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Characterization of exciplexes generated by excited *tris*-diimine–ruthenium(II) complexes and silver(I) ion of ground state

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Abstract

Luminescent bimolecular and termolecular exciplexes of $*[Ru(bpy)_3]^{2+}$ and $*[Ru(phen)_3]^{2+}$ (bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline) formed by silver ions have been characterized and compared. Formation constants, luminescence lifetime, radiative and non-radiative decay constants were determined at room temperature. Oxidative quenching measurements in the $[Ru(bpy)_3]^{2+}$–Ag^+ system using MV^{2+} (MV^{2+} = 1,1′-dimethyl-4,4′-bipyridinium) as an electron acceptor resulted in quenching rate constants, $(3.1 \pm 0.2) \times 10^9$, $(3.1 \pm 0.3) \times 10^9$, $(1.6 \pm 0.3) \times 10^9$ and cage escape efficiencies, 0.11 ± 0.01, 0.05 ± 0.01, 0.06 ± 0.01, for $*[Ru(bpy)_3]^{2+}$, $*[Ru(bpy)_3]Ag^{3+}$ and $*[Ru(bpy)_3]Ag_2{}^{4+}$, respectively. Temperature-dependent luminescence lifetime measurements in aqueous solutions revealed that the exciplex formation causes a considerable change in the deactivation pathways of the excited species. Exciplex formation results in a decrease in the efficiency of the thermally activated decay through MLCT → dd transition and in an increase of the efficiency of deactivation to the ground state via other non radiative processes. The thermodynamic parameters of the exciplex formation have been estimated. © 1998 Elsevier Science S.A.

Keywords: Photophysics; Luminescence dynamics; Quenching; Exciplex

1. Introduction

The $[Ru(bpy)_3]^{2+}$ ion has emerged as one of the most, if not the most, studied inorganic compounds since the discovery of the excellent redox properties of the complex in its luminescent excited state [1–6]. Although exciplexes have rarely been observed among transition metal complexes, exciplex formation of $*[Ru(bpy)_3]^{2+}$ and related α-diimine complexes, such as $*[Ru(phen)_3]^{2+}$, $*[Ru(Me_2phen)_3]^{2+}$ and $*[Ru(bpz)_3]^{2+}$ (bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline, Me_2phen = 4,7-dimethyl-1,10-phenanthroline and bpz = 2,2′-bipyrazine), with silver(I) ion has been reported recently [7–10]. These investigations revealed that $*[RuL_3]^{2+}$ (where L = bpy, phen and Me_2phen) forms bimolecular and termolecular exciplexes with silver(I) ion, while $*[Ru(bpz)_3]^{2+}$ was shown to react with silver ion in aqueous or acetonitrile solution to form exciplexes with up to six silver ions per excited cation [8]. The bimolecular and termolecular exciplexes were characterized by luminescence spectra, luminescence lifetime, formation constants and thermodynamic parameters for formation of $*[Ru(bpy)_3]\cdots Ag_n{}^{(2+n)+}$. In order to examine the detailed mechanism and the intrinsic nature of the interaction between the excited ruthenium complex and the silver ion in the ground state we performed time-resolved spectroscopy, quenching measurements at room temperature and temperature-dependent lifetime studies on aqueous solutions of $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ in the presence of silver(I) ion at 3 M ionic strength.

In this article, at first, attention is focused on time resolved luminescence and absorption spectroscopy and quenching by methylviologen then we present the results obtained by extensive investigations of the temperature dependence of the luminescence dynamics governed by the equilibrium reactions of the excited ruthenium complex and silver ions in ground state.

2. Experimental details

2.1. Materials and solutions

$AgNO_3$ (Reanal) and $NaNO_3$ (Reanal) were used without further purification. Analytical grade Aldrich $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$, $[Ru(phen)_3]Cl_2 \cdot xH_2O$ and methylviologen dichloride (1,1′-dimethyl-4,4′-bipyridinium

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dichloride; $MVCl_2$) were converted to diperchlorate salts by the method described in the literature [7,11]. Water purified by a Millipore Super-Q system was used to prepare aqueous solutions. The concentration of the ruthenium complex was 10^{-4} M and the concentration of methylviologen changed between zero and 2×10^{-2} M, while the concentration of silver ion was varied from 0 to 1.5 M. A suitable amount of $NaNO_3$ was added to the reaction mixture to adjust the ionic strength to 3 M. The excitation of the samples was performed in a quartz cuvette of optical path length 1 cm and a volume of 4 cm^3 (Hellma) in anaerobic conditions.

2.2. Equipment and methods

Room-temperature absorption spectra were obtained using a Specord M40 (Zeiss) spectrophotometer connected to an IBM/AT compatible PC. Luminescence excitation and emission spectra were recorded on a Perkin-Elmer LS50B fluorimeter using a front-surface accessory since the absorbance of the solutions was much higher than 0.05 at the excitation wavelengths. Emission spectra were corrected using quinine sulfate as the luminescent standard between 400 and 630 nm, and $Ru(bpy)_3^{2+}$ as another reference material for longer wavelengths. Luminescence quantum yields were estimated using $Ru(bpy)_3^{2+}$ as the reference emitter considering the dependence of the refraction index on ionic strength and C_{AgNO_3}/C_{NaNO_3} ratio. The quantum yield of this complex is 0.042 [12] in dilute aqueous solution at ambient temperature. Time-resolved measurements were performed by a laser flash photolysis system described previously [13]. The third harmonic (355 nm, 15 mJ/pulse, fwhm 15 ns) of a Nd:YAG laser (Spectron SL-402) was used for excitation. Temperature-dependent lifetime measurements were carried out by the use of a temperature controlled MLW MK 70 cryostat over the 1–75°C range. Luminescence quenching experiments were performed by MV^{2+} as the electron acceptor. Lifetimes were calculated by fitting to a monoexponential model using commercial software (MS Excel 5.0) based on the Marquardt–Levenberg algorithm. Reported values are averages for 3 measurements.

3. Results

3.1. Luminescence spectra and luminescence lifetime at ambient temperature

Fig. 1 shows the absorption and the uncorrected luminescence spectra of the $[Ru(phen)_3]^{2+}$–silver(I) system in aqueous solution at 3 M ionic strength. The absorption spectra observed at $[Ag^+]=0$ and $[Ag^+]=1.5$ M are almost indistinguishable. On the other hand the intensity of the excitation spectra, matching the absorption spectrum with respect to the position of the maximum and the shape, decreases with silver ion concentration. The decrease in the intensity of luminescence is accompanied by a red shift in the emission spectra.

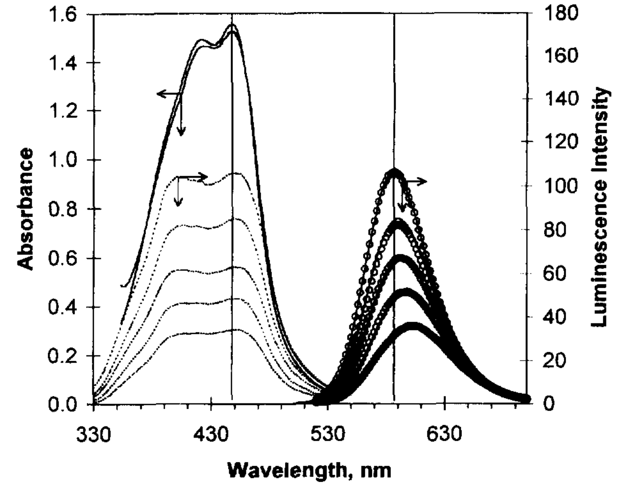


Fig. 1. The absorption and the luminescence excitation and emission spectra of $[Ru(phen)_3]^{2+}$–Ag^+ system in aqueous solution at 3 M ionic strength and ambient temperature. The concentration of ruthenium complex is 1.0×10^{-4} M and the silver ion concentrations are 0 and 1.5 M for absorption measurements and 0, 0.2, 0.4, 0.8, 1.5 M for luminescence measurements. The circles represent the fitted data and solid (absorption and emission spectra) and dashed (excitation spectra) lines are the experimental data.

