



Photophysical and acid–base properties of bis(2,2'-bipyridine) (3,3'-dicarboxy-2,2'-bipyridine) ruthenium(II) chloride

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Abstract

A new mixed-ligand complex $[\text{Ru}(\text{bpy})_2(3,3'\text{-dcbpy})]^{2+}$ (compound **1**) was synthesized, where $\text{bpy} = 2,2'$ -bipyridine and $3,3'$ - $\text{dcbpy} = 3,3'$ -dicarboxy-2,2'-bipyridine. The ground state $\text{p}K_{\text{a}1}$ and $\text{p}K_{\text{a}2}$ of compound **1** were 0.2 and 2.2, respectively. The ground state $\text{p}K_{\text{a}1}$ and $\text{p}K_{\text{a}2}$ values of 1.7 and 2.9 for compound **2** ($[\text{Ru}(\text{bpy})_2(4,4'\text{-dcbpy})]^{2+}$, where $\text{bpy} = 2,2'$ -bipyridine and $4,4'$ - $\text{dcbpy} = 4,4'$ -dicarboxy-2,2'-bipyridine) were also measured. The stronger acidity of compound **1** was attributed to intramolecular hydrogen-bonding interaction. The excited state $\text{p}K_{\text{a}}^*$ values of compound **1** and **2** were determined by means of spectrophotometric titration. Compared to the ground state $\text{p}K_{\text{a}}$ s of compound **1** and **2**, the higher values for $\text{p}K_{\text{a}}^*$ s revealed that the excited state species was a slightly stronger base than its ground state analog. Compound **1** had shorter emission lifetime and smaller quantum yield than those of the compound **2**. These results implied that the substituted positions of carboxylic acid in the 2,2'-bipyridine ligand had effect on the photophysical properties of the complexes. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ruthenium polypyridyl complex; Spectrophotometric titration; Ground state acid–base properties; Excited state acid–base properties

1. Introduction

Synthesis and characterization of electrochemical and photochemical properties of various polypyridyl transition-metal complexes have been of prime focus in numerous research groups because of their potential use in solar energy conversion schemes in recent years [1–3]. Particularly, ruthenium(II) polypyridyl complexes have been employed as efficient photosensitizers for the past two decades. In this class of sensitizers, *cis*-(NCS)₂bis(2,2'-bipyridyl-4,4'-dicarboxylate) ruthenium(II) has been proven to be the most efficient. A solar-to-electric energy conversion efficiency of 10% was achieved with nanocrystalline TiO₂ film coated with a monolayer of this complex [4]. However, these complexes show very weak luminescence in solution. For example, the emitting state of the above complex has luminescence quantum yield of only 0.4% (125 K) and a 50 ns lifetime (298 K) [5]. Therefore, it is difficult to study photophysical properties of this complex.

The acid–base properties of transition metal complexes containing dicarboxylic acid substituent pyridine ligands can provide important information about the nature of

excited states. For this purpose, bis(2,2'-bipyridine)(3,3'-dicarboxy-2,2'-bipyridine) ruthenium(II) chloride (compound **1**) was synthesized. Detailed photophysical studies of the acid–base properties of this complex were reported in this paper. For comparative purposes, the parallel measurements on bis(2,2'-bipyridine)(4,4'-dicarboxy-2,2'-bipyridine) ruthenium(II) chloride (compound **2**) were carried out. These experimental results may provide further insight into the photoelectrochemical and excited state photophysical properties of the *cis*-(NCS)₂bis(2,2'-bipyridyl-4,4'-dicarboxylate) ruthenium(II) and *cis*-(NCS)₂bis(2,2'-bipyridyl-3,3'-dicarboxylate) ruthenium(II).

2. Experimental

2.1. Materials

All chemicals and solvents were of reagent grade and used as received without further purification.

