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pH Dependence of Absorption and Emission Spectra of $Ru(phen)_2(phenOH)^{2+}(PF_6)_2$ Complex

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Abstract

A ruthenium complex of the 4-hydroxy-1,10-phenanthroline ligand was synthesized, and the variation of its absorption and emission intensity and litetime with pH characterized. Excited state lifetime, luminescence intensity, and emission properties were determined. The complex exhibits a maximum at 460nm, and a small red shift at higher pH. The spectra show a well defined isobestic point. Luminescence intensity exhibited a sigmoidal relationship with pH, a behaviour that is similar to those of other ruthenium complexes carrying protonable functional groups. This characteristic is suggestive of the suitability of this complex for pH sensor design for medical practices as well as industrial processes. pH dependence is more evident in the emission than the absorption spectra, a behaviour characteristic of higher pH dependence on the excited than the ground state of the complex. Emission lifetimes of 165.4 ns and 3.08 ns for the protonated and deprotonated states respectively, were determined and the pK^*_a value calculated as 3.68.

Key words: Ruthenium; Phenanthroline; pH; Intensity; Sensor; Spectroscopic

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INTRODUCTION

In recent times, complexes of transition metals of d^6 configuration, particularly ruthenium polypyridyl complexes (Sheeba et al., 2013), have gained extensive photochemical, photophysical (Helena et al., 2008) and electrochemical research interests in the design of solar energy-driven water-oxidizing photoanodes (Robin et al., 2010), molecular probes (Ajay et al., 1998; Szmacinski et al., 1996; Wong et al., 2014) luminescence-based sensors (Sarah et al., 2010; Heather et al., 2002; Ronald et al., 1994), molecular machine devices (Sylvestre & Jean, 2008; Wu et al., 1999; Henrique, 2003) organic light emitting diodes as well as in construction of solar cells (Hong et al., 2004; Hartmut et al., 2002; Santos et al., 2008; Kohjiro et al., 2001; Yu et al., 2013; Yuancheng & Qiang, 2012) and in solar energy research aiming to mimic photosynthesis (Giarikos, 2013; Concepcion et al;2012; Sun et al., 2001). These applications are tied to the high emission quantum yields and attractive excited state properties of the complexes, making them highly suitable for frequency domain luminescence sensing (Lin & Brown, 2000), Other interesting characteristics include a unique combination of spectroscopically distinguishable metal redox states, tunable electronic properties (Sheeba et al., 2013), good aqueous solubility, high chemical and photo stability, large stokes shift, and long emission (Zhang et al., 2015). The spectral and redox properties of ruthenium polypyridyl complexes can be tuned in two ways. First, by introducing a ligand with a low-lying π^* molecular orbital, and second, by destabilization of the metal t_{2g} orbital through the introduction of a strong donor ligand (Nazeeruddin et al., 2001). A careful choice of substituents and systematic ligand design has facilitated adequate exploitation of the properties of these complexes (Ellerbrock et al., 2002). Interesting sensing ability by ruthenium complexes for pH, chloride, CO_2 and oxygen concentrations, temperature (Higgins & DeGraff, 2005) as well as indirect measurement of K^+,

Na^+, Ca^{2+}, NH_4^+, urea and glucose via energy transfer (Wolfbeis et al., 1998) have been reported in literature. For example, complexes with hydroxyl, carboxyl, and amino-functionalised ligands have exhibited spectroscopic properties affected by change in pH, therefore, influencing their applicability in molecular sensing (Ellerbrock et al., 2002). pH measurement is very important in areas ranging from physiology to lake, river, and seawater monitoring, industrial process monitoring, power plant cooling water salinity control, mud/sediment analysis and fermentation. Therefore measurement using luminescent sensors has become an area of considerable research attraction.

Ruthenium (II) complexes based on the 4,7-dihydroxy-1,10-phenanthroline ligand and its derivatives have been researched for the pH dependence of their luminescence properties (Ellerbrock et al., 2002). This is because, for direct pH sensing by a luminescent indicator, the indicator must include a pH-sensitive functionality which is capable of reversible protonation-deprotonation and changes the emissive properties of the indicator with pH changes (Kim et al., 2009). These complexes are strongly emissive, and the protons on the hydroxyl groups of the ligand are acidic, hence the absorption and emission spectra of the complexes are dependent on the pH of the environment (Chan et al., 1998), since the protonation – deprotonation equilibrium of the complexes involve the dissociation of the protons (Ellerbrock et al., 2002). Studies on complexes of mono-hydroxy analogues of this ligand, such as 3-carbethoxy-4-hydroxy-1,10-phenanthroline have proven similar properties (Ellerbrock et al., 2002).

