

## Bi-1,10-phenanthrolines and Their Mononuclear Ru(II) Complexes

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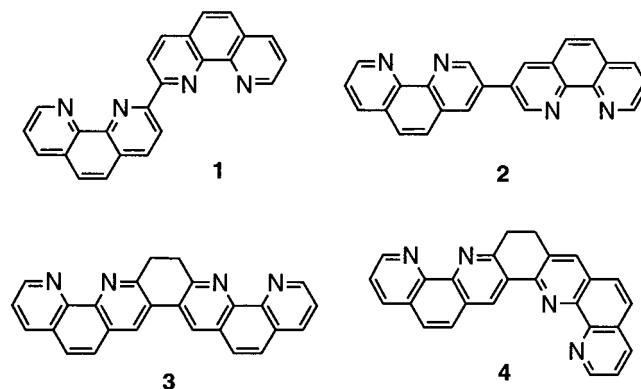
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A series of four biphen (phen = 1,10-phenanthroline) ligands, 2,2'-biphen (**1**), 3,3'-biphen (**2**), 2,2'-dimethylene-3,3'-biphen (**3**), and 2,3'-dimethylene-3,2'-biphen (**4**), is prepared by coupling and Friedländer methodology. The corresponding mononuclear Ru(II) complexes,  $[\text{Ru}(\mathbf{1-4})(\text{Mebpy})_2]^{2+}$  where Mebpy = 4,4'-dimethyl-2,2'-bipyridine, are prepared. These complexes show long wavelength electronic absorptions at 441–452 nm and emissions at 622–641 nm. Metal-based oxidations occur in the range 1.18–1.21 V, and ligand-based reductions, at –1.20 to –1.30 V. The addition of  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ , or  $\text{Hg}^{2+}$  ions results in a strong enhancement and red shift of the luminescence of complex **Ru-3**. Alkali and alkaline earth metal ions barely affect the luminescence of **Ru-3** while transition metal ions such as  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Mn}^{2+}$  lead to efficient quenching of the **Ru-3** luminescence. The luminescence of **Ru-2** and **Ru-4** is quenched in the presence of  $\text{Zn}^{2+}$  because of a conformationally induced reduction in electronic communication between the two phen halves of the ligand. The addition of  $\text{Zn}^{2+}$  has only a slight effect on the luminescence of **Ru-1** because of steric hindrance toward complexation.

## Introduction

Luminescence quenching and enhancement can be used effectively for the design of chemical sensors.<sup>1</sup> This concept involves constructing molecules with two functional components, a specific receptor for the intended substrate and a reporter that will change its luminescent properties in the presence of the receptor–substrate interaction.<sup>2</sup> Transition

metal complexes have been widely employed as luminescent sensors because their emissive state is readily influenced by altering the steric or electronic environment of the metal center. Ru(II) diimines have proved to be particularly versatile in sensor applications, because their emitting state energies and excited state redox properties are quite sensitive to variations in the coordinating ligands and the local environment.<sup>3</sup> Herein, we report the design and syntheses of four bi-1,10-phenanthrolines (**1–4**), their mononuclear Ru(II) complexes (Chart 1), and the spectroscopic properties of these complexes in response to various metal ions.

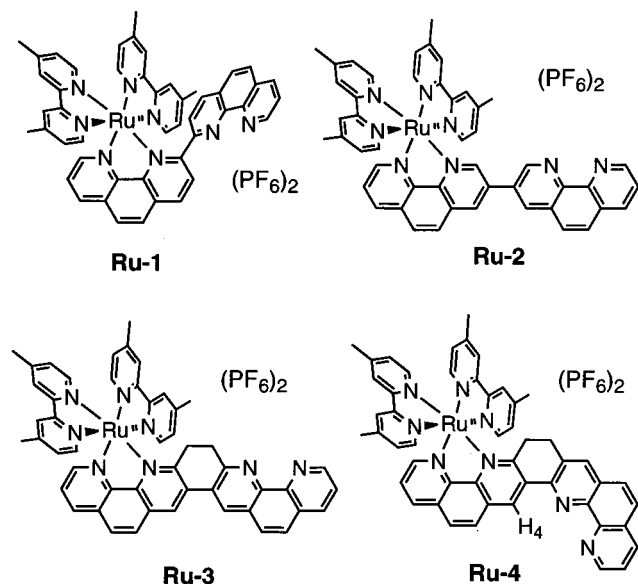


Ligands **1** and **2** involve two 1,10-phenanthroline (phen) subunits joined at their 2,2'- and 3,3'-positions. In solution,