Synthesis of the 3,3'-Dicarboxy-2,2'-bipyridine(3,3'- dcbpy) was described in the literature [6]. The product was characterized by means of elementary analysis. Anal. Calcd. for C₁₂H₈N₂O₄ C, 59.0; N, 11.5; H, 3.3. Found: C, 59.0; N, 11.8; H, 3.5.

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4,4'-Dicarboxy-2,2'-bipyridine was prepared by the method of Whitten et al. [7].

Compound **1** was synthesized as described for compound **2** [8], by using 3,3'-dicarboxy-2,2'-bipyridine as a starting material. Anal. Calcd. for $[\text{Ru}(\text{bpy})_2(3,3'\text{-dcbpy})]\text{Cl}_2 \cdot 12\text{H}_2\text{O}$: C, 40.6; N, 8.8; H, 5.0. Found: C, 41.2; N, 8.5; H, 3.9.

$[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ was prepared as described in the literature [9].

2.2. Measurements

UV-Vis absorption spectra were recorded on a HITACHI U-2001 UV/Vis spectrophotometer and emission spectra on a HITACHI-850 fluorescence spectrophotometer with a computer for data collection and analysis. Emission quantum yields were calculated by comparison with the integrated intensity of the emission spectrum of an absorbance-matched solution of $[\text{Ru}(\text{bpy})_3]^{2+}\text{Cl}_2$ ($\Phi_{\text{em}} = 0.042$) [10] in water. The fluorescence lifetimes were measured at room-temperature with a time-resolved spectrofluorimeter (Horiba NAES-1100), which was based on the single-photon-counting method. The light source (2 ns FWHM) for the excitation was a high-pressure hydrogen flash lamp of free-running type. The excitation wavelength was 460 nm. Each sample was bubbled with N_2 for 30 min prior to use.

Acid–base titration experiments were performed on samples dissolved in 1 mol/l NaCl to keep a constant ionic strength. The ground $\text{p}K_{\text{a}}^0$ was determined by spectrometric titration, and the excited state $\text{p}K_{\text{a}}^*$ was measured by fluorescence titration. Ground-state absorption spectra were obtained from samples having an absorbance of ca. 0.7 at 460 nm. The acidity of these solutions was adjusted by the addition of solutions of HCl and/or NaOH (0.1–0.8 mol/l). The total volume change of the sample was negligible (<1%). The Hammett acidities (H_0) of these dilute solutions were assigned using a pH glass electrode calibrated with standard aqueous buffers and by assuming $\text{pH} = H_0$ [11]. In the strongly acidic regimes ($H_0 < 0.5$), absorption spectra were obtained by titrating with 98.6% H_2SO_4 . Estimated errors in the reported values are as follows: absorption and

emission maximums, ± 1 nm (± 5 nm for weak emitters); emission lifetime, $\pm 10\%$; $\text{p}K_{\text{a}}$, $\text{p}K_{\text{a}}^*$, ± 0.1 .

3. Results and discussion

3.1. UV-Vis spectra and the ground state $\text{p}K_{\text{a}}^0$

The UV-Vis absorption spectra for $[\text{Ru}(\text{bpy})_2(3,3'\text{-dcbpy})]^{2+}$ in aqueous solution as a function of pH are shown in Fig. 1(a). The absorption bands near 450 nm were assigned to metal-to-ligand charge-transfer (MLCT) transitions by analogy to the parent compound $[\text{Ru}(\text{bpy})_3]^{2+}$. As the pH decreased, the absorbance of the MLCT band decreased and broadened. Then a new, low-energy shoulder appeared at ca. 500 nm. As the pH increased, the energy maximum of the MLCT band became sharper and red-shifted. The changes of these spectra were completely reversible, and the compound was stable at each pH. Two isosbestic points at 427 nm and 496 nm were in the figure at pH between 2 and 7. Below pH 2, the spectra changed little.