We detected rather similar spectral features for $[Ru(bpy)_3]^{2+}$–silver(I) system in accordance with earlier observations [7,10]. Time-resolved luminescence spectra indicate very similar changes (Fig. 2). The analysis of the luminescence decay curves over the investigated wavelengths at any concentration of silver ion were performed by last-squares fitting procedure. The emission decays were found to be first order, and no emission wavelength dependence to the lifetime was observed. These results provide evidence for the rapid equilibration among the excited species.

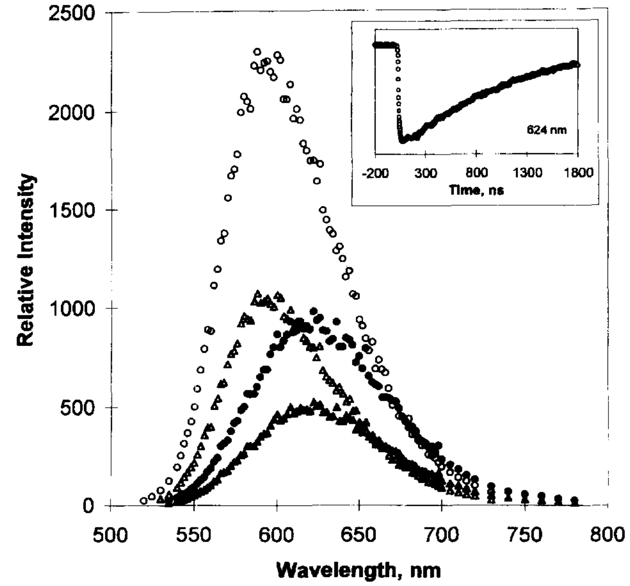


Fig. 2. Transient emission spectra detected in aqueous solution of $[Ru(phen)_3]^{2+}$–Ag^+ system at 3 M ionic strength; $[Ag^+]=0$, 60 ns (○) and 700 ns (△) time delays, $[Ag^+]=1.5$ M, 60 ns (●) and 700 ns (▲) time delays. Inset shows a typical transient signal detected at 624 nm.

Distinct differences have been observed between the nature of luminescence-lifetime vs. silver-ion-concentration data for bpy and phen derivatives at ambient temperature (see (○) data on Figs. 5 and 6). The decrease in lifetime is monotonic in the case of the $^*[Ru(bpy)_3]^{2+}$–Ag^+ system, while a maximum is observed in the τ-$[Ag^+]$ curve for the $^*[Ru(phen)_3]^{2+}$–Ag^+ system at room temperature. Such substantial changes in the luminescence spectra and the luminescence lifetime are in accordance with the results reported earlier [7,9,10], and strongly suggest exciplex-formation in both systems. Moreover, the phenomena observed for the phenanthroline complex are consistent with a model involving both bimolecular and termolecular exciplexes.

$$^*[Ru(L)_3]^{2+} + Ag^+ \rightleftharpoons {}^*[Ru(L)_3]Ag^{3+} \qquad (1)$$

$$^*[Ru(L)_3]Ag^{3+} + Ag^+ \rightleftharpoons {}^*[Ru(L)_3]Ag_2^{4+} \qquad (2)$$

3.2. Time-resolved absorption spectra

The transient absorption spectra detected at 50 ns delay time in aqueous solutions of $[Ru(phen)_3]^{2+}$ containing 3.0 M $NaNO_3$ and 1.5 M $NaNO_3$/1.5 M $AgNO_3$ are depicted in Fig. 3. Both spectra show bleaching between 370 and 480 nm, in the range of the MLCT absorption of the ground state complex, and an absorption peaking at 350 nm, which is assigned as an intraligand transition of the coordinated diimine ligand possessing the promoted electron on its π^* orbital [14]. The disappearance of bleaching and the decay of transient absorption obey first order kinetics with the same lifetime as observed for luminescence. The difference between spectra is very small; the transient absorption at 350 nm is slightly stronger in the presence of silver than that obtained for solution containing ruthenium complex and 3 M $NaNO_3$. The spectral changes are consistent with an exciplex interaction which originates from the affinity of silver ion for the electron localized on the partially filled π^* orbital of polypyridyl ligands [7,9,14].

3.3. Quenching experiments

Oxidative quenching studies were performed using MV^{2+} as the electron acceptor. The first step of the reaction between the excited complex and MV^{2+} is the formation of the primary redox pair;

$$^*[Ru(L)_3]^{2+} + MV^{2+} = \{^*[Ru(L)_3]^{3+} \cdots MV^+\}, \qquad (3)$$

and in the presence of an exciplex,

$$^*[Ru(L)_3]Ag_n^{(2+n)+} + MV^{2+} = \{^*[Ru(L)_3]Ag_n^{(3+n)+} \cdots MV^+\} \qquad (4)$$

The constituents of the primary redox pair can then escape from the solvent cage, resulting in $\cdot MV^+$ and ruthenium(III) complex and the products of exciplex decomposition in the presence of silver(I) ions;

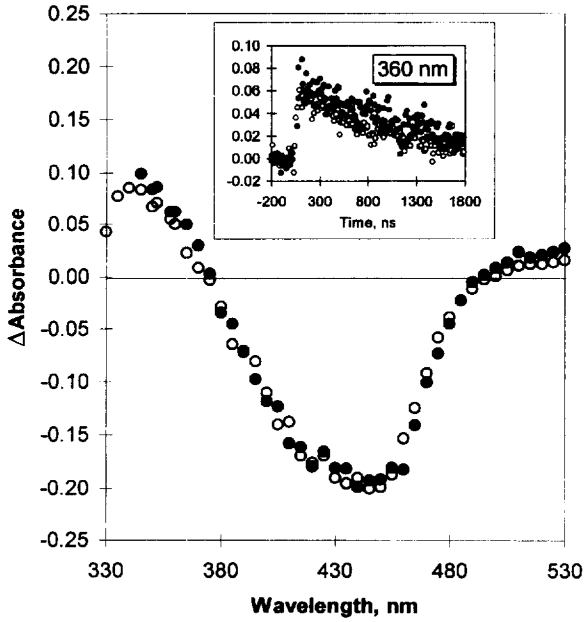


Fig. 3. Transient absorption spectra detected in aqueous solution of $[Ru(phen)_3]^{2+}$–Ag^+ system at 3 M ionic strength, 50 ns after the laser pulse. Averages of three decay curves were used to evaluate the Δ-Absorbance values 50 ns after the laser pulse by a fitting procedure using single exponential decay. The inset shows the decay of transient absorptions obtained by a single laser pulse; $[Ag^+]=0$ M (○) and $[Ag^+]=1.5$ M (●).

$$\{^*[Ru(L)_3]^{3+} \cdots MV^+\} = [Ru(L)_3]^{3+} + \cdot MV^+ \qquad (5)$$

$$\{^*[Ru(L)_3]Ag_n^{(3+n)+} \cdots MV^+\} = [Ru(L)_3]^{3+} + nAg^+ + \cdot MV^+. \qquad (6)$$

