Luminescent pH Sensors Based on $Ru(bpy)_2L^{2+}$ Where L Are Imidazo[f]1,10-phenanthrolines

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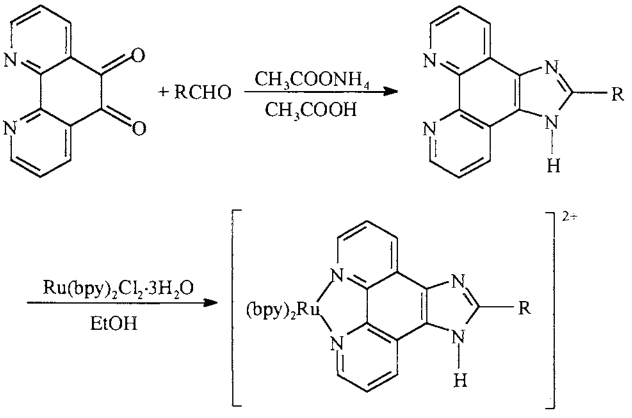
The luminescence quantum yield of $Ru(bpy)_2L^{2+}$ complexes where L are imidazo[f]1,10-phenanthrolines is strongly controlled by pH due to intramolecular photoinduced electron transfer.

Transition metal complexes (TMCs) can be employed as luminescence-based sensors, and Ru-polypyridine complexes have proven particularly versatile in the applications owing to their excellent photophysical and photochemical properties.[1-5] Further, their emitting-state energies and excited-state redox properties can be exquisitely sensitive to variations in the coordinating ligands, and local enviroment.[6,7] Ruthenium-polypyridine have been applied to the chemical sensors such as oxygen sensors,[8,9] pH sensors,[10,11] carbon dioxide sensor,[12,13] specific metal ion sensors,[1] etc.. 1,10-Phenanthroline has been used as an useful bridging ligand for preparation of functional ruthenium (II) complexes.[14,15] This communication reports the synthesis of several new ruthenium (II) complexes containing a ligand of imidazo[f]1,10-phenanthrolines and discusses the mechanism of their pH-sensitivity.

Complexes **1-3** were synthesized from $[RuCl_2(bpy)_2]\cdot 3H_2O$ in ethanol and isolated as the perchlorate (Scheme 1), and the phenthronline derivative ligands were prepared from 1,10-phenanthroline-5,6-dione (phendione) and ammonium acetate and corresponding aldehyde in glacial acetic acid.



Complexes **1-3**
1 R = H
2 R = 4-N,N-Dimethylaminophenyl
3 R = 4-Hydroxyl-3-methoxyphenyl

Scheme 1. The synthetic route and structures of Complexes **1-3**.

The absorption spectra of the three complexes showed reversible changes in various pH conditions. In the low pH range (pH<3), the metal to ligand charge transfer (MLCT) bands of all the complexes are flat and wide, compared to their normal shapes in neutral water or in acetonitrile. However, with pH increasing up to 3, the shapes of MLCT bands gradually turned into normal with slight red shift of absorption maximum. Meanwhile, their absorption intensity also slightly increase and the maximum absorption wavelengths of MLCTs are red shifted 21, 25, and 25 nm for complexes **1**, **2**, and **3**, respectively, with pH going from 0.55 to 3. In contrast to MLCT, their absorption in ultraviolet region has very little variation.

In high pH range (pH 3-12), the MLCTs bands of the three complexes show little changes in shape except a bit bathochromic shift of the absorption onset with a gradually increasing molar extinction coefficient for **1** and decreasing molar extinction coefficient for **2** and **3**. Besides, the three complexes show significant variations of absorption spectra in ultraviolet region, especially for **2** and **3** and the distinct isosbestic points of 376 nm for **1**, 364 and 471 nm for **2**, 472 nm for **3** were observed. From their plots of absorbance *vs.* pH, the ground state pK_a values of compounds **1-3** could be estimated (Shown in Table 1).