The absorption changes at 453.5 nm as a function of pH between -0.6 and 10.5 for compound **1** at room-temperature showed titration curves with two inflection points ($\text{p}K_{\text{a}1}^0 = 0.2$ and $\text{p}K_{\text{a}2}^0 = 2.2$) in Fig. 1(b). Thus in Fig. 1(b) the spectrum at $\text{pH} = 4.7$ represented that of the deprotonated form, at $\text{pH} = 1.9$, the monoprotonated form, and at $\text{pH} = 0$, the diprotonated form. The observations of two of isosbestic behavior and two inflection points in the titration plot demonstrated that two different protonation steps occurred in compound **1** (Eq. (1) and Eq. (2)), which could be used to describe the acid–base behavior of this compound:

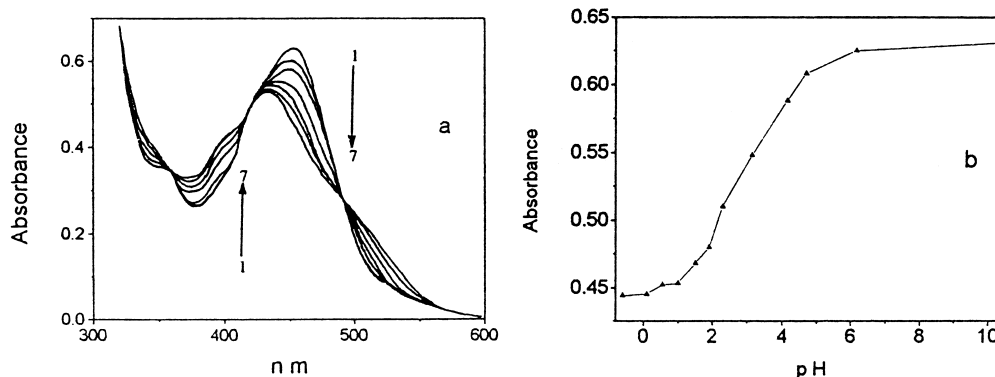
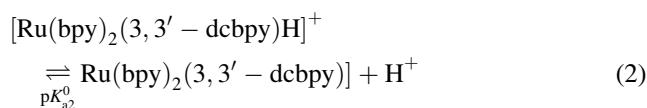
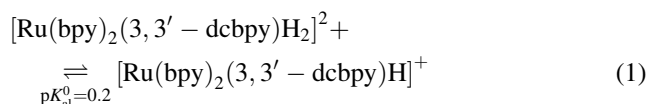


Fig. 1. (a) Absorption spectra of **1** in aqueous solution for the following values of pH: 1, 6.16; 2, 4.70; 3, 4.15; 4, 3.14; 5, 2.60; 6, 2.3; 7, 2.11. Spectrophotometric titration of **1** showing absorbance change at 453.5 nm for various values of pH.

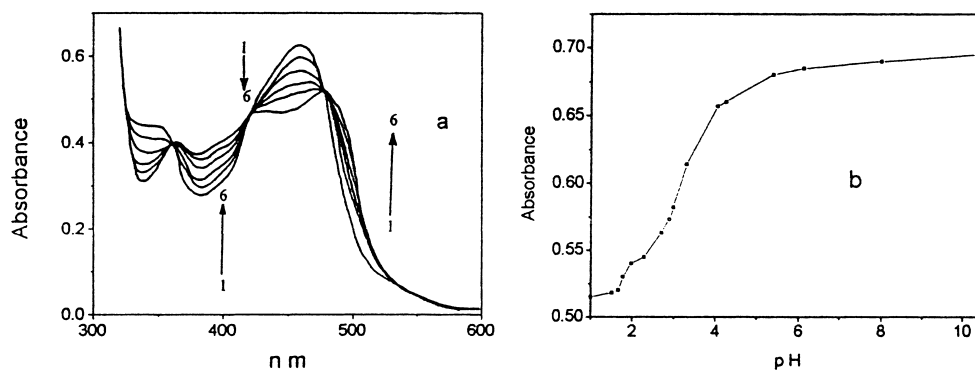


Fig. 2. (a) Absorption spectra of **2** in aqueous solution for the following values of pH: 1, 5.38; 2, 4.25; 3, 4.04; 4, 3.31; 5, 2.99; 6, 2.12. (b) Spectrophotometric titration of **2** showing absorbance change at 459 nm for various values of pH.