The backward electron transfer within the solvent cage competes with the redox pair escape resulting in the original ground state species.

$$\{^*[Ru(L)_3]^{3+} \cdots MV^+\} = [Ru(L)_3]^{2+} + MV^{2+} \qquad (7)$$

$$\{^*[Ru(L)_3]Ag_n^{(3+n)+} \cdots MV^+\} = [Ru(L)_3]^{2+} + nAg^+ + MV^{2+}. \qquad (8)$$

Since, in solutions of high silver concentration, some silver deposit was also observed at the front surface of the cuvette after several hundreds of laser shots, it is reasonable to consider some side reactions such as;

$$\{^*[Ru(L)_3]Ag_n^{(3+n)+} \cdots MV^+\} = [Ru(L)_3]^{3+} + (n-1)Ag^+ + Ag^\circ + MV^{2+}, \qquad (9)$$

$$\cdot MV^+ + Ag^+ = MV^{2+} + Ag^\circ. \qquad (10)$$

In order to avoid the influence of these side reactions we exposed the samples to only several laser pulses. Although the luminescence lifetimes of the bimolecular and the termolecular exciplexes formed from $^*[Ru(bpy)_3]^{2+}$ with silver ion(s) are smaller than that of the excited complex, the observed lifetime at $[MV^{2+}]=0.01$ M increases with silver ion concentration, which is accompanied by a decrease in the yield of $\cdot MV^+$ (Fig. 4). These results clearly demonstrate that an increase in the positive charge of the luminescent species, due to the exciplex formation, leads to a definite decrease in quenching efficiency. Since the yield of free $\cdot MV^+$ monotonically decreases with silver ion concentration and the reduction is approximately 50% at $[Ag^+] = 1$ M, a considerable decrease in cage escape efficiency is also expected.

3.4. Temperature dependence of luminescence lifetime

Luminescence lifetimes were measured between 1 and 72°C at different silver ion concentrations for bpy and phen complexes. A dramatic decrease in luminescence lifetime of the bpy derivative has been observed at high $[Ag^+]$ near 0°C (Inset of Fig. 5: $\tau \sim 700$ ns at $[Ag^+] = 0$ M and $\tau \sim 200$ ns at $[Ag^+] = 1.5$ M). The remarkable feature of this system is that the luminescence lifetime is almost constant between 1 and 50°C ($\tau \simeq 200$ ns). The τ–T curves obtained for $[Ru(phen)_3]^{2+}$ solutions at various silver concentrations cross each other; the lifetimes of the exciplexes are smaller than that of $^*[Ru(phen)_3]^{2+}$ at low temperature, while the data obtained at higher temperature suggest that the bimolecular and the termolecular exciplexes have a longer lifetime than that of the excited ruthenium(II) complex (inset of Fig. 6). It is also observed that the τ–T curves cross each other at three different temperature, which can be considered as an experimental evidence of the appearance of three luminescent species in the system.

The lifetime titration data for $^*Ru(bpy)_3^{2+}$, in accordance with the τ–T values, indicate a monotonicly decreasing with increasing concentration of silver ion (Fig. 5). The decrease is less, however, at higher temperature, and the lifetime values are very similar for $[Ag^+] > 0.5$ M at any temperature. Fig. 6 shows the lifetime titration data for *tris*-phenathroline com-

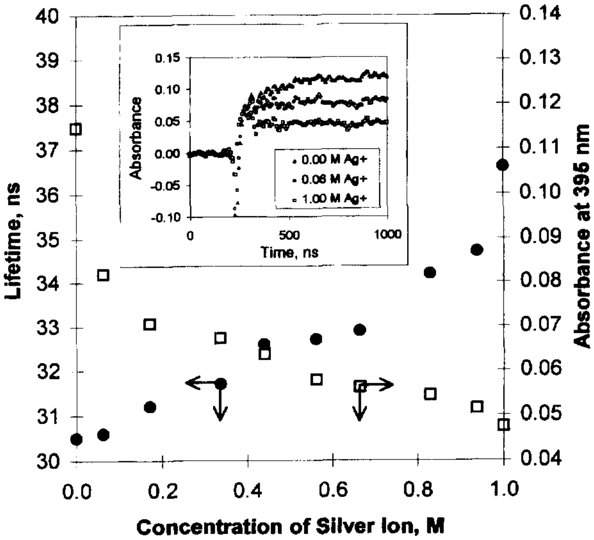


Fig. 4. Dependence of luminescence lifetime and the absorbance at 395 nm detected in aqueous solution of $[Ru(bpy)_3^{2+}] = 10^{-4}$ M, $[MV^{2+}] = 10^{-2}$ M, 500 ns after the laser pulse of 355 nm. The inset shows the transient absorptions detected at 395 nm and various silver ion concentrations.

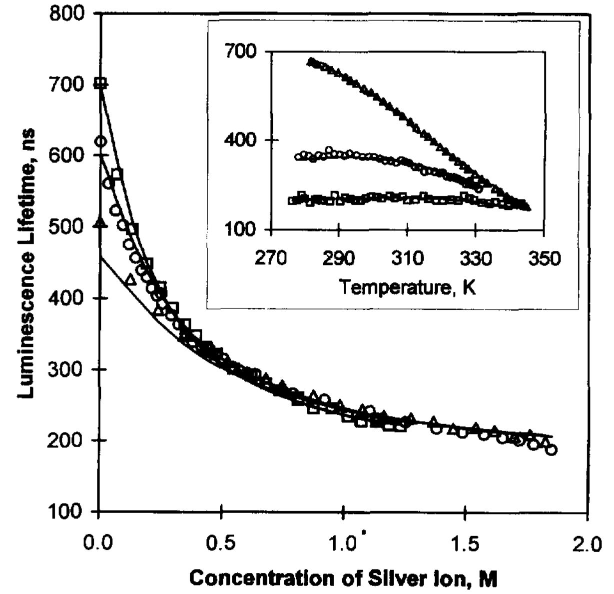


Fig. 5. Lifetime titration of $Ru(bpy)_3^{2+}$ vs. $[Ag^+]$ at different temperatures in aqueous solution at 3 M ionic strength. Symbols are experimental points; (□) 10°C, (○) 25°C and (△) 40°C. Inset shows the luminescence lifetime vs. temperature at different concentration of silver ion; (△) $[Ag^+] = 0$ M, (○) $[Ag^+] = 0.3$ M and (□) $[Ag^+] = 1.5$ M. Solid lines represent the best fits using the model described in the text.

