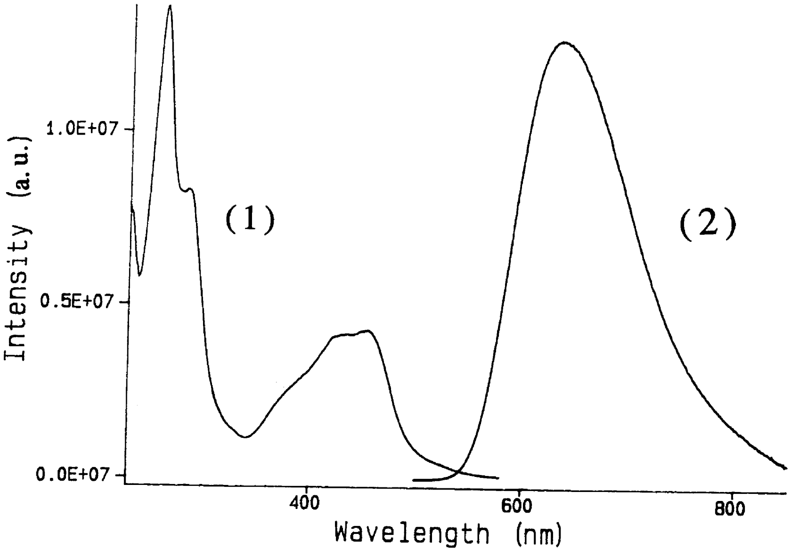


Fig. 2. Luminescence excitation (1) and emission (2) spectra of $[Ru(phen)_2(bpyC8N)]^{2+}$ in Tris buffer at room temperature.

Table 3
Photophysical data for the ruthenium complexes of the phen series in Tris and ethanol, at room temperature

Complex	Solvent	λ_{max}^{em} (nm)	Φ_{em}	τ (ns)	k_r ($10^4\,s^{-1}$)	k_{nr} ($10^4\,s^{-1}$)
$[Ru(bpy)_3]^{2+}$	Tris	606	0.038	640	5.88	150
	Ethanol	602	0.075	870	8.60	106
$[Ru(phen)_3]^{2+}$	Tris	590	0.052	770	9.87	188
	Ethanol	587	0.023	340	6.78	288
$[Ru(phen)_2(dmbpy)]^{2+}$	Tris	603	0.058	1050	5.47	90
	Ethanol	594	0.055	1005	5.47	94
$[Ru(phen)_2(bpyC10)]^{2+}$	Tris	602	0.055	1150	4.80	82
	Ethanol	596	0.050	880	5.67	108
$[Ru(phen)_2(bpyC8N)]^{2+}$	Tris	615	0.039	900	4.30	107
	Ethanol	596	0.057	850	6.68	111
$[Ru_2(phen)_4(bpy_2C10)]^{4+}$	Tris	603	0.061	1160	5.20	81
	Ethanol	595	0.053	900	5.90	105
$[Ru_2(phen)_4(bpy_2C10N2)]^{4+}$	Tris	615	0.031	890	3.48	109
	Ethanol	599	0.053	900	5.89	105
$[Ru_2(phen)_4(bpy_2C8N3Me)]^{4+}$	Tris	615	0.039	895	4.32	107
	Ethanol	605	0.064	1025	6.24	91

λ_{max}^{em}: corrected emission maximum; Φem: emission quantum yield (error ± 15%); τ: emission lifetimes (error ± 5%); k_r: radiative rate constant; k_{nr}: non-radiative rate constant.

The excited state is stabilized in the presence of amine groups by about 340 cm^{-1}. The same phenomenon is observed to a lesser extend in ethanol and in particular for bimetallic compounds with two or three amine functions. Moreover a very pronounced hypsochromic shift is observed in ethanol compared to Tris buffer, indicating that the excited state of charge transfer nature, i.e. the ^{3}MLCT excited state is stabilized in polar solvents (Scheme 1) [24,25].

