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# New Quinone Diimine Complex of Zinc with pH-Dependent Emission in the Visible Region

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## Introduction

Molecules and polymers that possess pH-dependent luminescence have been explored extensively owing to their potential application as tunable-wavelength light-emitting diodes,[1−3] as optical pH sensors and switches,[4−7] and in solar energy conversion.[8,9] Examples of metal complexes exhibiting pH-dependent emission include Ru(II) systems possessing 2,2′-bipyridine (bpy) ligands substituted with carboxylic and phosphoric acids,[8,10,11] substituted Ir(III) bis-terpyridine complexes,[12] and *trans*-$O_2Re(py)_4^+$ (py = pyridine).[13] In addition, the luminescence from Pt(II) complexes of quinoxaline-2,3-dithiolate is quenched by proton donors in various aprotic solvents.[14] Similar behavior was observed for Ru(II), Os(II), and Pt(II) complexes of dppz (dppz = dipyrido[3,2-*a*:2′,3′-*c*]phenazine)[15−17] and for *trans*-$O_2Re(py)_4^+$.[13]

Additional interest in metal complexes possessing a pH-sensitive excited state arises from their potential usefulness as probes of DNA structure and in photoinduced DNA chemistry. These complexes include the 9,10-phenanthrenequinone diimine (phi) ligand coordinated to Ru(II) and Rh(III) metal centers, previously characterized in the protonated and deprotonated forms.[18] The $Rh(L)_{3-n}(phi)_n^{3+}$ (L = bpy, phen =1,10-phenanthroline; *n* = 1, 2) complexes have been shown to photocleave duplex DNA and to photorepair thymine dimers.[19] Other DNA binding quinone diimine complexes include $Ru(L)_2phi^{2+}$ (L = bpy, phen), $Ru(phi)_2bpy^{2+}$, $Rh(NH_3)_4phi^{3+}$, and $Rh(en)_2phi^{3+}$ (en = ethylenediamine).[20] Although no emission was observed for these systems or for the related $Zn(phi)Cl_2$ complex at room temperature, transient absorption spectra of the complexes reveal ligand-centered excited states with lifetimes of ∼200 ns and 2.0 $\mu$s for various Rh(III) phi complexes and $Zn(phi)Cl_2$, respectively.[21b] The spectral characteristics of both the ground and excited states of the Rh(III) complexes, as well as their photoreactivity, are pH dependent.[21]

In the present work we explore the photophysical properties of the emissive $BF_4^-$ salt of the related complex $Zn(bqdi)(H_2O)_2^{2+}$ (bqdi = 1,2-benzoquinone diimine), whose structure is shown in the inset of Figure 1a. Numerous complexes possessing the bqdi ligand have been previously prepared,[22] including those of Fe(II)[23] and Ru(II).[24−26] However, to our knowledge, emission from these complexes was not reported. The pH-dependent emissive properties of $Zn(bqdi)(H_2O)_2^{2+}$ may prove useful as a DNA probe and in sensing applications.

$Zn(bqdi)(H_2O)_2^{2+}$ was prepared from $Zn(bqdi)(Cl)_2$ by adaptations to previously reported methods.[20] $ZnCl_2$, 1,2-phenylenediamine (PDA), $AgBF_4$, and hydrazine monohydrochloride were purchased from Aldrich and used without further purification. $Zn(bqdi)(Cl)_2$ was synthesized by dissolving PDA (0.5 mmol) in anhydrous DMF (15 mL) containing hydrazine monohydrochloride (0.025 mmol) in a three-neck flask. $ZnCl_2$ (0.5 mmol) was dissolved in anhydrous ethanol (20 mL) in a separate round bottom flask. Both solutions were bubbled with argon for 30 min separately. The $ZnCl_2$ solution was slowly added to the faint brown PDA solution under argon. The clear, light amber solution was refluxed overnight and turned dark red after stirring in air for ∼1 h at room temperature. Following solvent removal, the solid collected was washed on a filter frit with water and ether to remove excess $ZnCl_2$ and free ligand, respectively. The pale red-brown $Zn(bqdi)(Cl)_2$ was collected in 71.4% yield. Elemental analysis (Galbraith Laboratories) of the product corresponds to $Zn(bqdi)(Cl)_2\cdot DMF$ with each element found (calculated) as follows: Zn 20.66% (20.72%), H 4.29% (4.15%), C 36.22% (34.26%), N 13.50% (13.32%), Cl 22.40% (22.47%). The $BF_4^-$

