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Effect of the pH in the luminescence of ruthenium tris-bipyridine derivatives

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Abstract

The effect of pH on the electronic absorption spectra and luminescence behavior of the $[Ru(bpy)_3]^{2+}$, $[Ru(bpy)_2(mbpy)–NHCH_3]^{2+}$ and $[Ru(bpy)_2(mbpy)–acrd]^{3+}$ complexes, where bpy = 2,2′-bipyridine, mbpy = 4-methyl-4′-carbonyl-2,2′-bipyridine and acrd = 9-aminoacridinyl, has been investigated with special attention in the amide connection. The pH-dependent photophysical properties were investigated by steady state and time-resolved luminescence spectroscopy.

Keywords: pK_a; Ru(II) complexes; Luminescence; Amide

1. Introduction

Because of their photophysical properties, polypyridyl ruthenium complexes have been provided basis for the study of photoinduced electron or energy transfer in solution and in molecular assemblies [1]. The properties of the excited states of these complexes can be varied systematically by introducing a range of appropriate ligands. For instance, several compounds have been prepared with amide bridges, especially concerning peptides and protein modified by using metal complex chromophores such as polypyridyl ruthenium complexes [2–4]. A key feature of these applications is the change in the photophysical properties of ruthenium chromophores on changing the microenvironment provided by biological macromolecules. To better use the metal chromophores in this kind of application, it is of fundamental importance to study the mechanism of the underlying phenomena. Aiming to achieve this goal, the emission spectroscopy technique has been frequently used by several research groups [5]. In order to improve and fully exploit the wealth of information provided by this technique, a considerable number of studies dealing with medium effects such as changing solvent polarity or pH on the excited-state properties of polypyridyl ruthenium complexes has been investigated [4,6,7]. The ability to reversibly modify the luminescence properties of a given chromophore by changing the periphery of such complexes (i.e. protonation/deprotonation or coordination of a metal ion) is of particular interest for the possible development of switching mechanisms in future photochemical molecular devices [8]. Thus, if photoinduced electron or energy transfer between a chromophore and a quencher through a conjugated bridge is thought to be across a simple molecular wire; then, the ability of its reversible behavior constitutes a switching mechanism for the long-distance electron or energy transfer. The acid–base properties of these types of compounds can differ significantly in the excited state comparatively to the ground state. These changes in acidity can be explained by the differences in electron distribution between the ground and excited states.

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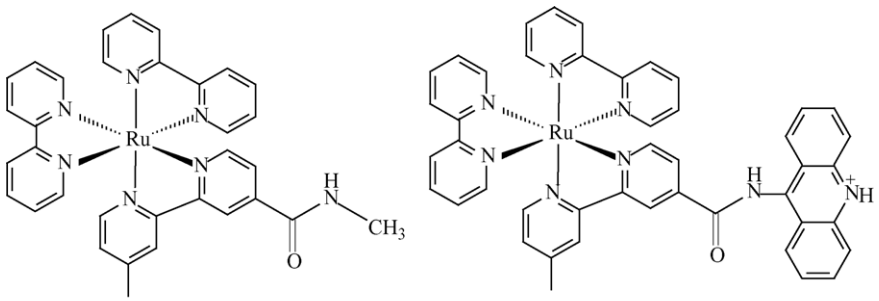


$[Ru(bpy)_2mbpy\text{-}NHCH_3]^{2+}$ $[Ru(bpy)_2mbpy\text{-}acrd]^{3+}$

Scheme 1. Planar representation of the $[Ru(bpy)_2(mbpy)–NHCH_3]^{2+}$ and $[Ru(bpy)_2(mbpy)–acrd]^{3+}$ complexes.

We report here the results related to the investigation of the influence of the pH in the spectroscopic and luminescent properties of the $[Ru(bpy)_2(mbpy)–NHCH_3]^{2+}$ and $[Ru(bpy)_2(mbpy)–acrd]^{3+}$ complexes, where bpy = 2,2′-bipyridine, mbpy = 4-methyl-4′-carbonyl-2,2′-bipyridine and acrd = 9-aminoacridinyl (Scheme 1), with special attention to the amide state protonation. The results are discussed in a comparative form with the well known spectroscopic behavior of the $[Ru(bpy)_3]^{2+}$ complex [1].

