

A Wide-range Luminescent pH Sensor Based on Ruthenium(II) Complex

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The measurement of pH is of great importance in biological, chemical and industrial areas, such as biological and chemical analyses, environmental monitoring, and process control. In recent years, the optical pH sensing technique based on the luminescence of certain indicators has received increasing attention because it offers many advantages over the potentiometric method employing a glass electrode,¹ such as small probe size, high sensitivity, electrical safety, the absence of any requirement for a reference electrode, and a wide selection of available indicator dyes.²

Various luminescent dyes have been explored for the development of optical pH sensors, including fluorescein derivatives,³ corrole derivatives,⁴ coumarin derivatives⁵ and ruthenium(II) polypyridyl complexes.⁶ Of these, derivatives of the latter have been used extensively for optical pH sensors because they display high photochemical stability, high molar absorptivity, long luminescence lifetime derived from the metal to ligand charge transfer (MLCT) excited states, and large Stokes shift.⁷

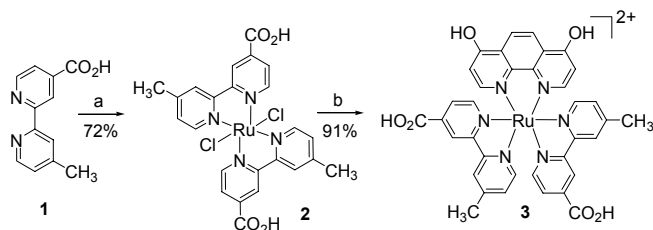
For direct pH sensing by a luminescent indicator, the indicator must include a pH-sensitive functionality which is capable of reversible protonation-deprotonation and altering the emissive properties of the indicator with pH changes. This concept has been successfully applied to several ruthenium(II) polypyridyl complexes $[\text{Ru}(\text{bipy})_2\text{L}]^{2+}$ (bipy = 2,2'-bipyridine derivatives) where L is a ligand possessing protonatable/deprotonatable functional groups.⁸ Similarly to most pH indicators, however, these $[\text{Ru}(\text{bipy})_2\text{L}]^{2+}$ complexes have a narrow pH sensing range. Therefore, the development of luminescent chemosensors with a wide-range pH sensing function continues to be an interesting research area.

With the aim of preparing a Ru(II) complex covering a broad pH sensing range, we designed a ruthenium complex consisting of two different polypyridyl ligands, each possess-

ing different protonatable/deprotonatable functionalities: -OH and -CO₂H. Herein we report on the synthesis and luminescent properties of $[\text{RuLL}'_2]^{2+}$ where L is 4,7-dihydroxy-1,10-phenanthroline and L' is 4'-methyl-2,2'-bipyridine-4-carboxylic acid. Ru(II) complexes containing 4,7-dihydroxy-1,10-phenanthroline show luminescent pH sensitivity.^{8f}

4'-Methyl-2,2'-bipyridine-4-carboxylic acid (**1**)⁹ was reacted with RuCl₃ in dimethylformamide following Wrighton's method^{8f} with minor modification to provide the ruthenium complex **2** as a dark violet solid in 72% yield.¹⁰ Reaction of complex **2** with 4,7-dihydroxy-1,10-phenanthroline in a mixed solvent of EtOH and 1 M NaOH solution afforded the ruthenium complex **3** at a 91% yield as a red crystalline solid, which was an inseparable mixture of stereoisomers.¹¹ The formation of complex **3** was confirmed by the presence of resonance peaks (¹³C NMR) for CO₂H at 165.6 ppm, CH₃ at 20.2 ppm and all aromatic carbons, as well as an indicative molecular ion peak (MALDI-TOF MS) at *m/z* 786.12 (M-2Cl).

The 2D emission spectra of complex **3** in buffer solutions of pH 10.0 and 2.0 are shown in Figure 1. In the former (Figure 1a), complex **3** was almost deprotonated and displayed a strong emission at 620 nm when excited by radiation of 485 nm and overlapped emissions maximized near 470 nm with the excitation wavelength of 335 nm. The emission at 620 nm was attributed to MLCT of Ru(II) complexes and the emission near 470 nm to the ligand-centered transition.¹² In figure 1b, where complex **3** is fully protonated, a weak emission was observed at around 635 nm with a red shift and a significantly reduced intensity compared to the 620 nm band in Figure (1a). The reduced intensity of the MLCT band on the increased acidity of the media was observed similarly in the MLCT of $[\text{Ru}(\text{bipy})_2\text{L}]^{2+}$, where L is 4,7-dihydroxy-1,10-phenanthroline^{8f}



Scheme 1. Reagents and conditions: (a) RuCl₃·3H₂O, dimethylformamide, reflux, 2 h; (b) 3,4-dihydroxy-1,10-phenanthroline, EtOH/1 M NaOH, reflux, 3 h.