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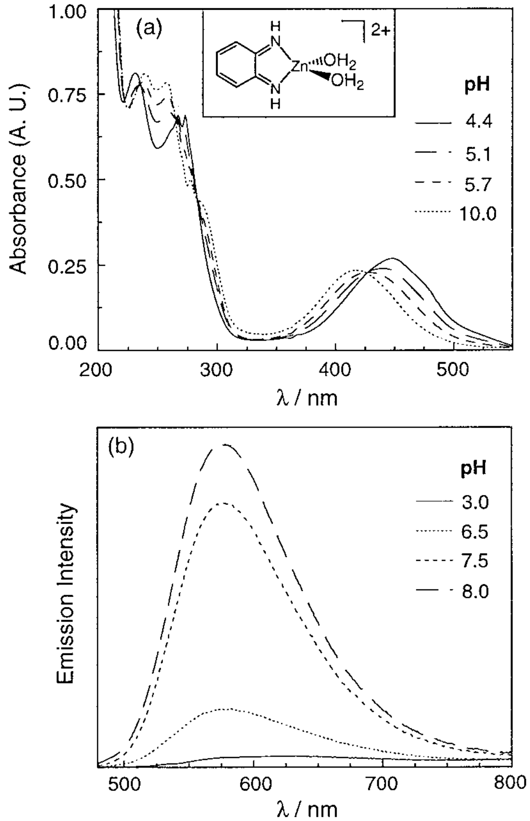

**Figure 1.** Room temperature (a) electronic absorption and (b) and emission ($\lambda_{exc} = 420$ nm) spectra of $Zn(bqdi)(H_2O)_2^{2+}$ at various pH values. The structure $Zn(bqdi)(H_2O)_2^{2+}$ is shown in the inset of part a.

salt of $Zn(bqdi)(H_2O)_2^{2+}$ was prepared from $Zn(bqdi)(Cl)_2$ through the addition of $AgBF_4$, resulting in the precipitation of AgCl. The highly water soluble orange $Zn(bqdi)(H_2O)_2 \cdot 2BF_4$ was separated from insoluble AgCl and remaining $Zn(bqdi)(Cl)_2$ through filtration, and the deep red solid was isolated following the removal of the solvent. The $^1H$ NMR spectrum (400 MHz) of $Zn(bqdi)(H_2O)_2 \cdot 2BF_4$ in $D_2O$ exhibits peaks at 9.03 (s, =NH), 7.77 (m, bqdi), 7.55 (m, bqdi), 7.02 (s, broad, $H_2O$); these assignments are consistent with those of related complexes.[26,27] FAB-MS peaks were observed at $m/z = 211$ ($Zn(bqdi)(H_2O)Na^+$), 207 ($Zn(bqdi)(H_2O)_2^+$), and 193 ($Zn(bqdi)Na^+$).

The absorption and emission maxima of the water soluble $Zn(bqdi)(H_2O)_2^{2+}$ at pH = 3.0 and pH = 8.0 are listed in Table 1, along with the respective molar extinction coefficients. The pronounced changes in the absorption and emission spectra of $Zn(bqdi)(H_2O)_2^{2+}$ as a function of pH are shown in Figure 1. The emission, shown in Figure 1b, is weak at pH = 3.0 with a maximum at 638 nm ($\tau = 131$ ps), but an 8-fold increase in intensity is observed as the pH is raised to 8.0 with a shift in the maximum to 576 nm ($\Phi_{em} = 0.026$, $\tau = 1.6$ ns).[28] This behavior is indicative of the existence of ground state protonated and deprotonated species that possess different luminescence properties. Plots of the absorption at 418 and 453 nm and emission intensity at 576 nm vs pH exhibit inflection points at pH ~ 5.2, consistent with the $pK_a$ value obtained from a potentiometric titration of the complex. The amount of base consumed in the titration is consistent with the exchange of a single proton. In addition, the absorption changes in the pH = 4.4 to pH = 10.0 range shown in Figure 1a give rise to five isosbestic points at 223, 235, 266, 284, and 426 nm, consistent with the process involving only two species. Deprotonation of the water molecules coordinated to Zn(II) can be ruled out, since typical $pK_a$ values for these processes range from 7 to 8.[29,30] Furthermore, such deprotonation is not expected to result in changes in the absorption and emission of the complex. The proton exchange is similar to that reported for the related Rh(III) complexes possessing phi ligands, where loss of a single proton from the quinone diimine ligands takes place with $pK_a$ values that range from 4.7 to 9.2 depending on the nature of the ancillary ligands.[21a] The variations in absorption and emission of $Zn(bqdi)_2(H_2O)_2^{2+}$ are completely reversible in the range $2.1 \leq pH \leq 11.0$.