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Chart 1



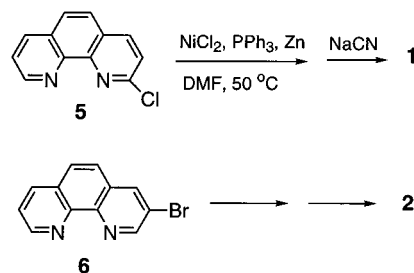
neither ligand is expected to be planar, and rotation about the biaryl bond will have a low energy barrier. The transoid conformation of **1** will be favored to avoid a putative H3...H3'-interaction<sup>4</sup> while the cisoid and transoid forms of **2** should be of approximately equal energy. Ligand **3** is a 2,2'-dimethylene bridged derivative of **2** wherein the cisoid conformation is enforced. Ligand **4** is a 2,3'-biphen with a 3,2'-dimethylene bridge which now enforces a transoid conformation. In **1**–**3**, the bidentate binding sites are equivalent while in **4** one site is more sterically encumbered.

For the mononuclear Ru(II) complexes of these four ligands (Chart 1), the luminescent metal center is located near a vacant bidentate coordination site that remains accessible to added cations. Thus, these complexes fit the general model of a sensor system, and it will be demonstrated that for certain cations luminescence is enhanced, for some, it remains nearly unchanged, and for others, it is diminished or quenched.

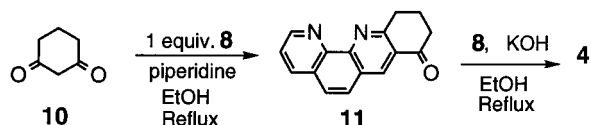
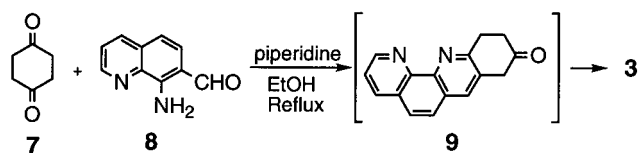
### Synthesis and Characterization

The two unbridged biphen **1** and **2** were synthesized in 70%–80% yields by the Ni(0) coupling of 2-chlorophen (**5**)<sup>4,5</sup> or 3-bromophen (**6**).<sup>6</sup> The reaction initially yielded a Ni(II) complex of the coupling product which may be demetalated by treatment with NaCN, thereby liberating the free ligand. Although 3,3'-biphen **2** is previously unknown, 2,2'-biphen **1** had been earlier prepared by Case in 24% yield, using an Ullmann coupling of 2-chlorophen.<sup>7</sup> When care is

taken to remove the complexed nickel, Ni(0) coupling dramatically improved the yield.<sup>4,8</sup>