The emission lifetimes for the phen series of complexes are reported in Table 3. We observe for $[Ru(phen)_2(dmbpy)]^{2+}$ and the complexes with a hydrocarbon chain, that the emission lifetimes are relatively higher in Tris buffer than in ethanol, whereas the complexes having an amino chain have similar lifetimes in both solvents. These results are in agreement with the literature [17,26].

The emission quantum yields follow the same variations as the emission lifetimes. In ethanol, these values are similar whereas in Tris buffer, they are slightly lower for the complexes having an amino chain than for their homologous complexes with a polymethylene chain or for the reference complex and remain close to that of $[Ru(bpy)_3]^{2+}$. Regardless of the solvent, we do not observe any significant difference between the quantum yields and lifetimes for the mononuclear complexes and the corresponding binuclear ones. Assuming that the intersystem crossing quantum yield (ϕ_T) for the formation of the ^{3}MLCT triplet state of our system is unity as for polypyridyl Ru(II) complexes $\phi_T = 1$ [27] and knowing the lifetimes (τ) and emission quantum yields (ϕ_{em}), the radiative (k_r) and non-radiative (k_{nr}) rate constants for the phen series of complexes can be calculated using the following expressions:

$$k_r = \frac{\phi_{em}}{(\phi_T \tau)}, \qquad k_{nr} = \tau^{-1} - k_r$$

These rate constants determined at room temperature (Table 3) are very comparable with those of $[Ru(phen)_2(dmbpy)]^{2+}$.

3.4. Excited-state absorption

The absorption spectra of the complexes in the excited state have been determined by laser flash spectroscopy (Figs. 3 and 4).

Fig. 4 shows that the differential transient absorption spectra of the mononuclear and binuclear complexes are similar to that of the reference complex $[Ru(phen)_2(dmbpy)]^{2+}$ in Fig. 3. They display a maximum at 340 nm, a minimum at 450 nm corresponding to the bleaching of the ground-state

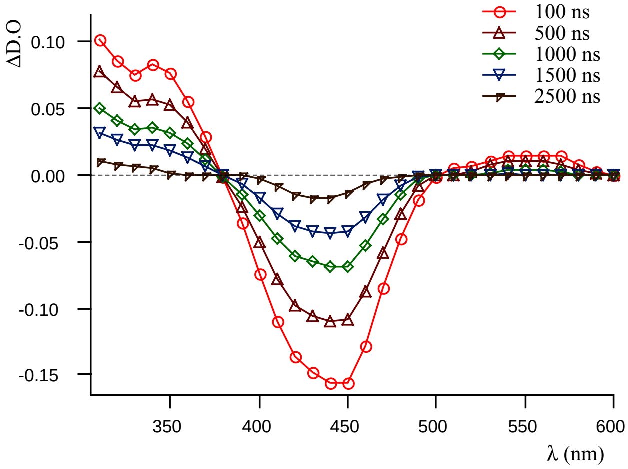


Fig. 3. Differential excited-state absorption spectrum of $[Ru(phen)_2(dmbpy)]^{2+}$ (2.9×10^{-5} M) in deaerated Tris buffer, observed at different times after the laser pulse.