2. Experimental section

2.1. Equipments

Absorption spectra were measured with a HITACHI U-2000 spectrophotometer, and the corrected steady-state emission spectra were recorded using a CD-900 Edinburgh spectrofluorimeter with the excitation wavelength (λ_{exc}) specific for each sample. Emission quantum yields (Φ_{em}) in aerated aqueous solutions were calculated relatively to $[Ru(bpy)_3]^{2+}$ in oxygen free aqueous solution, assuming a standard value of $\Phi_{em} = 0.042$. Luminescence decays were measured by time-correlated single photon counting technique using a CD-900 Edinburgh spectrometer operating with a hydrogen-filled nanosecond flash lamp at 40 kHz pulse frequency and a cooled PMT Hamamatsu R955. The decays were analyzed by monoexponential or biexponential fitting using reconvolution of the δ-function with the instrument response function (pulse width of 1 ns FWHM). ^1H and ^{13}C NMR spectra were obtained in the designated solvents on a BRUKER (400 MHz) spectrometer. Syntheses were monitored by HPLC (High Performance Liquid Chromatography) technique using a Shimadzu LC-10AD chromatograph with SPD-10A UV–vis detector. The pH values were measured by using a CORNING pH meter 440 equipped with a 3-in-1 Combo W/RJ Ag/AgCl reference electrode. Low pH values were adjusted with calculated volumes of 2–12 M HCl, and high pH values with 2 M NaOH. The final complex concentration was 5.0×10^{-5} M in all cases.

2.2. Materials

Acetonitrile, 9-aminoacridine (acrd), tetrafluorborate acid, 1,3-diisopropilcarbodiimide, 4,4′-dimetil-2,2′-bipyridine, selenium dioxide, 1-hydroxybenzotriazole hydrate and *N*-methylmorpholine, purchased from Aldrich, were used as received. Chloride acid, dicloromethane, ethanol, acetone, ammonium hydroxy, sodium hydroxy, and methanol, acquired from Mallinckrodt were used as received except for acetone that was treated with sodium sulfate and then distilled and stored with 4 Å molecular sieves. Trifluoracetic acid, silver nitrate, methylamine, from Merck, and trisbipyridine of ruthenium chloride, from G. Frederick Smith Chemical Co., were used without further purification. Dimethylformamide (Merck) was distilled under reduced pressure at 75 °C and dried with 4 Å molecular sieves. Ether (Synth) was treated with sodium, and then distilled twice before use.

The 4′-methyl-2,2′-bipyridine-4-carboxylic acid was prepared by the method described by McCafferty et al. [2], and the $[Ru(bpy)_2(mbpy)–OH](BF_4)_2$ and the $[Ru(bpy)_2(mbpy)–NHCH_3](BF_4)_2$ complexes were prepared following the method of Peek and et al. [9]. The $[Ru(bpy)_2(mbpy)–acrd](BF_4)_2$ complex was prepared as previously described [10]. All these compounds were characterized by NMR spectroscopy and elemental analysis. The results are consistent with those reported in the literature [2,9,10].

3. Results and discussion

The absorption spectra of the $[Ru(bpy)_2(mbpy)–NHCH_3]^{2+}$ and $[Ru(bpy)_2(mbpy)–acrd]^{3+}$ complexes in aqueous or in methanol solution are typical for polypyridyl ruthenium complexes [1]. The most significant features are the band and the shoulder observed at 456 and 426 nm, respectively, for both complexes (see Fig. 1). The solvatochromism observed for these absorption bands is consistent with the assignment of metal to ligand charge transfer transitions [10]. Additionally, a strong absorption at 285 nm assigned to the bpy intraligand $\pi^* \leftarrow \pi$ transitions was observed in the spectra of the complexes. One point