**Table 1.** Absorption ($\lambda_{abs}$) and Emission ($\lambda_{em}$) Maxima of $Zn(bqdi)(H_2O)_2^{2+}$ in Aqueous Solutions at pH = 3.0 and pH = 8.0

| pH | $\lambda_{abs}$/nm ($\epsilon/\times 10^3$ $M^{-1}$ $cm^{-1}$)[a] | $\lambda_{em}$/nm[b] |
|---|---|---|
| 3.0 | 231 (6.07), 273 (4.32), 453 (1.49) | 638 |
| 8.0 | 238 (5.97), 257 (5.07), 285 (3.28), 418 (1.41) | 576 |

[a] Determined using Beer's law ($\pm 10$ $M^{-1}cm^{-1}$). [b] Emission corrected for instrument and detector response ($\lambda_{exc} = 420$ nm).

It is well-established that excited states resulting from complexes of Zn(II) are typically ligand-centered (LC) in nature, owing to the inability of the $d^{10}$ metal center to participate in low energy charge transfer or metal-centered transitions.[31] Therefore, the emission from $Zn(bqdi)_2(H_2O)_2^{2+}$ is believed to arise from an excited state centered on the bqdi ligand. In the related nonemissive complex $Zn(phi)Cl_2$, the transient absorption spectrum was previously assigned as an LC excited state, similar to those observed for the Rh(III) complexes $Rh(phi)_2L^{3+}$, $Rh(L)_2phi^{3+}$, and $Rh(phi)_3^{3+}$ (L = phen, bpy).[21] The ground state electronic absorption and emission spectra of $Zn(bqdi)(H_2O)_2^{2+}$ under acidic and basic conditions are both red shifted relative to those observed for the purified precursor ligand, 1,2-phenylenediamine ($\lambda_{abs} = 277$ nm, $\lambda_{em} = 360$ nm). Such a shift is not unexpected, since the complex possesses the quinone diimine form of the ligand. In $Zn(phi)Cl_2$, the LC absorption of the 9,10-phenanthrenequinone diimine ligand in the complex is also found at lower energy compared to the uncoordinated 9,10-diaminophenanthrene precursor.[20,21]

The shifts in the ground state electronic absorption spectra with variations in pH measured for $Zn(bqdi)_2(H_2O)_2^{2+}$ are similar to those observed for the related $Rh(phi)_2L^{3+}$ and $Rh(L)_2phi^{3+}$ complexes (L = phen, bpy) arising from the protonation of the phi ligand at low pH values.[20,21] For example, a red shift in the phi-centered transition centered at 348 nm at pH = 9.0 to 378 nm at pH = 4.0 was previously reported for $Rh(phi)_2bpy^{3+}$.[20b] However, the Rh(III) complexes are nonemissive at room temperature.[21] Experiments designed to elucidate the identity of the excited states of the protonated and deprotonated forms of the complex and their respective deactivation pathways are currently underway.

To our knowledge, $Zn(bqdi)(H_2O)_2^{2+}$ is the first example of an emissive quinone diimine ligand coordinated to a transition metal. $Zn(bqdi)(H_2O)_2^{2+}$ represents a new complex whose emission can be "turned on" through variation in pH, which may prove useful in switching or sensing applications.

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