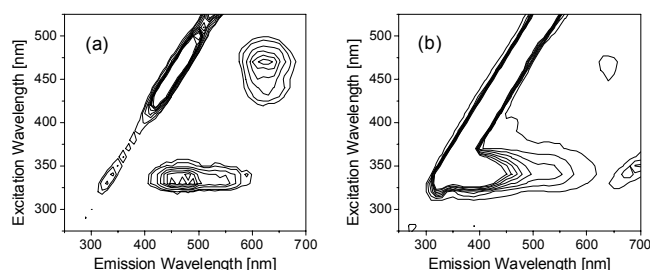


Figure 1. 2D Emission spectra of complex **3** (2.5×10^{-4} M) in phosphate buffer solutions at the following pH: (a) 10.0 and (b) 2.0.

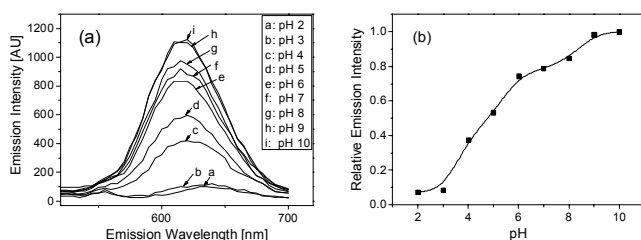


Figure 2. (a) Emission spectra of complex **3** in buffer solutions between pH 10.0 and 2.0 at 25 °C. (b) Relative emission intensity vs. pH of complex **3** in buffer solutions. All points are relative to the highest intensity point at pH 10.0. The line is provided to aid visualization and has no physical significance.

and 3-carboxy-2,2'-bipyridine.^{6b,8b}

To determine the response of complex **3** to H^+ ions, we exposed it (2.5×10^{-4} M) to various phosphate buffer solutions (0.1 M) between pH 2.0 and 10.0, and observed the emission intensity at 620 nm with excitation at 485 nm. As shown in Figure 2, the emission intensity was strongly dependent upon pH over the broad range of pH from 3 to 9. This wide range of pH response was attributed to the multiple protonation-deprotonation equilibria arising from the acidic functionalities ($-CO_2H$ and $-OH$) with different pK_a values in the complex. Such multiple protonation-deprotonation equilibria of complex **3** are clearly evident in Figure 2b, where the plots of the relative emission intensity vs. pH have two inflection points near pH 4.5 and 8.0, owing to the stepwise deprotonation of CO_2H and OH groups in the ligands.

Complex **3** exhibited an increase in the emission intensity in the direction of deprotonation. The blue shift of the MLCT band of complex **3** in basic medium was inexplicable because the MLCT emission could be affected by any combination of numerous factors including the solvent polarity, stereochemistry of the ligand-metal complex, spin-orbital coupling, electron density or oxidation state of core metal. In the literature, however, the MLCT band of $[Ru(bipy)_2L]^{2+}$ is red-shifted for the ligand 4,7-dihydroxy-1,10-phenanthroline^{8f,13} and blue-shifted for 3-carboxy-2,2'-bipyridine^{8b} upon an increase of pH. Thus, the blue shift of MLCT emission of Ru complex **3** in basic medium was attributed to the strong influence of the two CO_2H groups in 4'-methyl-2,2'-bipyridine-4-carboxylic acid on the blue-shifted emission of complex **3** over the 4,7-dihydroxy-1,10-phenanthroline inducing red-shifted emission.

In summary, we synthesized the Ru(II) complex consisting of polypyridyl ligands possessing different acidic functionalities, CO_2H and phenolic OH . This complex, which was capable of multiple equilibria of protonation and deprotonation, displayed excellent luminescent pH sensitivity to extend the operating pH range, thereby suggesting the promising potential of this luminescent dye as an indicator for optical pH

sensing applications over a wide pH range of 3-9. The development of optical pH sensing membranes containing this indicator is in progress and will be reported soon.

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- Mp >300 °C (decomp.); 1H NMR (DMSO- d_6) δ 8.84 (d, 1H), 8.79 (d, 1H), 8.55 (d, 1H), 8.22 (dd, 1H), 7.84 (dd, 1H), 7.30 (dd, 1H), 2.40 (s, 3H, CH_3); ESI-MS m/z 623.06 $[M + Na]^+$ (calcd 622.98).
- Mp >280 °C (decomp.); 1H NMR (DMSO- d_6) δ 9.04-8.89 (m, 4H), 8.81 (s, 2H), 7.95-7.70 (m, 6H), 7.52-7.18 (m, 6H), 2.52 (s, 6H); ^{13}C NMR (DMSO- d_6) δ 165.6, 156.7, 151.4, 150.6, 148.2, 142.8, 127.7, 126.2, 125.0, 123.3, 118.5, 110.4, 20.2; MALDI-TOF MS: m/z 786.12 $[M - 2Cl]^{2+}$ (calcd 786.17).
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