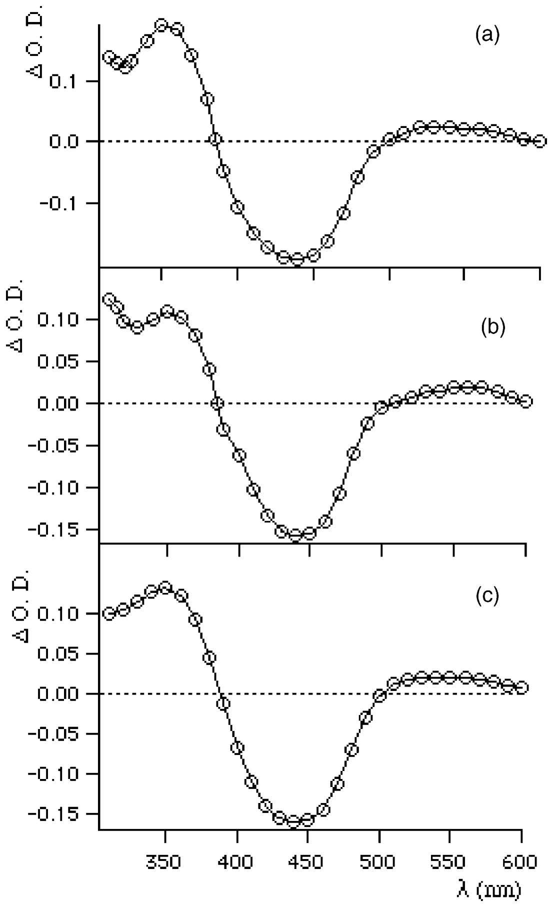


Fig. 4. Differential excited-state absorption spectra of (a) $[Ru(phen)_2(bpyC8N)]^{2+}$ (9.5×10^{-5} M), (b) $[Ru_2(phen)_4(bpy_2C10N2)]^{4+}$ (5×10^{-5} M) and (c) $[Ru_2(phen)_4(bpy_2C8N3Me)]^{4+}$ (5×10^{-5} M) in deaerated Tris buffer, observed immediately after the laser pulse.

absorption, and another maximum at about 560 nm. The analysis of the spectra as a function of time shows a monoexponential decay and the existence of only one species. We observe the recovery of the ground state on all spectra with a similar lifetime independent of wavelength. This result also shows that the complexes did not degrade during laser photolysis. In addition, the decay lifetime of the absorption signal is equal to the luminescence lifetime. The transient absorption and luminescence involve the same excited state. Like emission, transient absorption is deactivated efficiently in the presence of oxygen. In addition, the significant Stokes shift (about 5600–5900 cm^{-1}) between the maxima of absorption and emission suggests that the excited state is of triplet character. Consequently, we have attributed all the transient spectra to the ^{3}MLCT excited state.

3.5. Photophysical properties at 77 K

The photophysical results determined at low temperature for the complexes bearing an amino chain are given in Table 4. These results allow us to estimate the energy level for the lowest triplet state and consequently to calculate its redox potential, which is useful for the study of the photoactivity of these complexes in the presence of DNA [28].

It has been shown that the emission of mixed-ligand complexes of phen and bpy at 77 K arises from a ^{3}MLCT triplet state [22]. The emission spectra of mono and binuclear complexes are all similar to that of $[Ru(phen)_2(dmbpy)]^{2+}$. However, we notice a slight bathochromic shift (about 180 cm^{-1}) of the main band of $[Ru_2(phen)_4(bpy_2C8N3Me)]^{4+}$ (Table 4). The spectra display three bands with a vibration progression of about 1200 cm^{-1}. The ^{3}MLCT energy levels E_T estimated from the maxima of the first emission band are approximately 2.17 eV (50 kcal mol^{-1}). These E_T values as well as the excited-state lifetimes and the non-radiative rate constants k_{nr} (Table 4) are similar and intermediate between those of $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$. We have estimated k_{nr} at 77 K for the complexes of the phen series by assuming that k_r at 77 K is identical to the value of k_r determined at room temperature.