Table 1. The acid-base balance constants (pK_a) of compounds **1-3** from titration curves[a]

compound	pK_{a1}[b] /abs.	pK_{a2}[b] /abs.	pK_{a3}[b] /abs.	pK_{a1}[c] /lum.	pK_{a2}[c] /lum.	pK_{a3}[c] /lum.
1	1.97[d]	10.48[d], 10.46[e]		2.88	10.66	
2	1.97[d]	3.75[e]	10.56[e]		4.22	10.71
3	1.97[d]	8.5[e]	10.61[e]		6.71	

[a] Solutions were made up in phosphate buffers, pH range 0.55-12.6. pK_a were calculated using the Henderson-Hasselbalch-type mass action equation. [b] Obtained from absorption titration: $\log[(A_{max}-A)/(A-A_{min.})]=pK_a(abs.)-pH$. [c] Obtained from luminescence titration: $\log[(\Phi_{max}-\Phi)/(\Phi-\Phi_{min.})]=pK_a(lum.)-pH$. [d] From MLCT. [e] From ultraviolet region absorption variation.

From pH 0.55 to pH 13, the shapes of emission spectra of **1-3** are preserved with obvious hyperchromic shift of emission maximum with the pH increasing in low pH range and slight red shift in the high pH range. Going from pH 0.55 to pH 7, the emission spectra shifted blue 17, 16, and 12 nm for complexes **1**, **2**, and **3**, respectively. As a model, the emission intensity of complex **1** showed small change with pH variation, exhibiting two inflection points in the titration curve of emission. Compared with complex 1, luminescence intensity of complexes **2** and **3** decreased violently with pH increasing, especially for complex **3**. From their plots of luminescence *vs.* pH, two inflection points for complex 2 and one for complex 3 are observed (Figure 1).

The emission of complex **1** mainly comes from the protonated form (pH<1), and from neutral form (pH 3-8), while the deprotonated form is responsible for luminescence above pH 12. For complex **2**, the emission also comes from the protonated form (pH<1). However with pH increasing, the tert. N on imidiazole ring is deprotonated (pK_a=1.97), and then the N of N,N-dimethylaniline (DMA) is deprotonated with a pK_a of 3.7 with further pH rising. Compared with **1**, the emission of complex **2** is very weak during pH 3-7, caused by the intramolecular electron transfer from DMA to excited-state Ru central. DMA is well known to be a strong electron donor and can cause efficient

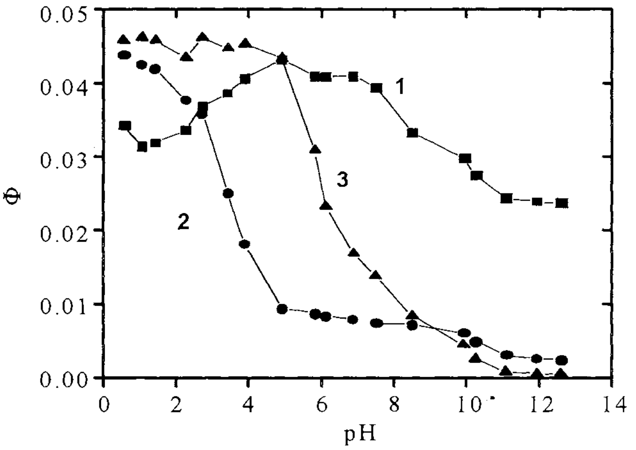


Figure 1. Luminescence quantum yields (Φ) for complexes **1**-**3** *vs.* pH in phosphate buffers. Quantum yields were measured on aerated solutions by comparison with [Ru(bpy)$_3$$^{2+}$] in aerated water when samples were excited at 450 nm.[11]

photoinduced electron transfer with Ru(II) complexes.[11] With pH increasing from 7 to 13, the emission was further quenched with another inflection (pK_a=10.71), consistent with the second dissociation constant of imidazole.

With pH increasing, the luminescence of complex **3** is violently quenched with a pK_a of 6.7, which is smaller than that obtained from absorption titration, demonstrating that phenol in the excited-state **3** is stronger acid than it in ground-state **3**. Phenoxide anion formed in base solution is a strong electron donor and the electron transfer reactions between phenols and Ru (II) polypyridine complexes have been already reported,[10,16] and used in the determination of ionization balance constants of phenols.[17] Formation of the phenoxide anion causes photoinduced intramolecular electron transfer to take place from the phenoxide ion to the polypyridine Ruthenium (II) moiety.

Summarily, the use of MLCT lumophores results in luminescent pH sensor through electron transfer mechanism.

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