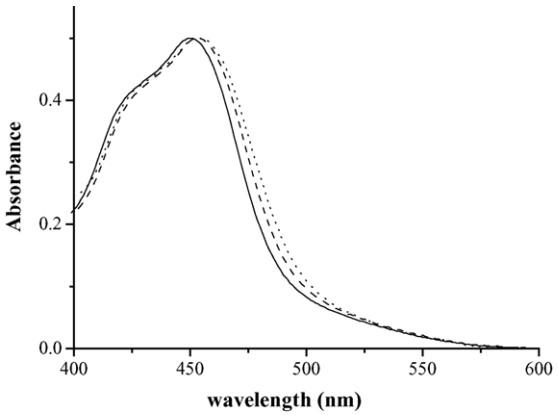


Fig. 1. MLCT absorption bands of the complexes: $[Ru(bpy)_3]^{2+}$ (—), $[Ru(bpy)_2(mbpy)–NHCH_3]^{2+}$ (- - -), and $[Ru(bpy)_2(mbpy)–acrd]^{3+}$ (· · ·) in acetonitrile.

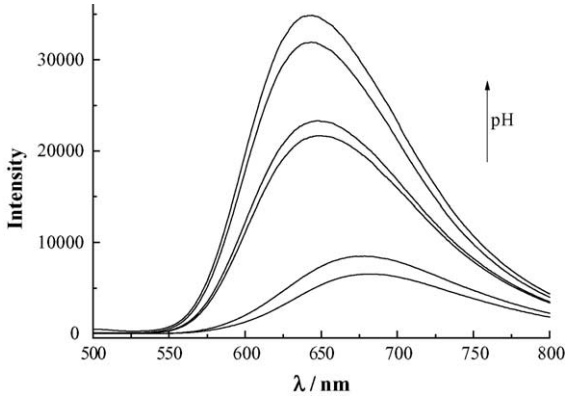


Fig. 2. Emission spectra of the $[Ru(bpy)_2(mbpy)–acrd]^{3+}$ at different pH values at 298 K, and λ_{exc} = 450 nm.

that must be addressed is that no significant absorption spectral changes were observed at pH values ranging from 2.0 to 12.0. Similar behavior was observed by Geisser et al. [4] for the $[Ru(bpy)_2(m–Net_2)]^{2+}$ complex, m–Net_2 = 4-*N*,*N*-diethylcarboxamido-4′-methyl-2,2′-bipyridine. The results obtained for this compound indicates that the amide oxygen pK_a value of the complex in its ground state is below zero [4].

The redox potentials ($E_{1/2}$) for the title complexes, obtained by cyclic voltammetry in 0.1 M TBAP acetonitrile solution, were reported early [10]. The potential of the Ru oxidation in $[Ru(bpy)_2(mbpy)–NHCH_3]^{2+}$ and $[Ru(bpy)_2(mbpy)–acrd]^{3+}$ complexes are 1.28 and 1.29 V, respectively, while the potentials for the sequential reductions of the bpy ligand are −1.20, −1.36, −1.54 V and −0.87, −1.15, −1.38, −1.54 V, respectively. In the case of $[Ru(bpy)_2(mbpy)–acrd]^{3+}$, the $E_{1/2}$ = −0.87 V is ascribed to the reduction of the acrd heterocycle moiety. Considering that the potential remaining values are close to the redox potentials of the $[Ru(bpy)_3]^{2+}$ complex, it is expected that the electronic spectra of these complexes present MLCT absorption bands in the same region. In fact, small differences of only 6 nm are observed in the absorption maximum of these bands. Also, there is an enlargement of the MLCT band in the red region due to the expected low energy of the amide-substituted bipyridine ligand (Fig. 1). In the ruthenium similar system containing bipyridine-modified amino acids ligands, no significant changes in the redox potentials were observed, and the MLCT transitions involving the derivative ligand are largely overlapped with the MLCT transitions from the metal to the unsubstituted bipyridines [11].