The UV-Vis absorption spectra for $[\text{Ru}(\text{bpy})_2(4,4'\text{-dcbpy})]^{2+}$ (compound **2**) in aqueous solution as a function of pH are shown in Fig. 2(a). The absorption bands near 460 nm were attributed to MLCT transitions. Upon lowering of pH, the MLCT band located at 460 nm showed a small decrease in intensity. Two isosbestic points at 422 nm and 478 nm were also found in the plot at pH between 1 and 6. Below pH 1, the spectra traced slightly off the isosbestic and changed little (not shown). The absorption changes at 459 nm as a function of pH between 1 and 11 at room-temperature yielded two pK_a values for the ground state as 1.7 and 2.9 (see Fig. 2(b)).

The stronger acidity of compound **1** as compared to its 4,4'-dcbpy analog could be explained in terms of intramolecular hydrogen-bonding interaction between the two carboxylic acid substituents in 3,3'-positions. The hydrogen-bonding interaction could occur between one of the oxygen atoms bonded to the carbonyl carbon atom in the 3 position with the hydrogen atom bonded to the carboxyl group in the 3' position in compound **1**. The distance of 3,3'-positions might fall within the hydrogen-bonding domain, which was more favorable than that of 4,4'-positions. The hydrogen-

bonding interaction might withdraw the electron from the carboxyl groups, then increase the electron withdrawing effect of the carboxyl groups. The above effect would decrease the electron density on the carboxyl group and increase the acidity of compound **1**. So the pK_a values of compound **1** were accordingly smaller than those of compound **2**.

3.2. Emission properties

Fig. 3(a) shows the emission spectra for compound **1** at various pH conditions. The luminescence intensity was almost pH independent above pH 7. Unlike the absorption intensities, the emission intensities of compound **1** varied mildly in dilute acidic solutions. The intensity decreased rapidly in middle acidic solutions and the emission was almost unchanged in strong acidic (below pH 2) solutions showing independent of pH again. The luminescence peaks at 615 nm in solutions of pH 6.17 and at 635 nm in pH 1.9 were assigned to deprotonated form and the monoprotinated form of **1** in the excited state, respectively, suggesting that proton transfer occurred within the lifetime of the excited