The 4-hydroxy-1,10-phenanthroline ligand was prepared in two steps from 3-carbethoxy-4-hydroxy-1,10-phenanthroline following the synthetic route of the latter. It contains one hydroxyl group whose proton imparts a simple pH dependence on the absorption and emission behaviour of the complex (Chan et al., 1998; Wacholtz et al., 1986). The luminescence properties of the complex, Ru(phen)$_2$(phen-OH)$^{2+}$(PF$_6$)$_2$, (phen = 1,10-phenanthroline and phen-OH = 4-hydroxy-1,10-phenanthroline), as a function of pH changes, is akin to those of other ruthenium complexes bearing protonable functionalities.

In this article, we report on the synthesis, characterization, and pH dependence of absorption and emission spectra of the complex, Ru(phen)$_2$(phen-OH)$^{2+}$(PF$_6$)$_2$. The main incentive for this investigation is that the result provides useful information relevant to the design of pH sensing materials based on ruthenium.

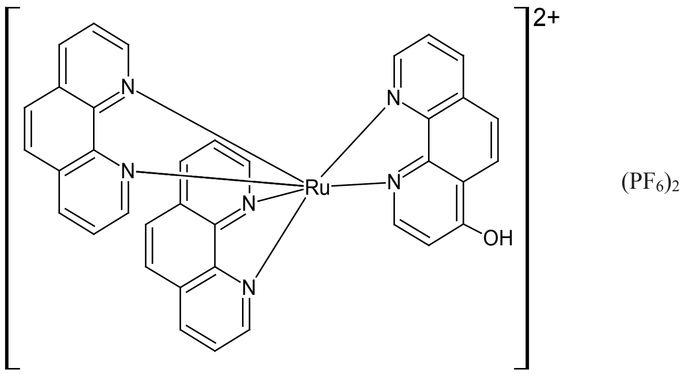


Figure 1
Structure of Ru(phen)$_2$(phen-OH)$^{2+}$(PF$_6$)$_2$

1. EXPERIMENTAL

All chemicals were of analytical grade and used as purchased from Aldrich Chemicals without further purification.

The ligand, 4-hydroxy-1,10-phenanthroline, was prepared following a two steps synthesis from 3-carbethoxy-4-hydroxy-1,10-phenanthroline. The latter was obtained according to a published procedure used by Ellerbrock and co-workers (Ellerbrock et al., 2002).

15.36 g (0.058 mol) of 3-carbethoxy-4-hydroxy-1,10-phenanthroline was refluxed in 10% ethanolic solution of potassium hydroxide to produce 3-carboxyl-4-hydroxy-1,10-phenanthroline followed by sublimation at 180 °C to yield 90 g (85%) of 4-hydroxy-1,10-phenanthroline ligand. Ru(phen)$_2$Cl$_2$ was prepared from RuCl$_3$.xH$_2$O and 1,10-phenathroline using a literature procedure (Giordano et al., 1978).

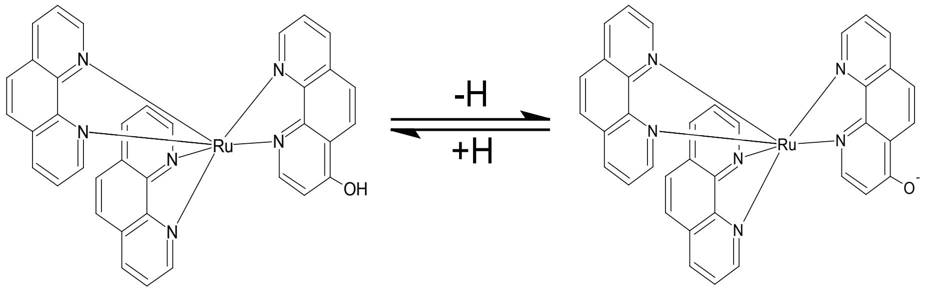
300 mg (0.47 mmol) of Ru(phen)$_2$Cl$_2$ was refluxed in 30 ml dimethyl formamide with 608 mg (0.611mmol) of ligand under argon for 18 h to produce the complex, [Ru(phen)$_2$(phenOH)]$^{2+}$. After cooling the reaction mixture to room temperature, 50 ml of water was added and the complex precipitated upon treatment with saturated NH$_4$PF$_6$. The precipitate was collected, washed with water, and dried. Further purification was done by dissolving in 5ml acetonitrile which was added dropwise into diethyl ether. This precipitate was filtered and dried in a vacuum oven to yield 351mg (78%) of Ru(phen)$_2$(phenOH)$^{2+}$(PF$_6$)$_2$ (λ_{abs} = 460 nm, ε = 18,517, λ_{em} = 595 nm, and Φ_{em} = 0.085). All measurements were