Accounting for the well-established emission spectrum profile of the complex $[Ru(bpy)_3]^{2+}$ [1], this species was taken as standard for comparative analysis with the emission results obtained for the $[Ru(bpy)_2(mbpy)–NHCH_3]^{2+}$ and $[Ru(bpy)_2(mbpy)–acrd]^{3+}$ compounds. The excitation processes result in the excited MLCT triplet states, ^{3}MLCT, which are the responsible states for the emission luminescence processes and bimolecular reactions observed for these complexes. In fact, the ^{3}MLCT excited state is the mostly frequently observed for the bulky majority of the polypyridinic ruthenium complexes reported in the literature [12] with appropriate lifetimes and properties to act as electron or energy donor or acceptor.

The emission intensities of the $[Ru(bpy)_3]^{2+}$ species do not experiment significantly changes at a large range of pH values. However, the emission spectra of the $[Ru(bpy)_2(mbpy)–NHCH_3]^{2+}$ and $[Ru(bpy)_2(mbpy)–acrd]^{3+}$ complexes present a blue shift and an intensity increase as the pH value is changed from 2.0 to 12.0. This behavior is illustrated in Fig. 2 for the complex $[Ru(bpy)_2(mbpy)–acrd]^{3+}$. Also, an increase in the emission quantum yield with pH is observed for both complexes, and the values obtained are reported in Table 1.

For the $[Ru(bpy)_3]^{2+}$ complex, the changes in the pH values do not cause any ordered shift of its emission spectrum but only a fluctuation of about 2 nm of its maximum emission wavelength. Conversely, decreases of about 37 and 41 nm in the maximum emission bands of the $[Ru(bpy)_2(mbpy)–NHCH_3]^{2+}$ and $[Ru(bpy)_2(mbpy)–acrd]^{3+}$ complexes, respectively, were observed at the expense of the increase of the pH values. These different ^{3}MLCT emission behaviors might be related to the acid–base equilibrium of amide group of the

Table 1
Wavelength of emission maximum (λ_{max}) and quantum yield (Φ_{em}) of the complexes as a function of pH in aqueous solution at 298 K

pH	$[Ru(bpy)_2(mbpy)–NHCH_3]^{2+}$		$[Ru(bpy)_2(mbpy)–acrd]^{3+}$	
	λ_{max} (nm)	Φ_{em}	λ_{max} (nm)	Φ_{em}
2.0	679	0.006	684	0.006
4.0	673	0.007	680	0.008
6.0	647	0.019	647	0.023
8.0	644	0.029	648	0.032
10.0	643	0.030	644	0.034
12.0	642	0.033	643	0.038

*pH: 2.0–12.0; λ_{max} ($[Ru(bpy)_3]^{2+}$): 622 ± 2 nm; Φ_{em} ($[Ru(bpy)_3]^{2+}$ in water): 0.042.

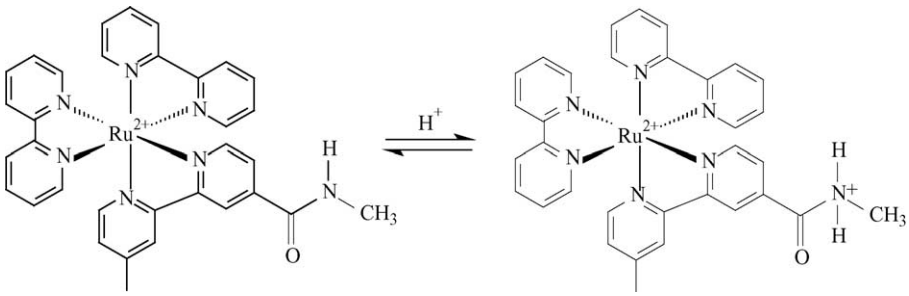


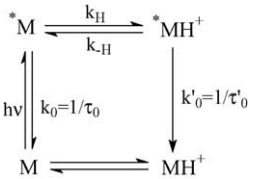
Fig. 3. Protonation scheme of the amide group of the $[Ru(bpy)_2(mbpy)–NHCH_3]^{2+}$ complex.

functionalized ligands, once these moieties are the basic differences between the model system and the synthesized complexes, as can be visualized in Scheme 1. The $[Ru(bpy)_3]^{2+}$ species does not posses basic nitrogen atoms on its periphery, while for the other complexes the ground and excited states are capable of being protonated, as illustrated in Fig. 3. This fact may lead to a specific effect of the amide bridge in the bipyridine-arylcarboxamide, which changes the electronic energy of the localized ^{3}MLCT electronic state and breaks the symmetry among the bipyridyl ligands.