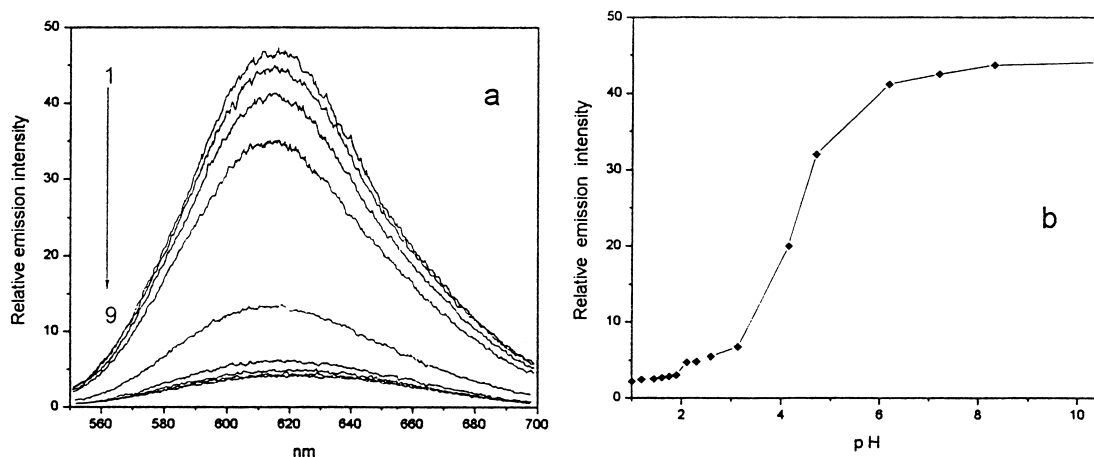


Fig. 3. (a) pH dependence of room-temperature emission for **1**. From 1 to 9, the values of pH are 10.47; 4.15; 3.14; 2.60; 2.30; 2.11; 1.90, respectively. Titration curves for relative emission intensity variation with pH for **1** (615 nm).

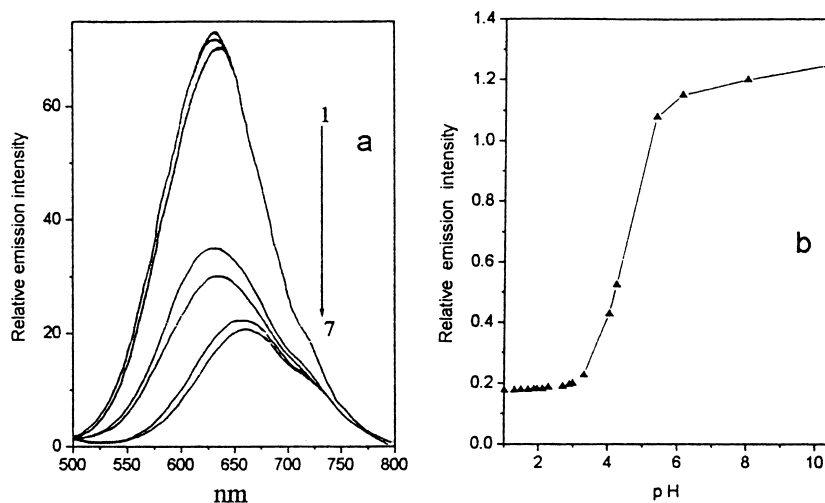


Fig. 4. (a) pH dependence of room-temperature emission for **2**. From 1 to 7, the values of pH are 7.99; 6.12; 5.38; 4.25; 4.04; 3.31; 2.12, respectively. (b) Titration curves for relative emission intensity variation with pH **2** (645 nm).

state. The emission intensity of the monoprotonated form was very weak (ca. 7%) as compared to that of the deprotonated one.

Fig. 4(a) shows the emission spectra for compound **2** as a function of pH. At pH above 5.38, the emission maxima and intensities were independent of pH. As pH decreased from 5.38 to 4.25, a sudden decrease occurred. Then between pH 4.25 and 2.99, the emission intensities decreased gradually and slowly; at pH below 2.99, the emission maximums and intensities were again almost independent of pH.

As the pH decreased from 5.38 to 2.72, the luminescence peak of compound **2** at 645 nm red-shifted to 685 nm, which was assigned to the excited states of the deprotonated and monoprotonated species, respectively. The emission intensity for the monoprotonated species was weak (ca. 17%) compared to that for the basic one.

A summary of the emission quantum yields and lifetimes of compound **1** and **2** at different pH were listed in Table 1. These data suggested a profound influence of the substituted positions of carboxyl group at the 2,2'-bipyridine ligand on the photophysical properties of the compounds. As shown in Fig. 3(a) and Fig. 4(a) and Table 1, compound **1** emitted at shorter wavelength, and had a shorter emission lifetime and smaller quantum yield than compound **2**. This behavior is opposite to the predicted trend by the energy gap law (Eq. (3)) [12].

$$K_{\text{nr}} \propto e^{-CE_{\text{em}}} \quad (3)$$

where C is the slope in cm and E_{em} is the energy in cm^{-1} at the emission maximum. According to Eq. (3), k_{nr} of compound **1** should be smaller than that of compound **2** and, therefore, the emission quantum yield of compound **1** should be higher than that of the compound **2**. This may be attributed to a thermal population of high-lying ligand field (^3LF) state (Fig. 5) [13].