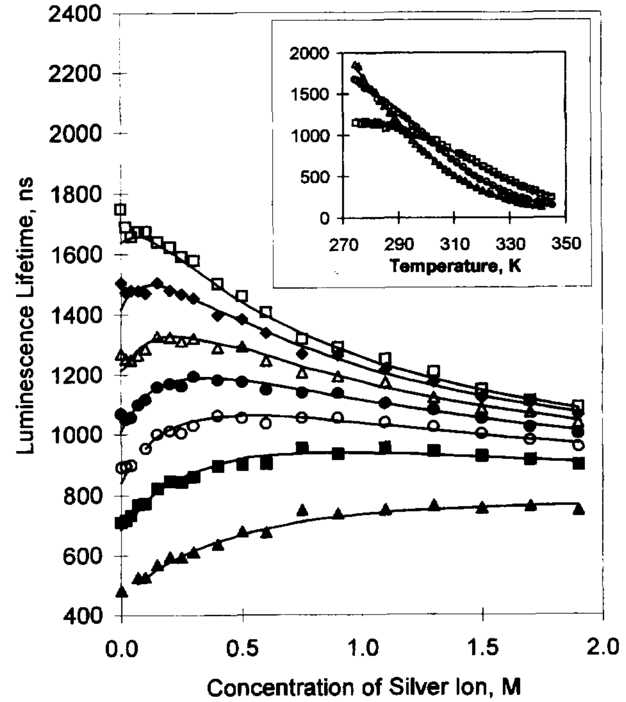


Fig. 6. Luminescence lifetime vs. concentration of silver at different temperature in aqueous solution of $Ru(phen)_3^{2+}$ at 3 M ionic strength; (□) $t = 5.9$°C, (◆) $t = 10.5$°C, (△) $t = 15.5$°C, (●) $t = 20.2$°C, (○) $t = 24.8$°C, (■) $t = 30.1$°C, (▲) $t = 39.5$°C. Inset shows the luminescence lifetime vs. temperature at different concentration of silver ion; (△) $[Ag+] = 0$ M, (○) $[Ag+] = 0.3$ M and (□) $[Ag+] = 1.5$ M. Solid lines represent the best fits using the model described in the text.

plex. As can be seen, the luminescence lifetime first increases and then decreases with an increase in silver ion concentration, with the value of τ_{max} dependent on the temperature; it shifts to higher concentration when the temperature is increased. This corresponds rather well to the change in mole fraction of the three luminescent species supposing a longest lifetime for bimolecular exciplex.

4. Discussion

4.1. Stepwise formation constants and luminescence lifetimes of exciplexes

The analysis of luminescence emission spectra and luminescence lifetime data confirms that the model proposed by Ayala et al. [7,9] describes the phenomena observed in both systems. The most important feature of this model is that it involves the formation of bimolecular and termolecular exciplexes (Eqs. (1) and (2)) and the decay of all luminescent species via radiative and non-radiative processes:

$$^*[Ru(L)_3]^{2+}=[Ru(L)_3]^{2+}+h\nu \text{ or } \Delta \quad (11)$$

$$^*[Ru(L)_3]Ag^{3+}=[Ru(L)_3]^{2+}+Ag^{+}+h\nu \text{ or } \Delta \quad (12)$$

$$^*[Ru(L)_3]Ag^{3+}=[Ru(L)_3]^{3+}+Ag^{\circ} \quad (13)$$

$$^*[Ru(L)_3]Ag_2^{4+}=[Ru(L)_3]^{2+}+2Ag^{+}+h\nu \text{ or } \Delta \quad (14)$$

$$^*[Ru(L)_3]Ag_2^{4+}=[Ru(L)_3]^{3+}+Ag^{+}+Ag^{\circ} \quad (15)$$

The model can be summarized in Scheme 1.Since the equilibration between the three excited species is very rapid compared with the decay rates, k_i $(i=0,1,2)$ the luminescence lifetime observed in solutions containing silver ion can be expressed by a very simple equation.

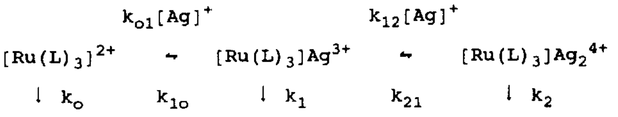
$$1/\tau_{obs}=\sum\alpha_i/\tau_i \quad (16)$$

where α_i is the mole fraction of the luminescent molecular entity $(\alpha_i=\beta_i[Ag^+]^i/\Sigma\beta_i[Ag^+]^i$; β_i is the overall formation constant $\beta_o=1$, $\beta_1=K_1=k_{01}/k_{10}$, $\beta_2=K_1K_2$, $K_2=k_{12}/k_{21}$ and K_i is the stepwise formation constant at ambient temperature), τ_{obs} is the observed lifetime and $\tau_i=1/k_i$ is the lifetime of the luminescent species.

The characteristic constants (K_i, β_i) for L = bpy and L = Me_2phen were determined by Ayala et al. [7] using a procedure based on fitting Eq. (16) and

$$I(\lambda)=\sum\alpha_i I_i(\lambda) \quad (17)$$

where $I(\lambda)$ is the observed luminescence spectrum and $I_i(\lambda)$ are the luminescence spectra of the excited species. In order to obtain reliable formation constants, luminescence spectra and data related to the intrinsic nature of the bimolecular and termolecular exciplexes, we also performed luminescence lifetime measurements at various temperature (0–70°C). Hence we had three series of data for the fitting procedure; (a) luminescence spectra at various silver concentration and room temperature, (b) luminescence lifetime vs. silver concentration at different temperatures, and (c) luminescence lifetime vs. temperature at different concentration of silver ion. Using the temperature dependent expression for luminescence lifetime given elsewhere [15,16] and Eqs. (16) and (17) for least squares fitting we meet some inconsistencies. Namely, we were able to get good fitting with the same parameter sets either for data series (a) and (c) or (b) and (c) but it was not possible to get one parameter set for all data. Hence, we decided to reveal the source of inconsistencies by checking the fundamental equations (Eqs. (16) and (17)). We found that Eq. (16) is correct since the excited state equilibration processes occur much faster than the decay of emitting molecular entities, which was confirmed by the experimental observations. However, we had to modify Eq. (17) according to the considerations summarized in Appendix A.



Scheme 1.

$$I(\lambda)=\tau_{obs}\sum\alpha_i I_i(\lambda)/\tau_i \quad (18)$$

The fitting procedure using Eqs. (16) and (18) resulted in a parameter set of reasonable precision for all experimental data and the luminescence spectrum of the exciplexes. Fig. 7 shows the corrected luminescence spectra of $^*Ru(bpy)_3^{2+}$, $^*Ru(bpy)_3Ag^{3+}$ and $^*Ru(bpy)_3Ag_2^{4+}$, which clearly indicate a considerable red shift: ~30 nm and ~40 nm for bimolecular and termolecular exciplex, respectively. Very similar changes have been observed for phenanthroline complex: ~30 and 35 nm. The results obtained for room tem-

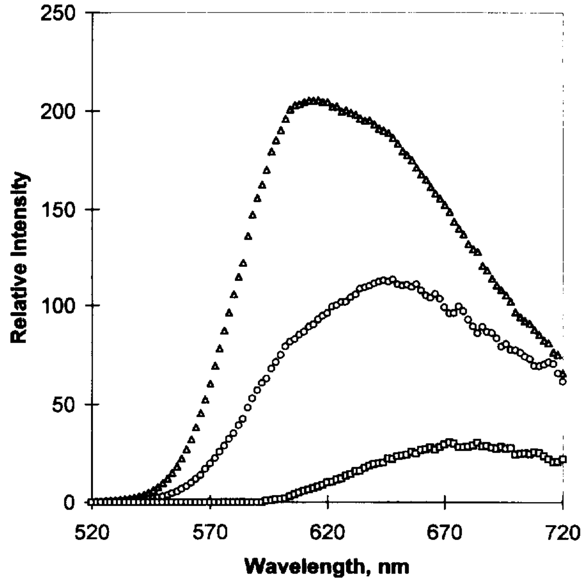


Fig. 7. The corrected emission spectra of $^*[Ru(bpy)_3]^{2+}$ (△), $^*[Ru(bpy)_3]Ag^{3+}$ (○) and $^*[Ru(bpy)_3]Ag_2^{4+}$ (□) obtained for aqueous solution at 3 M ionic strength.

perature measurements are summarized and compared with literature data in Table 1. The lifetimes and formation constants of the $*[Ru(bpy)_3]^{2+}$–Ag^+ system are in good agreement with those reported by Ayala et al. [7]. An increase in the nonradiative decay is consistent with the observed red shift according to the energy gap law. Comparing the figures of the $*[Ru(phen)_3]^{2+}$–Ag^+ and $*[Ru(Me_2phen)_3]^{2+}$–Ag^+ systems, however, a remarkable difference in the lifetime values is observed. The formation of bimolecular and termolecular exciplexes results in a considerable decrease in luminescence lifetime for the Me₂phen complex, similarly to that obtained in the $*[Ru(bpy)_3]^{2+}$–Ag^+ system, but the bimolecular exciplex of $*[Ru(phen)_3]^{2+}$ possesses longer lifetime than the parent complex. This suggests that the exciplex formation from the excited *tris*-phenanthroline complex leads to a decrease in one of the non-radiative decay processes. This effect provides an overcompensation of the increase in efficiency of the direct deactivation channel to the ground state due to the decrease in the energy gap.