carried out in air-equilibrated acetonitrile medium. Elemental analysis (Oneida Research Services) found C: 44.12 %, H: 2.85 %, and N: 9.54%. Calculated for $C_{36}H_{24}N_6ORuP_2F_{12}$ is C: 44.92%, H:2.55%, and N:8.74%.

Investigations on the pH effect on absorption and emission intensity were carried out with a solution of 10.0mg of the complex in 20 ml of methanol which was further diluted to 200 ml with deionised water. In order to obtain solutions with various pH values, drops of 20% NaOH or 20% HCl was added. Hitachi U-2000 spectrophotometer was employed in absorption spectra measurement while emission spectra were recorded on a Perkin-Elmer LS50B spectrofluorometer following excitation at 460 nm. Lifetime decays were obtained at Tulane University using time correlated single photon counting on a homebuilt system employing an IBH flash lamp running with hydrogen gas. Solutions containing 0.2 M HCl in methanol and 0.2 M ammonium hydroxide in methanol were used for acidic and basic lifetime measurements respectively. Decay spectra in both solutions were found to fit a single exponential at 95% confidence limit of ±2 ns, with lifetimes of 165.4 and 3.08 ns for acidic and basic solutions, respectively.

2. RESULTS AND DISCUSSION

From acid-base equilibrium, Scheme I, the absorption and emission spectral changes of the complex depend on the effect of pH variation on either its ground or excited state. A change in emission spectra depends on whether the excited state of the complex is affected by pH or not, while absorption spectral changes are caused by pH effects on the ground state. Since optical pH sensors are based on pH dependent changes of the absorbance or luminescence of indicator molecules, complexes with only absorption or emission spectral changes with pH are better candidates for pH and CO_2 sensor design Compared to absorption-based methods (Ellerbrock et al., 2002), luminescence is particularly more important due to its higher sensitivity and good specificity. Luminescence method has sensitivity that is 1,000 times greater than spectrophotometric methods. Also, lower limits of detection can be achieved for the desired analytes (Guilbault, 1990; Schulman, 1988; Wolfbeis, 2005).