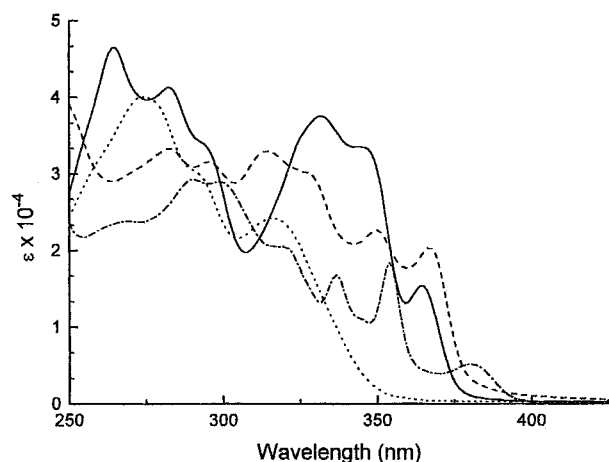
The previously unreported bridged biphen **3** and **4** were synthesized by the Friedländer condensation<sup>9</sup> of 8-amino-7-quinolinecarbaldehyde (**8**) with 1,4-cyclohexanedione (**7**) or 1,3-cyclohexanedione (**10**).<sup>10</sup> The condensation of **7** and **8** in a 1:1 or 1:2 molar ratio with piperidine as the catalyst gave only the doubly condensed product **3**; the monocondensed product could not be obtained. This is understandable if one realizes that the condensations with **8** occur in a stepwise fashion. Only one monocondensation product is available from **7**, thus activating the methylene group closest to the phen ring in **9** and directing the formation of **3**. In 1,3-cyclohexanedione, **10**, the methylene group at the 2-position is activated by two carbonyl groups and hence is more reactive than the other methylene groups.<sup>11</sup> Thus, the condensation of **8** and **10** in a 1:1 molar ratio using a mildly basic catalyst such as piperidine only gave 5,6,7,8-tetrahydro-[2,3-*b*]pyridoaclid-8-one (**11**) in 94% yield. The condensation of **11** with 1 equiv of **8** in the presence of ethanolic KOH provided the doubly condensed species, 2,3'-dimethylene-3,2'-biphen (**4**). However, the condensation of **8** with 2 equiv of **10** using ethanolic KOH or piperidine as the catalyst did not readily afford **4**.



Mononuclear complexes **Ru-3** and **Ru-4** were prepared by treating the appropriate biphen with 1 equiv of [Ru(Me<sub>2</sub>bpy)<sub>2</sub>Cl<sub>2</sub>] (Me<sub>2</sub>bpy = 4,4'-dimethyl-2,2'-bipyridine) in refluxing ethanol. The dimethylene bridge in both ligands offers some steric hindrance to complexation so that **Ru-3**

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**Figure 1.** Electronic absorption spectra of bi-phen ligands **1** (—), **2** (···), **3** (---), and **4** (-·-·-),  $10^{-5}$  M in MeOH.

and **Ru-4** were obtained in yields of 30% and 51%, respectively. When **2** and 1 equiv of  $[\text{Ru}(\text{Me}_2\text{bpy})_2\text{Cl}_2]$  were refluxed in ethanol, however, only the dinuclear complex of **2** was formed, and no mononuclear complex was observed. To facilitate formation of the mononuclear complex, 1 equiv of  $[\text{Ru}(\text{Me}_2\text{bpy})_2\text{Cl}_2]$  in EtOH–H<sub>2</sub>O (3:1) was added dropwise to a refluxing solution of **2** over 2 h. Complex **Ru-2** was obtained in 20% yield and displayed a single set of <sup>1</sup>H NMR resonances indicating free rotation about the 3,3'-bond. Attempts to prepare **Ru-1** in refluxing ethanol or ethanol–H<sub>2</sub>O were unsuccessful, probably because of steric hindrance from the 2'-phen group. Complex **Ru-1** was ultimately prepared in 16% yield by heating **1** and  $[\text{Ru}(\text{Me}_2\text{bpy})_2\text{Cl}_2]$  in ethylene glycol for 30 min in a microwave reactor.<sup>12</sup> The complex evidenced two sets of NMR resonances in a 2:1 ratio indicating the existence of two diastereomers, depending on the orientation of the appended, uncomplexed 2'-phen group. The appearance of two diastereomers for a series of 2-arylphens has been noted in earlier work.<sup>13</sup>

The two bidentate sites in ligands **1–3** are equivalent so that there is no uncertainty about the position of metal binding. For biphen **4**, however, two isomers are possible for the mononuclear Ru(II) complex. Binding at the less hindered (unprimed) ring is verified by NMR. The protons H<sub>4</sub>, H<sub>9</sub>, and H<sub>9'</sub> on **4** are all located near nitrogen and thus shifted downfield, resonating at 9.65, 9.15, and 9.10 ppm for the free ligand. Binding of the  $\text{Ru}(\text{Me}_2\text{bpy})$  moiety is expected to strongly shield these protons and shift them to higher field. In **Ru-4**, the signals for H<sub>4</sub> and H<sub>9'</sub> remain relatively unchanged at 9.74 and 9.14 ppm indicating that binding must be at the site nearer to H<sub>9</sub>.