In order to reveal the intrinsic feature of luminescence dynamics, we calculated the radiative and non-radiative rate constants of $*[Ru(L)_3]Ag_n^{(2+n)+}$ exciplexes by fitting $k_{robs}([Ag^+]) = \Sigma\alpha_i k_{ri}$ to $k_{robs}([Ag^+]) = \Phi_{lum}/\tau_{lum}([Ag^+])$ values. The results of this procedure are also summarized in Table 1. The formation of bimolecular and termolecular exciplexes leads to a monotonic decrease in radiative rate constants for bpy and phen complexes, while a minimum for this rate constant is obtained for the bimolecular exciplex of $*[Ru(Me_2phen)_3]^{2+}$. The bimolecular and termolecular exciplex formation is accompanied by a considerable increase in non-radiative rate constants of bpy and Mephen complexes, which is contrary to the very small change in this rate constant estimated for phen complex.

4.2. Quenching constants and escape efficiencies

In the presence of methylviologen the luminescence lifetime decreases due to the efficient electron transfer quenching. In solutions containing silver ions three luminescent species are present: the excited complex, the bimolecular exciplex, and the termolecular exciplex. These species have different lifetimes. In principle, their reaction with methylviologen should be characterized by various rate coefficients due to the different structure and charge of the emitting molecular entities. The observed luminescence lifetime (τ_{obsq}) can be described by the following equation.

$$1/\tau_{obsq} = \sum \alpha_i (k_{qi}[MV^{2+}] + 1/\tau_i) \qquad (19)$$

where k_{qi} represents the quenching rate constants of $*[Ru(bpy)_3]^{2+}$ ($i=0$), $*[Ru(bpy)_3]Ag^{3+}$ ($i=1$) and $*[Ru(bpy)_3]Ag_2^{4+}$ ($i=2$). The fitting of this equation to the lifetime data measured at $[MV^{2+}] = 0.01$ M (Fig. 4) resulted in $k_{q0} = (3.1 \pm 0.2) \times 10^9$ M^{-1} s^{-1}, $k_{q1} = (3.1 \pm 0.3) \times 10^9$ M^{-1} s^{-1} and $k_{q2} = (1.6 \pm 0.3) \times 10^9$ M^{-1} s^{-1}. The results suggest a strong interaction between the empty 5s orbital of silver ion and the π^* orbital of the bpy ligand possessing the electron promoted by photon absorption. This interaction results in the 'shielding' of the positive charge of the silver ion in the bimolecular exciplex. On the other hand, it can strongly influence the electronic frequency factor and the activation free energy of the electron transfer reaction. The silver ion can also act as a 'wire' hence the transfer of the electron through the silver ion to the MV^{2+} is

Table 1
Formation constants, lifetimes and rate constants for $*[Ru(L)_3]Ag_n^{(2+n)+}$ exciplexes at room temperature

n	β_n (M^{-n})	τ_n (ns)	$\phi_{lum} \times 10^2$	$k_{nr} \times 10^{-6}$, s^{-1}	$k_r \times 10^{-4}$ (s^{-1})
		L = bpy			
0		585 ± 20	4.4 ± 0.2	1.6 ± 0.2	7.5 ± 0.6
		600 [a]	4.8 ± 0.1 [a]	1.6 ± 0.1 [a]	8.0 ± 0.2 [a]
		580 [b]		1.6 ± 0.1 [b]	6.9 ± 1.0 [b]
1	3.4 ± 0.2	370 ± 40	2.1 ± 0.2	2.6 ± 0.3	5.7 ± 1.1
	6.9 ± 0.5 [a]	380 [a]	1.9 ± 0.1 [a]	2.6 ± 0.1 [a]	5.0 ± 0.1 [a]
2	3.5 ± 0.3	155 ± 7	0.65 ± 0.05	6.6 ± 0.3	4.2 ± 0.5
	7.6 ± 1 [a]	180 [a]	0.7 ± 0.1 [a]	5.5 ± 0.1 [a]	3.9 ± 0.1 [a]
		L = phen			
0		835 ± 20	5.9 ± 0.4	1.1 ± 0.1	7.1 ± 0.7
		906 [b]		1.0 ± 0.1 [b]	6.0 ± 1.0 [b]
1	4.9 ± 0.1	1300 ± 120	4.7 ± 0.3	0.7 ± 0.1	3.6 ± 0.6
2	2.9 ± 0.1	805 ± 15	2.1 ± 0.2	1.2 ± 0.1	2.6 ± 0.3
		L = DMphen			
0		1620 [a]		0.57 ± 0.01 [a]	5.1 ± 0.2 [a]
1	12 ± 1 [a]	980 [a]		1.0 ± 0.1 [a]	2.3 ± 0.1 [a]
2	12 ± 2 [a]	250 [a]		3.9 ± 0.1 [a]	4.0 ± 0.1 [a]

[a] From Ref. [7].
[b] From Ref. [17].
$k_{nr} = k_{nr0} + k_1 \exp(-\Delta E_1/RT)$.

facile. The quenching of the termolecular exciplex proceeds by a lower rate due to the increase in coulomb repulsion between the reactants.

Since, in the case of $[\mathrm{Ru(bpy)_3}]^{2+}$, the quantum yield for formation of the luminescent state is unity [18–21] the quantum yield of $\cdot\mathrm{MV}^+$, $\Phi_{\cdot\mathrm{MV}+}$, is equal to $\eta_q\eta_{ce}$. In this simple expression η_q is the efficiency of quenching reaction, $\eta_q = k_q[\mathrm{MV}^{2+}]/(1/\tau_o + k_q[\mathrm{MV}^{2+}])$ and η_{ce} is the cage escape efficiency, $\eta_{ce} = k_{ce}/(k_{ce} + k_{bet})$, where k_{ce} is the rate constant of the escape of the primary redox pair from the cage and k_{bet} is the rate constant of the back electron transfer reaction within the cage. However, in the presence of silver ion we have three luminescent species, hence $\Phi_{\cdot\mathrm{MV}+}$ can be written as

$$\phi_{\cdot\mathrm{MV}+} = \sum \alpha_i \{k_{qi}[\mathrm{MV}^{2+}]/(1/\tau_i + k_{qi}[\mathrm{MV}^{2+}])\}\eta_{cei} \tag{20}$$

where the values, η_{cei}, are the cage escape efficiencies of primary pairs having various transition metal constituents ($^*[\mathrm{Ru(bpy)_3}]^{2+}$ ($i=0$), $^*[\mathrm{Ru(bpy)_3}]\mathrm{Ag}^{3+}$ ($i=1$) and $^*[\mathrm{Ru(bpy)_3}]\mathrm{Ag_2}^{4+}$ ($i=2$)). Using Eq. (20), we estimated the values of η_{cei} from the data depicted in Fig. 4. We obtained $\eta_{ce0} = 0.11 \pm 0.01$, which is in good agreement with the literature data [22]. A considerable decrease in cage escape efficiency estimated for bimolecular ($\eta_{ce1} = 0.05 \pm 0.01$) and termolecular ($\eta_{ce2} = 0.06 \pm 0.01$) exciplexes can be interpreted by a very fast back electron transfer reaction, especially in the case of the bimolecular exciplex. These results also are in accordance with the strong charge transfer exciplex interaction.