Scheme I

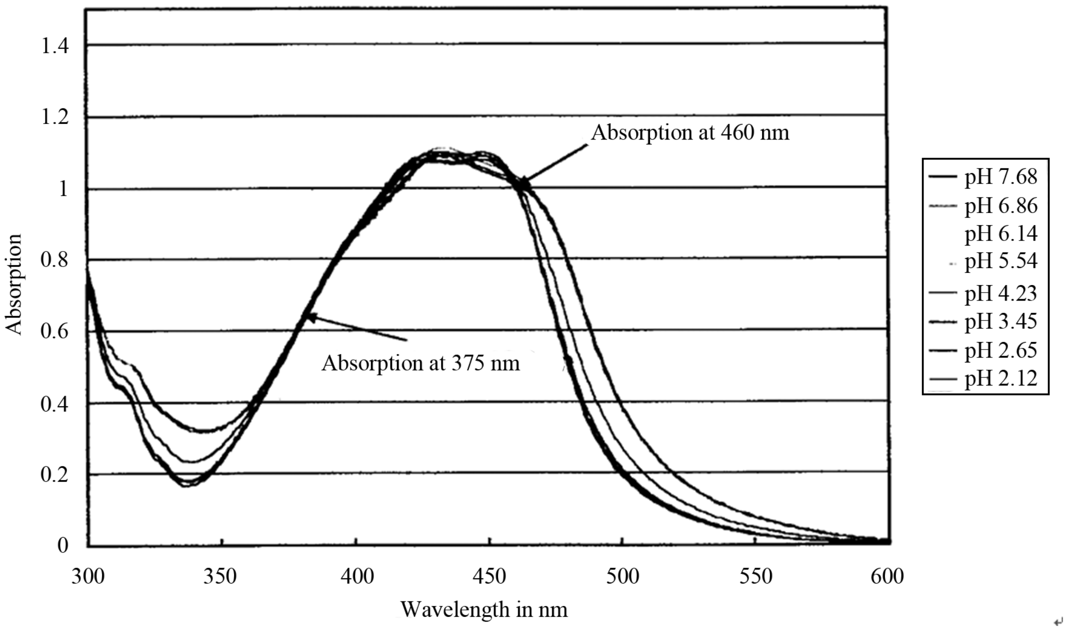


Figure 2
Effect of pH on the Absorption Spectra of Ru(phen)$_2$(phenOH)$^{2+}$(PF$_6$)$_2$

In aqueous solution, the absorption spectra (Figure 2) of the complex, $Ru(phen)_2(phen\text{-}OH)^{2+}(PF_6)_2$, exhibit a maximum at 460 nm, and a small red shift at higher pH. The spectra show a well defined isobestic point. This is important because it serves as the starting point for emission testing as luminescence intensity bears a large dependence on the amount of absorbed radiation. In other words, the emission spectra were recorded at 460nm excitation since it is the wavelength at which both the protonated and deprotonated species absorb the same amount of light, to avoid the effect of absorbance difference on the emission intensity of the two emitting species. The complex shows a very active and narrow range of emission intensity dependence on pH. Increase in intensity with decrease in pH from 7.68 to 2.12 is seen in Figure 3.

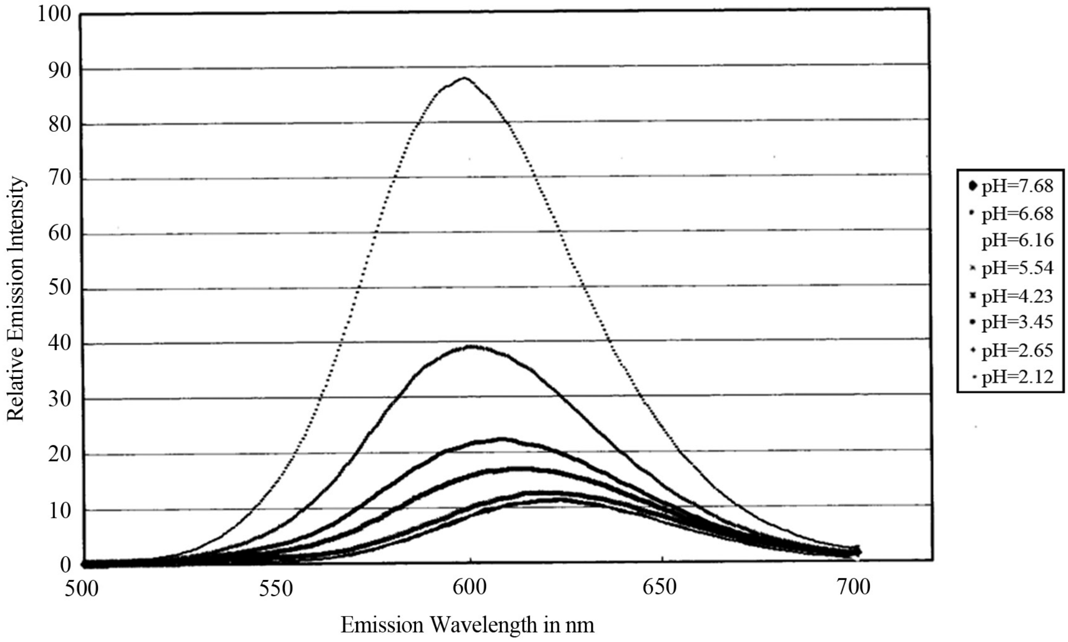


Figure 3
Effect of pH on the Emission Spectra of $Ru(phen)_2(phenOH)^{2+}(PF_6)_2$

The pH dependence of these spectra can be rationalized on the protonation-deprotonation equilibrium of the hydroxyl group of the ligand (Maman et al., 1999) Being more evident in the emission than the absorption spectra, this dependence is suggestive of higher pH dependence on the excited than the ground state. This behaviour is similar to that of the carboethoxy complex (Ellerbrock et al., 2002), but against many ruthenium complexes that involve protonation-deprotonation equilibria in which a decrease in pH result in increase in emission intensity (Kalyanasundaram et al., 1992; Zheng et al., 1996) especially $[Ru(bpy)_2(dhphen)]^{2+}$ immobilized in Nafion (Chan et al., 1998).