### Properties of the Complexes

The electronic absorption spectra of free ligands **1–4** all display strong absorption envelopes between 250 and 400 nm, associated with  $\pi-\pi^*$  transitions originating from the phen units (Figure 1). The lowest energy absorbances of **1**,

**Table 1.** Photophysical and Electrochemical Data for Ru(II) Complexes

complex	absorption <sup>a</sup>		emission <sup>a</sup>		$E_{1/2}^b$	
	$\lambda_{\text{max}}$ (nm)	$\epsilon$ , $\text{M}^{-1}\text{cm}^{-1}$	$\lambda_{\text{em}}$ (nm)	$\Phi_{\text{em}}$	ox.	red.
<b>Ru-1</b>	452 (12200)		622	$8.0 \times 10^{-4}$	1.19 (240)	-1.30 (180)
	284 (68000)					-1.62 (200)
<b>Ru-2</b>	441 (13300)		641	$8.2 \times 10^{-3}$	1.21 (170)	-1.21 (110)
	323 (33800)					-1.59 (160)
	283 (89500)					
<b>Ru-3</b>	445 (13000)		636	$3.1 \times 10^{-3}$	1.18 (77)	-1.20 (90)
	341 (47600)					-1.55 (87)
	283 (95200)					
<b>Ru-4</b>	444 (13700)		636	$4.4 \times 10^{-3}$	1.19 (78)	-1.21 (82)
	368 (32200)					-1.57 (93)
	348 (29900)					
	315 (35500)					
	286 (85500)					

<sup>a</sup>  $10^{-5}$  M in CH<sub>3</sub>OH at 25 °C. <sup>b</sup> Solutions were 0.1 M TBAP in CH<sub>3</sub>CN; the sweep rate was 200 mV/s. The number in parentheses is the difference (mV) between the anodic and cathodic waves.

**3**, and **4** appear at 380, 364, and 367 nm, respectively, considerably red-shifted from the 261 nm absorbance of 1,10-phenanthroline. This observation confirms a strong electronic interaction between the two phen halves of these ligands in which a planar conformation is either readily accessible (**1**) or enforced by dimethylene bridging (**3** and **4**). For ligand **2**, the two phen halves are twisted out of a common plane because of H<sub>2</sub>,H<sub>4'</sub> and H<sub>4</sub>,H<sub>2'</sub> interactions around the 3,3'-bond, and the absorption maximum is blue-shifted to 316 nm.

The electronic absorption and luminescence data for the mononuclear Ru(II) complexes are summarized in Table 1. For all four complexes, the absorption bands in the region 441–452 nm correspond to spin-allowed metal-to-ligand charge transfer (<sup>1</sup>MLCT) transitions. The absorption bands found in the region below 400 nm can be ascribed to ligand-centered (<sup>1</sup>LC) transitions. Complexes **Ru-2**, **-3**, and **-4** exhibit strong LC bands in the region 315–368 nm, similar to bands observed for the free biphen ligands (Figure 1) and implying strong electronic interaction between the two phen halves of the complexed ligand. However, the complex **Ru-1** does not show any clear LC absorption at 300–400 nm, although the free ligand absorbs strongly at 380 nm. This observation is consistent with the uncomplexed phen group being held approximately orthogonal to the complexed one leading to the interruption of electronic communication between these two halves of the molecule.<sup>14</sup>

An analogous series of dinuclear Ir(III), Ru(II), and Os(II) complexes of 5,5'-biphen has been prepared by Ni(0)-promoted homocoupling of the mononuclear complexes.<sup>15</sup> These species do not evidence any communication between the two metal centers because of nonplanarity of the ligand system enforced by unfavorable H<sub>6</sub>,H<sub>4'</sub> and H<sub>4</sub>,H<sub>6'</sub> interactions surrounding the 5,5'-bond.