4.3. Photophysics of excited complexes and exciplexes

To explain the influence of the interactions between the excited α-diimine Ru(II) complexes and silver ion we first summarize the prominent properties of the MLCT state of Ru(II) complexes in aqueous solution. The following information is available.

(a) Light absorption initially populates an MLCT state, which is mainly singlet in character [20]. Intersystem crossing to the emitting largely triplet states occurs with unit efficiency [18,19,21].

(b) In aqueous solutions, the MLCT state is best described as a Ru(III) center with a single reduced α-diimine ligand (coordinated radical anion) possessing the electron promoted by excitation, rather than as a state delocalized over all ligands [23–27]. This localization appears to originate from molecular distortion in the excited state that leads to lower the energy of one of the ligand localized states which can trap the electron.

(c) The emission occurs from a manifold of three ^{3}MLCT levels with a spacing between the states of ~10 and ~50 cm^{-1} for $\mathrm{Ru(bpy)_3}^{2+}$ and ~10 and ~40 cm^{-1} for $\mathrm{Ru(phen)_3}^{2+}$, respectively [28–31]. At temperature near ambient these lowest lying MLCT states being separated by small energy gaps have significant Boltzmann populations and behave kinetically as a single state, largely triplet in character, with decay properties dominated by the highest of the three states.

(d) Deactivation of the emitting state can occur directly to the ground state via radiative and nonradiative processes with first order rate constants k_{or} and k_{onr} ($k_o = k_{or} + k_{onr}$) or through a thermally activated surface crossing to low-lying dd states followed by rapid decay. The values of the energy gap fall in the range of 2500 to 4500 cm^{-1} depending on the nature of solvent and the ligands coordinated to the ruthenium center [32–35]; $k_{1nr} = k_1 \exp(-\Delta E_1/RT)$. The kinetic scheme for population and decay of the d–d excited state is given elsewhere [31,32]

$$\mathrm{MLCT} \underset{k_{-d}}{\overset{k_d}{\leftrightarrows}} \text{d–d} \xrightarrow{k_g} \text{ground state or photochemistry}$$

In the limit that $k_{-d} \gg k_g$ the two states are in equilibrium and the ΔE_1 can be interpreted as the internal energy difference between the ^{3}MLCT and d–d states and $k_1 \sim k_g$. In the other limit $k_{-d} \ll k_g$ and k_1 and ΔE_1 characterize the irreversible surface crossing.

(e) Thermal population and decay also occurs from an additional MLCT state possessing greater singlet character and several hundred cm^{-1} higher in energy than the lowest level MLCT states [36–39] (it should be noted that this process does not occur or has a very small efficiency for $^{\mathrm{MLCT}}[\mathrm{Ru(phen)_3}]^{2+}$). The rate coefficient of this process involves the energy gap between the three lower level states and the fourth MLCT states of mainly singlet character $k_{2nr} = k_2 \exp(-\Delta E_2/RT)$.

In principle, it is necessary to consider three nondegenerate states to describe the luminescence lifetime of *tris*-diimineruthenium(II) complex and its derivatives. Hence, the general kinetic expression for excited state decay [15,16] given by

$$\begin{aligned} 1/\tau(T) = \{&k_o + k_1\exp(-\Delta E_1/k_BT) \\ &+ k_2\exp(-\Delta E_2/k_BT)\}/\{1 + \exp(-\Delta E_1/k_BT) \\ &+ k_2\exp(-\Delta E_2/k_BT)\} \end{aligned} \tag{21}$$

In this equation, k_o is the rate constant of the decay from the low-lying ^{3}MLCT states consisting of a radiative, k_{or}- and a non-radiative, k_{onr}-term, k_1 is the coefficient of the temperature dependent decay characterized by the energy gap, ΔE_1, between the low-lying ^{3}MLCT states and d–d level, and k_2 is the coefficient of the temperature dependent decay occurring via the additional MLCT state which is higher in energy than the ^{3}MLCT states by a value of ΔE_2.

4.4. Evaluation of rate constants, energy gaps and thermodynamic parameters

In order to evaluate these parameters for the two ruthenium complexes, $[\mathrm{Ru(bpy)_3}]^{2+}$, $[\mathrm{Ru(phen)_3}]^{2+}$, and the bimolecular and termolecular exciplexes, $[Ru(bpy)_3]Ag^{3+}$, $[Ru(phen)_3]Ag^{3+}$, $[Ru(bpy)_3]Ag_2{}^{4+}$, $[Ru(phen)_3]Ag_2{}^{4+}$, we performed a fitting procedure in two steps using the data depicted in Figs. 5 and 6. At first, we estimated the parameters of the complexes; then, using these values the rate coefficients and the ΔE-values for exciplexes were calculated. It was considered that the solutions, other than $[Ag^+]=0$, contained three luminescent species; the excited complex, the bimolecular exciplex and the termolecular exciplex. Because the equilibration processes occur much faster than the decay of either luminescent species, they disappear at the same rate, which is determined by mole fraction and the lifetime of the excited complex and exciplexes. The temperature dependence of the observed lifetime, τ_{obs} results from the temperature dependence of both the lifetime of the three luminescent species and their mole fraction, $\alpha_i(T)$

$$k_{obs}(T)=1/\tau_{obs}(T)=\sum\alpha_i(T)/\tau_i(T) \quad (22)$$

where $\alpha_i(T)=\beta_i(T)[Ag^+]^i/\Sigma\beta_i(T)[Ag^+]^i$, ($\beta_i(T)$ is the overall formation constant, $\beta_o=1$, $\beta_1(T)=K_1(T)=k_{01}(T)/k_{10}(T)$, $\beta_2(T)=K_1(T)K_2(T)$, $K_2(T)=k_{12}(T)/k_{21}(T)$ and $K_i(T)$ is the stepwise formation constant), and $\tau_i(T)$ is the lifetime of the luminescent species. The stepwise formation constants were considered as a function of thermodynamic parameters (ΔH and ΔS) using the well known equation; $K=\exp[-(\Delta H-T\Delta S)/RT]$. In order to obtain reliable data for the formation constants the luminescence spectra were also involved in the procedure considering Eq. (18). Eqs. (21) and (22) were used for the multiparameter least-squares curve fitting procedure based on Marquardt method [40]. The error-matrix was also generated, from which uncertainty and the standard deviation in the final value of the estimated variables were also obtained.

The lifetime data for $^*Ru(bpy)_3{}^{2+}$ and $^*Ru(phen)_3{}^{2+}$ complexes were analyzed first. Eq. (20) contains five parameters; three rate constants and two energy gaps. Numerical values for these quantities were determined by finding a set of parameters that generated the 'best fit' to the τ–T data points measured by laser flash photolysis. Although we obtained reasonable data for ΔE_2 and k_2 the uncertainties of these variables were comparable with their absolute value, hence we decided to reduce the number of variables. The three-parameter-calculation (k_o, k_1, ΔE_1) resulted in excellent fit. The data listed in Table 2 are in good agreement with the literature figures.