The relative emission intensity presents a well shaped sigmoidal curve with pH changes (Figure 4), with one inflexion point corresponding to a monoprotic acid (Chan et al., 1998). The pK_a of the excited state, pK_a^*, can be obtained from the Henderson-Hasselbalch-type relationship:

$$pK_a=pH+\log\tau_{acid}/\tau_{base} .$$

(pH = inflexion point of the curve of emission intensity *versus* pH, τ_{acid} and τ_{base} are respective lifetimes of the protonated and deprotonated species).

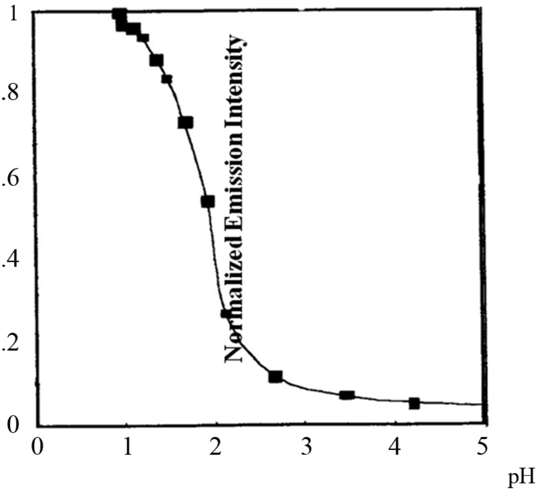


Figure 4
Effect of pH on the Relative Emission Intensity of $Ru(phen)_2(phenOH)^{2+}(PF_6)_2$

The validity of this equation holds if the protonated and deprotonated species have luminescence lifetimes that are longer than the rates of protonation/deprotonation equilibrium (Ellerbrock et al., 2002). The complex is quite responsive at lower pH ranges but not at all with high pH. This is evident in Figure 4 from pH higher than 3. Using the inflexion point (pH value) of 2.0 and lifetimes of 165.4 ns and 3.08 ns for the protonated and deprotonated states respectively, the pK$^*_a$ value is calculated for this complex as 3.68. Studies on similar ruthenium complexes suggest that the excited state pK$_a$ of this complex will be more acidic than its ground state pK$_a$ (Ellerbrock et al., 2002; Xie et al., 1999; Hicks et al., 2001).

The plot of emission intensity versus pH as shown in Figure 3 proves a decrease in intensity from 87 to 12 between the pH values of 7.68 to 2.12, while the corresponding lifetimes are 165.4 ns and 3.08 ns for the protonated and deprotonated species respectively. A similar behaviour has been reported for Ruthenium complexes of the carboethoxy- and 4,4'-dicarboxy-2,2'-bipyridine ligands (Ellerbrock et al., 2002; Xie et al., 1999) and has been rationalised on the basis of change in the radiative rate constant, which bears a close relationship with the molecular and electronic structure of the emitter (Hicks et al., 2001; Dollberg & Turro, 2001).

The non-linear change between the emission intensity and emission lifetime at low and high pH could be due to intermolecular hydrogen bonding at low pH and/or the possibility of delocalization of the negative charge on the phenolate anion, formed at high pH, onto one of the nitrogen atoms resulting in a partial quinoid character.

CONCLUSION

This study was undertaken to investigate the pH dependence of the spectroscopic behaviour of the Ru(phen)$_2$(phen-OH)$^{2+}$(PF$_6$)$_2$ complex. It has been established that the complex possesses several interesting spectroscopic characteristics: a large emission intensity change following a small spectroscopic change, dependence of emission intensity over extended ranges of pH, a protonable ligand, and an excited state pK$_a$ of 3.68. These properties support the choice of this complex as a favourable candidate for luminescence-based pH sensor design.

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