Aqueous solutions of the $[Ru(bpy)_2(mbpy)–NHCH_3]^{2+}$ and $[Ru(bpy)_2(mbpy)–acrd]^{3+}$ complexes present very low luminescence quantum yields (less than 1%) at pH ≤ 4.0, suggesting an increase of the nonradiative decay rate in low pH in addition to excited state deactivation by deprotonation kinetics. The kinetic considerations are better analyzed with reference to Scheme 2 [4,13], where k_H and k_{-H} are the rate constants for the protonation and deprotonation processes in excited state, respectively, and k_0 and k'_0 are the decay rate constants of these two species, respectively.

The emission decay for the $[Ru(bpy)_2(mbpy)–NHCH_3]^{2+}$ complex in acidic solution (pH ≤ 4.0) is biexponential, as can be seen from the lifetime data given in Table 2. In acidic medium, the emission decay may contain contributions from the protonated $*MH^+$ complex, which is the form responsible for the short decay time component observed, and from the deprotonated *M complex. For the $[Ru(bpy)_3]^{2+}$ complex, on the other hand, the decay is monoexponential with a lifetime practically independent on pH. In aerated aqueous solution with pH 2.0, and in basic solution with pH 12.0, the lifetimes are 359 and 386 ns, respectively.

The emission decay of $[Ru(bpy)_2(mbpy)–acrd]^{3+}$ has also a biexponential character but contrasting with the later system, this behavior occurs almost in the whole region of pH investigated (only at pH 12, a single lifetime is recovered from decay analysis). At pH values above 4.0, the deprotonated form *M prevails, as can be seen from the amplitude of the τ_1 value given in Table 2.



Scheme 2. Acid–base equilibria of the ground and excited states.

One approach to evaluate the excited state pK_a^* is from the Förster cycle [14], and the energies of the protonated and deprotonated ground and excited states. Indeed, if long-wavelength absorption or emission bands of acid–base forms and the pK_a of the ground state are known, the Förster cycle can be applied. Wrighton et al. [15] used this methodology to postulate that the lowest excited state of $Ru(bpy)_2(4,4'$-dicarboxylate-2,2′-bipyridine) is a stronger base than the ground state. For the $[Ru(bpy)_2(mbpy)–NHCH_3]^{2+}$ and $[Ru(bpy)_2(mbpy)–acrd]^{3+}$ compounds the difference in the 0–0 transition energies between the ground-state acidic and basic forms for the first equilibrium, $\Delta\bar{\nu}$, measured were 510 and 343 cm^{-1}, respectively. Such calculations give pK_a^* of 4.82 and 3.92 for $[Ru(bpy)_2(mbpy)–NHCH_3]^{2+}$ and $[Ru(bpy)_2(mbpy)–acrd]^{3+}$ complexes, respectively, according to Eq. (1):

$$pK_a^* = pK_a + \frac{\varepsilon_{HA} - \varepsilon_{\bar{A}}}{2.3RT} = pK_a + \frac{Nhc\Delta\bar{\nu}}{2.3RT} \quad (1)$$

For instance, if the excited state pK_a^* is observed above that of the ground state value for the same process, it can be suggested that the ^{3}MLCT state is localized on the ligand containing the acidic substituent. The excited state has its negative charge increased and is, therefore, a less acidic species. The pH dependence of the ^{3}MLCT state with the integrated emission intensity for the $[Ru(bpy)_2(mbpy)–NHCH_3]^{2+}$ and $[Ru(bpy)_2(mbpy)–acrd]^{3+}$ complexes are shown in Fig. 4.