In the next step, the energy gap for bimolecular exciplex and the rate constants for bimolecular and termolecular exciplexes were the variables and the data estimated in the former procedure were not varied. It was reasonable to suppose that the exciplex formation results in considerable change in the energy gap between the MLCT state and the d–d state and slightly influences the frequency factor of the irreversible surface crossing process (k_1) [41]. Hence, the k_1 rate constant of exciplexes was considered as a parameter with nearly the same value that obtained for the excited complex. The lifetime data measured at 1.5 M concentration of silver ion for bipyridine complex strongly suggested that the decay rate of the termolecular exciplex did not depend on the temperature over the 1–75°C range. Therefore we introduced only two variables for the bimolecular exciplex (k_o and ΔE_1) and one for termolecular exciplex (k_o). Considering the four thermodynamic data (ΔH_1, ΔS_1, ΔH_2, ΔS_2) the fitting procedure was performed for seven variables. The relatively large number of the lifetime data (τ–T and τ-$[Ag^+]$) combined with the luminescence spectra detected at different concentration of silver ion, however, provided an adequate condition for the reasonable estimation. It is important to note that an increase in the number of variables (k_1, k_2 or ΔE_2) resulted in a significant decrease in the precision of the estimated figures. The final results of the fitting is summarized in Table 2.

Table 2
Excited state parameters of $[RuL_3]^{2+}$ complexes (L = bpy or phen) and their bimolecular and termolecular exciplexes formed by silver ion ($[RuL_3]Ag_n{}^{(n+2)+}$ in aqueous solution at 3 M ionic strength

Excited species	$k_o\times10^{-5}$ (s^{-1})	$k_1\times10^{-13}$ (s^{-1})	ΔE_1 (cm^{-1})
$^*[Ru(bpy)_3]^{2+}$	13.2 ± 0.4	1.88 ± 0.02	3665 ± 10
	12.9 ± 0.3 [a]	1.00 ± 0.15 [a]	3560 ± 40 [a]
$^*[Ru(bpy)_3]Ag^{3+}$	25.2 ± 4.0	1.88	3815 ± 35
$^*[Ru(bpy)_3]Ag_2{}^{4+}$	64.5 ± 2.5	–	–
$^*[Ru(phen)_3]^{2+}$	3.37 ± 0.08	1.46 ± 0.30	3450 ± 45
	3.13 ± 0.06 [a]	1.22 ± 0.20 [a]	3390 ± 40 [a]
$^*[Ru(phen)_3]Ag^{3+}$	4.16 ± 0.11	1.46	3635 ± 10
$^*[Ru(phen)_3]Ag_2{}^{4+}$	12.40 ± 0.23	–	–

[a] Data from Ref. [41].

4.5. Origin of exciplex stabilization and thermodynamics

Although the procedure to extract physical parameters of the luminescent exciplexes from lifetime data and emission spectra is open to the criticism, we wish to emphasize that a high degree of self-consistency of the results was required. The data clearly indicate that k_o increases due to the formation of exciplexes. The effect is especially pronounced for termolecular exciplexes. It is consistent with the energy gap law suggesting an increase in k_{nro} as emission spectrum is red shifted. On the other hand the formation of bimolecular exciplex increases the energy gap for the temperature dependent deactivation resulting in a decrease in the efficiency of the *MLCT → dd interconversion: $k_1\exp(-\Delta E_1/k_BT)$ term is approximately 13% of k_o for bpy complex and it is higher than k_o for phen complex, while 4% and 40% of k_o is estimated for bimolecular exciplex of bpy and phen, respectively. It is reasonable to assume that ΔE_1 for termolecular exciplex is larger than that of the bimolecular exciplex, hence $k_1\exp(-\Delta E_1/k_BT)$ term is very small compared with k_o, especially in the case of bpy complex.

The rate constant characterizing the ^{3}MLCT → ground state process (k_o) is larger for $^3Ru(bpy)_3{}^{2+}$ than for

Table 3
Summary of thermodynamic data for the stepwise formation of bimolecular and termolecular exciplexes by the reaction of $*[Ru(bpy)_3]^{2+}$ and $*[Ru(phen)_3]^{2+}$ with silver ion of ground state

Excited species	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	K° (M^{-1})
$*[Ru(bpy)_3]Ag^{3+}$	-6.2 ± 2.5	-10 ± 9	3.4
$*[Ru(bpy)_3]Ag_2^{4+}$	-6.7 ± 1.6	-22 ± 6	1.1
$*[Ru(phen)_3]Ag^{3+}$	-14.0 ± 1.8	-34 ± 6	4.9
$*[Ru(phen)_3]Ag_2^{4+}$	-7.4 ± 1.3	-29 ± 4	0.6

$^3Ru(phen)_3^{2+}$. Moreover, the exciplex formation results in an increase of k_{obpy}/k_{ophen} ratio. A possible reason of this behavior is that the exciplex formation increases the efficiency of the deactivation process undergoing from the three triplet MLCT state through the so-called fourth MLCT state of enhanced singlet character in the case of bpy complexes.

The evaluated thermodynamic parameters are summarized in Table 3. The relatively small ΔH values indicate a weak charge transfer interaction, while the small negative entropy changes can be interpreted by the significant role of solvent reorganization. Using the ΔH and ΔS values we estimated the stabilization energy; 270 cm^{-1} and 323 cm^{-1} for the bimolecular exciplex of the bpy and phen complex, respectively.

5. Conclusions

Absorption and emission spectroscopic investigations using the time-resolved technique and temperature dependence has revealed the nature of the interaction between the silver ion in the ground state and $*[Ru(bpy)_3]^{2+}$ and $*[Ru(phen)_3]^{2+}$, respectively. The exciplex formation has been also confirmed by oxidative quenching using cationic quencher such as MV^{2+}. The data suggest that, as shown schematically in Fig. 8, there is a relatively strong interaction between the low-lying π^* level of one bpy or phen ligand and the empty 5s orbital of silver ion which results in two important changes in the energy surfaces of MLCT states.

(1) The first change is the stabilization of the MLCT excited states. This stabilization leads to a decrease in the energy of the MLCT levels resulting in an increase in the energy gap, ΔE_1, for the ^{3}MLCT → dd transition. The silver ion acts as an electron-withdrawing substituent of the bpy ligand; hence, the formation of 'bpyAg°' shows a very similar effect that was demonstrated by the electron-withdrawing X groups in the series of $[(tpm)Ru(4,4'-(X)_2-bpy)(py)]^{2+}$-complexes (tpm = tris(1-pyrazolyl)methane, py = pyridine) [39]. On the other hand, the formation of a bimolecular and termolecular exciplex from $*[Ru(L)_3]^{2+}$ leads to a decrease in the energy gap between the luminescent state and the ground state providing an increase in the decay rate. The exciplex stabilization can also result in a decrease in the energy difference between the three lowest-lying ^{3}MLCT states and the fourth MLCT state possessing a strong singlet nature in the case of bpy derivative.