In typical cases, photoexcitation of ruthenium polypyridyl complexes generates a singlet metal-to-ligand charge-transfer state (MLCT) which undergoes fast, highly efficient intersystem crossing ($\Phi_{\text{isc}} \approx 1$) to a manifold of closely spaced triplet state ($^3\text{MLCT}$) [14]. As shown in Fig. 5, these states can then decay back to the ground state through both radiative (k_r) and nonradiative (k_{nr}) mechanisms. Nonradiative deactivation of excited states includes two processes. One is the lowest excited state ($^3\text{MLCT}$) which decays to the ground state directly. The other is a thermal population of high-lying ligand field (^3LF) states. This ^3LF state undergoes fast nonradiative decay to the ground state or ligand dissociation [15].

In principle, the energy of LF excited state depends on the field strength, which depends on the σ -donor and π -acceptor properties of the ligand, the steric crowding around the metal and the bite angle of the polydentate ligands [14]. For compound **1**, the bite angle cannot be optimized because of the steric hindrance on the 2,2'-bipyridine which leads to weakening of the ligand field strength. Thus, the energy of LF excited state of compound **1** decreases. Furthermore, the

Table 1

The emission quantum yields and lifetimes at different pH for compound **1** and **2** ($\lambda_{\text{ex}} = 454 \text{ nm}$, $\lambda_{\text{em}} = 610 \text{ nm}$ for **1** and $\lambda_{\text{ex}} = 460 \text{ nm}$, $\lambda_{\text{em}} = 650 \text{ nm}$ for **2**)

Compound	1				2			
pH	13.38	6.16	1.90	-0.60	13.38	7.99	2.12	-0.60
τ (ns)	341	109	102	77	492	471	243	190
ϕ_{em} (10^{-3})	12	12	3.8	3.0	30	29	9.7	8.0

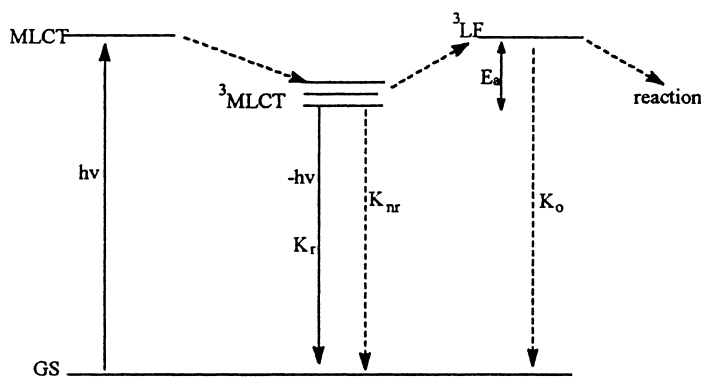


Fig. 5. Energy-level diagram showing the excited state processes occurring in ruthenium polypyridyl compounds.

MLCT energy of compound **1** is slightly higher than that of compound **2**. Therefore, k_{nr} increases exponentially with decreasing energy gap between MLCT and LF excited states. In addition, the formation of hydrogen band can lead to significant enhancement of nonradiate decay rates. An increase in k_{nr} may be the reason that the quantum yield of compound **1** is smaller than that of compound **2**. These results provide experimental support directly for the lower solar energy conversion efficiency of the *cis*-(NCS)₂bis(2,2'-bipyridyl-3,3'-dicarboxylate) ruthenium(II) than that of the *cis*-(NCS)₂bis(2,2'-bipyridyl-4,4'-dicarboxylate) ruthenium(II) [16].