Table 2
Emission lifetimes (τ) of the complexes as a function of pH

pH	$[Ru(bpy)_2(mbpy)–NHCH_3]^{2+}$		$[Ru(bpy)_2(mbpy)–acrd]^{3+}$	
	τ_1 (ns) ($\tilde{b}_1$)	τ_2 (ns)	τ_1 (ns) ($\tilde{b}_1$)	τ_2 (ns)
2.0	321 (0.311)	95	390 (0.202)	137.3
4.0	299 (0.174)	48	359 (0.185)	142.1
6.0	277	–	383 (0.772)	177.0
8.0	340	–	378 (0.852)	105.1
10.0	445	–	385 (0.963)	56.56
12.0	449	–	382	–

Errors in lifetimes are ±5%. The normalized pre-exponential factors of the biexponential decay are shown in parentheses ($\tilde{b}_1 + \tilde{b}_2 = 1$). Measures were performed in aqueous aerated solution at 298 K.

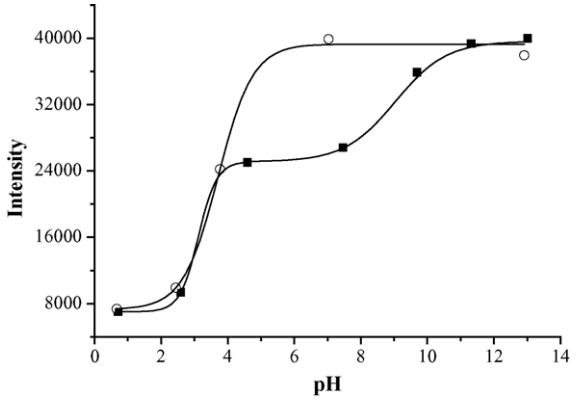


Fig. 4. pH dependence of the maximum emission intensities of the $[Ru(bpy)_2(mbpy)–NHCH_3]^{2+}$ (◯) and $[Ru(bpy)_2(mbpy)–acrd]^{3+}$ (■) complexes at 450 nm.

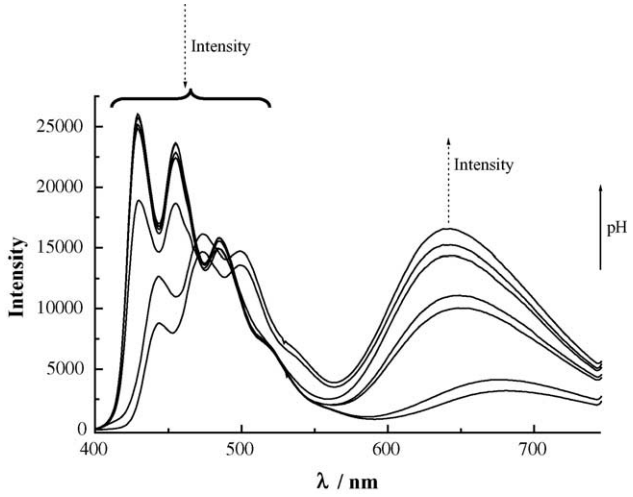


Fig. 5. Emission spectrum of the $[Ru(bpy)_2(mbpy)–acrd]^{3+}$ complex in aqueous solution at 380 nm as a function of pH at 28 K.

The $[Ru(bpy)_2(mbpy)–NHCH_3]^{2+}$ complex contains one protonation site, the amide group, with $pK_a = 3.75$, as indicated by the single inflection point in the fluorimetric titration curve (symbol (◯) in Fig. 4). For the complex with 9-aminoacridine ligand, two inflection points are observed (symbol (■) in Fig. 4) implying in two pK_a values: one at 3.20 and the other at 9.53. The first is ascribed to the amide protonation, and the second is related to the acid base equilibrium of the acridine heterocycle, after coordination.

The excited state pK_a (pK_a^*) values of the $[Ru(bpy)_2(mbpy)–NHCH_3]^{2+}$ and $[Ru(bpy)_2(mbpy)–acrd]^{3+}$ compounds, were obtained from the Förster cycle [14], and are 4.82 and 3.92, respectively. Comparatively to the pK_a values of the ground state, these results indicate a small increase in basicity in the excited state. These observations suggest that the MLCT transitions are located essentially on the bpy–$NHCH_3$ and bpy–acrd ligands for the $[Ru(bpy)_2(mbpy)–NHCH_3]^{2+}$ and $[Ru(bpy)_2(mbpy)–acrd]^{3+}$ complexes, respectively. This conclusion is consistent with the fact that the luminescence emissions of the complexes are observed at lower energy in acidic medium, i.e. at pH values below the first pK_{a1}^* for both complexes.