The luminescence excitation spectra of the complexes determined in ethanol at 77 K are similar to the absorption spectra observed in ethanol at room temperature, but they show better resolution. The spectra exhibit maxima in the visible at approximately 455 and 425 nm, and a shoulder at about 410 nm, with a vibration progression of 1440 cm^{-1} for the binuclear complexes and $[Ru(bpy)_3]^{2+}$, and 1520 cm^{-1} for the other complexes. These visible bands are attributed to MLCT charge transfer transitions. Hence, we can estimate the energy of the corresponding singlet states E_S (^{1}MLCT) from the long-wavelength absorption band which is assigned to the 0–0 transition (Table 4). As for the other photophys-

Table 4
Photophysical parameters at 77 K for ruthenium complexes in ethanol

Complex	λ_{max}^{em} (nm)			$\Delta\nu_{max}$ (cm^{-1})	τ (μs)	λ_{max}^{exc} (nm)	E_T (eV)	E_s (eV)	k_{nr} ($10^4\ s^{-1}$)
$[Ru(bpy)_3]^{2+}$	580	628	680 sh	1320	5.2	455	2.14	2.72	10.6
$[Ru(phen)_3]^{2+}$	560	606	648 sh	1360	10.3	451	2.21	2.75	2.93
$[Ru(phen)_2(dmbpy)]^{2+}$	572	619	662 sh	1330	9.2	452	2.17	2.74	5.40
$[Ru(phen)_2(bpyC8N)]^{2+}$	570	614	660 sh	1260	7.8	453	2.18	2.74	6.14
$[Ru_2(phen)_4(bpy_2C10N2)]^{4+}$	572	614	663 sh	1200	8.5	457	2.17	2.71	5.80
$[Ru_2(phen)_4(bpy_2C8N3Me)]^{4+}$	578	609	656 sh	880	8.1	455	2.15	2.72	6.10

λ_{max}^{em} is the corrected emission maxima, $\Delta\bar{\nu}_{max}$ is the vibrational progression, E_T is the energy of the lowest triplet state ^{3}MLCT, τ is the emission lifetime (error ± 5%), λ_{max}^{exc} is the corrected luminescence excitation maximum, E_S is the energy of the first-excited singlet state ^{1}MLCT, k_{nr} is the non-radiative rate constant estimated by assuming k_r identical at 77 and 298 K.

Table 5
Electrochemical data

Complex	E_{ox}	E_{red} (V/SCE)			E^*_{ox}	E^*_{red}
$[Ru(bpy)_3]^{2+}$	1.33	−1.33	−1.52	−1.78	−0.80	+0.81
$[Ru(phen)_3]^{2+}$	1.35	−1.36	−1.46	−1.80	−0.86	+0.86
$[Ru(bpy)_2(dmbpy)]^{2+}$	1.31	−1.37	−1.58	−1.83	–	–
$[Ru(phen)_2(dmbpy)]^{2+}$	1.33	−1.36	−1.53	−1.63	−0.84	+0.80
$[Ru(phen)_2(bpyC10)]^{2+}$	1.25	−1.40	−1.54	–	–	–
$[Ru(phen)_2(bpyC8N)]^{2+}$	1.29	−1.42	−1.54	–	−0.89	+0.76
$[Ru_2(phen)_4(bpy_2C10N2)]^{4+}$	1.29	−1.37	−1.55	–	−0.88	+0.80
$[Ru_2(phen)_4(bpy_2C8N3Me)]^{4+}$	1.40	−1.32	−1.50	−1.87	−0.75	+0.83

Redox potentials are obtained by cyclic voltammetry (error ± 20 mV) in acetonitrile vs. SCE at room temperature with 0.1 M $(n\text{-Bu})_4N(PF_6)$ as supporting electrolyte. E_{ox} and E_{red} are respectively the oxidation and reduction potentials in the ground state of the complexes. E^*_{ox} and E^*_{red} are respectively the oxidation and reduction potentials of the excited state, estimated by using the emission maximum as the 0–0 transition energy (see text).

ical data, the E_S values are similar and intermediate between those of the model compounds (2.72 and 2.75 eV for $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$, respectively).

3.6. Redox potentials

The redox potentials of the phen complexes, determined by cyclic voltammetry, are given in Table 5.