(2) The second considerable change in the energy surface of the MLCT state is the shift in the minimum along the nuclear coordinates. The energy minimum of the emitting excited state moves to a position above the ground state energy surface of the complex which is rather far from the minimum. However, it is reasonable to suppose that the radi-

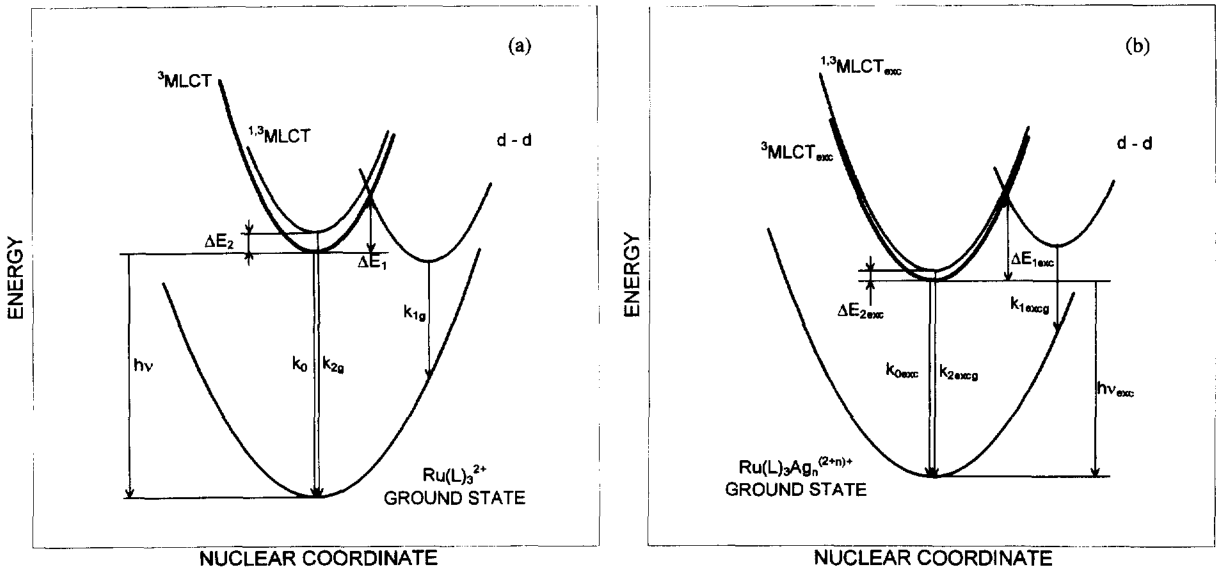


Fig. 8. Qualitative energy level diagrams for the $[Ru(L)_3]^{2+}$ complex (A) and $[Ru(L)_3]Ag_n^{(n+2)+}$ exciplexes (B) show the relative position of the ground, MLCT, and d–d states, and the paths of the energy degradation. ΔE_1 and ΔE_{1exc} are the energy barriers for the MLCT → d–d transition in $*Ru(L)_3^{2+}$ complex (A) and $Ru(L)_3Ag_n^{(n+2)+}$ exciplexes (B), while ΔE_2 and ΔE_{2exc} are the energy gaps between the three low-lying MLCT states and the fourth MLCT state for $*Ru(L)_3^{2+}$ complex (A) and $Ru(L)_3Ag_n^{(n+2)+}$ exciplexes (B) k_{1g} and k_{2g}, k_{1excg} and k_{2excg} are represent the rate of deactivation from d–d and the fourth MLCT sate.

ative and the non-radiative processes from the luminescent exciplex lead to the repulsive surface of the exciplex ground state and then to the ground state of the complex.

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Appendix A.

The differential equations for Scheme 1 are:

$$d[C]/\mathrm{d}t=k_{1o}[E_1]-(k_o+k_{o1}[A])[C] \tag{a1}$$

$$d[E_1]/\mathrm{d}t=k_{o1}[A][C]+k_{21}[E_2] -(k_1+k_{1o}+k_{12}[A])[E_1] \tag{a2}$$

$$d[E_2]/\mathrm{d}t=k_{12}[A][E_1]-(k_2+k_{21})[E_2] \tag{a3}$$

where $[A]$, $[C]$, $[E_1]$ and $[E_2]$ are the concentration of silver ion, excited complex, bimolecular exciplex and termolecular exciplex, respectively. Under steady state conditions, when the light absorbed by the ground state complex (I_a, mol photon s^{-1}) is constant and the light absorption by the exciplexes is negligible, the concentrations of excited species are also constant, hence;

$$-(k_o+k_{o1}[A])[C]+k_{1o}[E_1]=-I_a \tag{a4}$$

$$k_{o1}[A][C]-(k_1+k_{1o}+k_{12}[A])[E_1]+k_{21}[E_2]=0 \tag{a5}$$

$$k_{12}[A][E_1]-(k_2+k_{21}[E_2]=0 \tag{a6}$$

These yield the concentration of excited complex, bimolecular exciplex and termolecular exciplex, from which the luminescence intensity can be obtained using the rate of luminescence for the three species (k_{Lo}, k_{L1}, k_{L2}). Since the luminescence decay curves follow a single exponential curve at any silver ion concentration it is reasonable to suppose a much faster establishment of the excited state equilibrium, than the decays to the ground state ($k_{ij}\gg k_n$). Considering these, the steady state concentrations of the excited species derived from Eq. (a4), Eqs. (a5) and (a6) are

$$[C]=-I_a[(k_1+k_{1o})(k_2+k_{21})+k_{12}k_2[A]]/Det \tag{a7}$$

$$[E_1]=-I_a k_{o1}(k_2+k_{21})[A]/\mathrm{Det} \tag{a8}$$

$$[E_2]=-I_a k_{o1}k_{12}[A]^2/\mathrm{Det} \tag{a9}$$

where Det is the determinant of Eq. (a4), Eqs. (a5) and (a6),

$$\mathrm{Det}=-\{k_o[k_{1o}k_2+k_1k_2+k_1k_{21}+k_{1o}k_{21}] +[k_ok_{12}k_2+k_{o1}k_1k_2+k_{o1}k_1k_{21}][A] +k_{o1}k_{12}k_2[A]^2\} \tag{a10}$$

The observed emission intensity is proportional to the concentration of the emitting species,

$$I=I_a\{k_{Lo}[(k_1+k_{1o})(k_2+k_{21})+k_{12}k_2[A]] +k_{L1}[k_{o1}(k_2+k_{21})[A]] +k_{L2}(k_{o1}k_{12}[A]^2)\}/\mathrm{Det} \tag{a11}$$

Because the relation of the rate constants is $k_{ij}\gg k_n$, one can simplify this expression by omitting the very small constituents of the numerator and the denominator,

$$I=I_a\{k_{Lo}k_{1o}k_{21})+k_{L1}k_{o1}k_{21}[A] +k_{L2}k_{o1}k_{12}[A]^2\}/\{k_ok_{1o}k_{21}]+k_1k_{o1}k_{21}][A] +k_2k_{o1}k_{12}[A]^2\} \tag{a12}$$

Dividing both the numerator and the denominator by $k_{1o}k_{21}$,

$$I=I_a\{k_{Lo}+k_{L1}\beta_1[A]+k_{L2}\beta_2[A]^2\}/ \times\{k_o+k_1\beta_1[A]+k_2\beta_2[A]^2\} \tag{a13}$$

Introducing the mole fraction of different species we obtain

$$I=I_a\sum\alpha_ik_{L,i}/\sum\alpha_ik_i \tag{a14}$$

Substituting $\sum\alpha_ik_i=1/\tau_{obs}$ and $k_{L,i}=I_i/(\tau_iI_a)$ into Eq. (a14) yields

$$I(\lambda)=\tau_{obs}\sum[\alpha_iI_i(\lambda)/\tau_i] \tag{a15}$$

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