The above discussions enable us to infer that the protonation of the amide group leads to a strong stabilization of the ^{3}MLCT emissive state. This conclusion may be ascribed to solvent effect and a preferential charge location on the ligand with amide group due to the formation of two positive centers: the metal Ru^{II} and the protonated amide group. On the other hand, there is a higher competition with the non-radiative processes, leading to the decrease in the emission intensity with the pH values ≤ 4.0.

The ruthenium complex with the acridine peripherical group has a second excited-state equilibrium of the N–H of the acridine heterocycle, to which the value of $pK_{a2}^* = 9.6$ was evaluated from the Förster cycle (Eq. (1), $\Delta\bar{\nu} = 33\,cm^{-1}$). The existence of three possible species would explain the complexity of the behavior of this complex compared with the $[Ru(bpy)_2(mbpy)–NHCH_3]^{2+}$ species. Since three possible species are formed, a three exponential decay would be expected to occur, but the presence of biexponential decay instead of is supported by the fact that the difference in pK_a is of about 6 units. Therefore, only a given pair of species is responsible for the dynamics of protonation and deprotonation in ground and excited-state, in each region of pH.

The emission spectrum of the complex $[Ru(bpy)_2(mbpy)–acrd]^{3+}$ with excitation at 380 nm, shows the relative bands of the acridine (see Fig. 5). The structured band in the range of 400–550 nm are assigned to the fluorescence emission of the 9-aminoacridine moiety, and the broad band with maximum at 639 nm is the luminescence of the ^{3}MLCT state of the Ru complex [10]. The pH dependence of the emission spectra for the $[Ru(bpy)_2(mbpy)–acrd]^{3+}$ complex is shown in Fig. 4. The fluorescence of the acrd has three vibronic peaks and a shoulder at 355 nm [16]. The peaks located at 429, 456 and 485 nm at pH 2.0 shift to 443, 473 and 500 nm at pH 12, and the emission intensities decrease considerable. These changes are very similar to the spectral changes observed for acridine-9-*N*-methacrylamide in the protonated and neutral form, as reported recently [17]. This fact confirms the more complex acid–base equilibria of the $[Ru(bpy)_2(mbpy)–acrd]^{3+}$ species, previously discussed in terms of the luminescence properties of the MLCT state.

Finally, the difference in the pK_a values of the amide bridge group in ground ($\Delta pK_a = 0.55$) and excited state ($\Delta pK_a^* = 1.0$) observed for the $[Ru(bpy)_2(mbpy)–NHCH_3]^{2+}$ and $[Ru(bpy)_2(mbpy)–acrd]^{3+}$ complexes finds explanation on the effect of the charge resonance forming tautomeric isomers of acridinium cation. In fact, the amide–imine resonance of the acridinium (see Fig. 6) must bring the amide protonation to a more acidic region resulting in low pK_a values as observed from the comparison of the ground and excited state values of the two Ru complexes.

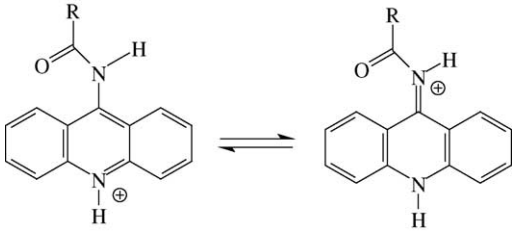


Fig. 6. Tautomeric forms of acridinium peripherical heterocycle, where R = $[Ru(bpy)_2(mbpy)]^{3+}$.

The results presented in this work show that the protonation of the pedant sites appended to the ruthenium (II) tris(bipyridyl) moiety lead to the luminescence quenching and red shift of the ^{3}MLCT state lowest energy. This conclusion hints that the emission from the complex with amide connection is strongly pH dependent.

Acknowledgments

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