In this study, the potential difference between the cathodic and anodic peak potential ranges between 60 and 85 mV with a scanning rate between 50 and 400 mV/s. Cyclic voltammetry of the complexes shows the existence of a reversible oxidation wave and 2–3 reversible reduction waves at potentials between −2.0 and +1.5 V. For the different complexes, mononuclear or binuclear, the redox potentials show similar values, as it is also observed for the emission lifetimes, and the quantum yields.

The redox potentials in the excited state are calculated from the redox potentials determined in acetonitrile at room temperature and using the energy E_T of the first band of the emission spectrum observed at 77 K in ethanol as the 0–0 transition energy. Whatever the complex is, mononuclear or binuclear, the values of the redox potentials are similar. In the excited state, Table 5 shows that the binuclear complex $[Ru_2(phen)_4(bpy_2C8N3Me)]^{4+}$ is clearly less reducing (−0.75 V) than the other complexes of the phen series and than $[Ru(phen)_3]^{2+}$ and $[Ru(bpy)_3]^{2+}$, whereas it is a better oxidant (+0.83 V) than the other complexes with an amino chain.

4. Discussion

The study of the electrochemical, spectroscopic and photophysical properties of the complexes of the phen series shows a great similarity between the mononuclear and binuclear complexes. The absorption spectra of the mononuclear and binuclear complexes are very similar and as already observed for the binuclear complexes of the bpy series [14], the molar absorption coefficients of the binuclear complexes are approximately twice those of the corresponding mononuclear complexes. If we consider the luminescence properties at room temperature, it should be pointed out that the binuclear complexes with a flexible chain may adopt a conformation which can favor the formation of an intramolecular excimer, but we do not observe any emission spectrum which can be ascribed to such a species. Moreover, the emission lifetimes of the complexes are very similar for the mononuclear complexes and their corresponding binuclear complexes. For instance, the excited state lifetimes of $[Ru(phen)_2(bpyC10)]^{2+}$ and $[Ru_2(phen)_4(bpy_2C10)]^{4+}$ in Tris buffer (Table 3) are 1150 and 1160 ns, respectively. In addition, either in Tris buffer or ethanol, we do not observe any significant difference between the quantum yields for the mononuclear complexes and the corresponding binuclear complexes. In the same way, we notice that the oxidation potentials of mononuclear and binuclear complexes also show great similarity. All these data demonstrate clearly that the nuclearity has no effect on these spectroscopic, photophysical and redox properties, including the excited-state absorption spectra. We can infer that, as for the complexes of the bpy series previously studied [14], there is no electronic interaction between the Ru–Ru sites in a binuclear complex, neither in the ground state nor in the excited state and that these systems behave as a dimer of $[Ru(phen)_2(dmbpy)]^{2+}$. Because of the electrostatic repulsion between the two Ru sites and the geometry around the metal center (octahedral), they probably adopt extended conformations, which make them interesting candidates for a double-interaction with the DNA helix. Furthermore, we can hope to obtain double-break for the reason that each metal site in the binuclear species is independent and can act as a photocleaver (on the same strand or on both strands) on DNA. Amine functions of the linker were chosen to further increase the affinity for DNA, by electrostatic interactions with the phosphate groups, especially in the case of bifunctional compounds.

In conclusion, because of their solubility in water, the presence of an intense absorption band in the visible, and a longer excited-state lifetime at room temperature than that of the corresponding complexes of the bpy series, complexes of the phen series may give rise to interesting properties as photosensitizers. In addition, knowing that $[Ru(phen)_3]^{2+}$ displays a better affinity for DNA than $[Ru(bpy)_3]^{2+}$ [9], we suppose that these systems may be good candidates as hydrosoluble photonucleases, better than $[Ru(bpy)_3]^{2+}$ and the complexes of the bpy series [12,14]. Indeed, preliminary results show that the luminescence quenching of the complexes of the phen series are highly sensitive to O_2 [25], and that a better efficiency of DNA photocleavage by the complexes containing amino linker especially the binuclear with three amine functions is expected. The detailed study of the phen series of complexes in the presence of DNA [28] is submitted.

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