3.3. Excited state pK_a^*

The titration curve of the luminescence intensity at 615 nm for **1** is shown in Fig. 3(b) over the pH range of 2–11 with one inflection point at 3.8. Since the two carboxylic acid groups also displayed two distinct pK_a s in the excited state. The inflection point represented the equilibrium between the deprotonated form and monoprotated form and indicated the value of pH for the other equilibrium (between monoprotated form and diprotated form) was lower than 1.9. The results illustrated that the excited complex could be protonated without electronic deactivation. As an example, when the deprotonated form of compound **1** was excited at pH 3.14, the emission of the monoprotated form was observed predominately.

The pK_a in the excited state (pK_{a2}^*) corresponding to the equilibrium between the deprotonated and monoprotated forms was evaluated in two empirical ways based on Forster's cycle, using the emission and absorption spectra and their titration curves [17,18].

First, in the titration method, the pK_{a2}^* was given as Eq. (4)

$$\text{pH} = pK_{a2}^* + \log\left(\frac{\tau_H}{\tau}\right) \quad (4)$$

Where the pH is taken at the inflection point of compound **1** in the luminescence curve. τ_H (102 ns) and τ (341 ns) are the excited state monoprotated and the deprotonated species,

respectively. Then, the pK_{a2}^* of compound **1** was determined to be 3.3.

Second, the Forster treatment results in Eq. (5), which described the relationship between ground and excited state pK_a s based on pure 0–0 transitions in wavenumbers (cm^{-1}) for the deprotonated (ν_B) and monoprotated (ν_{BH^+}), respectively. At room-temperature, the ground state pK_{a2}^0 of complex **1** was 2.2, the emission energy maximums for the deprotonated and monoprotated species were $\nu_B = 1.63 \times 10^4 \text{ cm}^{-1}$, $\nu_{BH^+} = 1.58 \times 10^4 \text{ cm}^{-1}$, then the predicted excited state pK_{a2}^* was 3.2 which agreed well with the value measured by fluorescence titration.

$$pK_a^* = pK_a^0 + \left(\frac{0.625}{T}\right)(\nu_B - \nu_{BH^+}) \quad (5)$$

Fig. 4(b) shows the titration of the emission in intensity at 645 nm for compound **2** over the pH range of 2–11, with one inflection point at pH 4.5. According to Eq. (4), and the lifetimes of the deprotonated form ($\tau = 471 \text{ ns}$) and monoprotated form ($\tau = 243 \text{ ns}$) of compound **2**, the pK_{a2}^* of compound **2** was 4.2. And using $\nu_B = 1.538 \times 10^4 \text{ cm}^{-1}$, $\nu_{BH^+} = 1.47 \times 10^4 \text{ cm}^{-1}$, the resulting value of pK_{a2}^* was 4.3 according to Eq. (5).

The higher apparent values for pK_a^* of compound **1** and **2** as compared to the ground-state pK_a indicated that the excited-state deprotonated forms of compound **1** and **2** were slightly stronger base than the ground-state analogues. The pK_{a2}^* of the complex suggested that the ligand electron density be significantly higher in the excited state than in the ground state.

4. Conclusions

A new mixed-ligand polypyridylruthenium(II) complex $[\text{Ru}(\text{bpy})_2(3,3'\text{-dcbpy})]^{2+}$ was synthesized. The ground state pK_{a1} and pK_{a2} of compound **1** were 0.2 and 2.2, respectively. The ground state pK_{a1} and pK_{a2} values of 1.7 and 2.9 for compound **2** were also measured. The stronger acidity of compound **1** could be attributed to intramolecular hydrogen-bonding interaction. Compared to the ground state pK_a , the

higher value of pK_a^* revealed that the excited state species was a slightly stronger base than its ground state analog. This result can be expected from the MLCT character of the excited state. The substituted positions of carboxy group in the 2,2'-bipyridine ligand had effect on the photophysical properties of the complexes. The compound **1** had shorter emission lifetime and smaller quantum yield than those of the compound **2**. The results can be interpreted in terms of an additional nonradiative decay pathway by thermally populating a 3LF state. To further understand the above mechanism, experiments are planned to study the temperature effect of the emission properties for compound **1**.

Acknowledgements

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