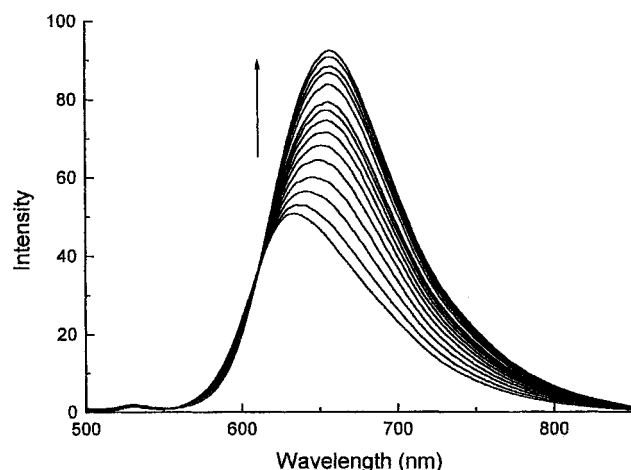
The room-temperature, steady-state luminescence spectra of **Ru-1**, **-2**, **-3**, and **-4** show maxima at 622, 641, 636, and

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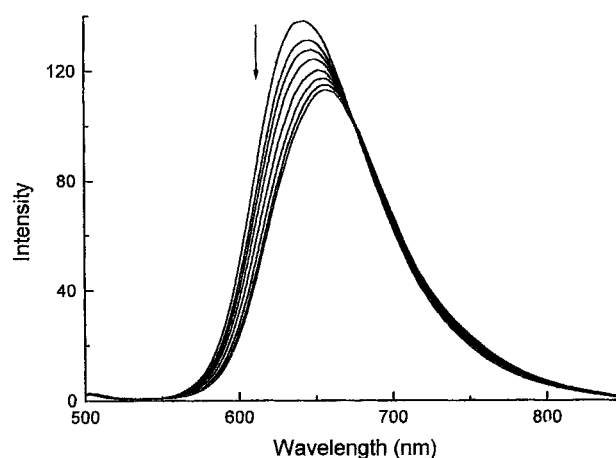
**Figure 2.** Luminescence titration spectra of **Ru-3** ( $1 \times 10^{-5}$  M) with added  $\text{ZnCl}_2$  ( $0\text{--}4.5 \times 10^{-4}$  M) in MeOH at room temperature.

636 nm, respectively, which are typical for Ru(II) polypyridyl emission from a triplet MLCT excited state. The emission maxima of **Ru-2**, **-3**, and **-4** are red-shifted compared with that of **Ru-1**, further confirming the more extensive electronic delocalization in these three complexes. Among the four complexes, **Ru-2** is the most luminescent, and **Ru-1** has the lowest luminescence quantum yield.

The half-wave redox potentials for the four complexes were measured in  $\text{CH}_3\text{CN}$ , and these data are summarized in Table 1. The oxidation potentials are all very similar, falling in the range 1.18–1.21 V. These oxidations are metal-based and indicate, as expected, that the electronic nature of the Ru(II) in all four complexes is nearly the same. The oxidations are just slightly less positive than the value of +1.23 V<sup>16</sup> recorded for  $[\text{Ru}(\text{phen})(\text{bpy})_2]^{2+}$ , because of the somewhat better charge stabilizing ability of the  $\text{Me}_2\text{bpy}$  ligand as compared to bpy. The reduction potentials are typically ligand-based, and the complexes **Ru-2**, **-3**, and **-4** all show similar values for the addition of the first and second electron. These systems all experience some delocalization in the bridging ligand due to the accessibility of a relatively planar conformation of **2**, **3**, and **4** in their complexes. **Ru-1** prefers a considerable twist between the two phen halves of **1** leading to a more negative reduction potential, which approaches the value of  $-1.36$  V<sup>16</sup> recorded for  $[\text{Ru}(\text{phen})(\text{bpy})_2]^{2+}$ .

### Tuning the Electronic Properties of the Mononuclear Complexes by Metal Binding

When  $\text{Zn}^{2+}$  was added to a methanol solution of **Ru-3**, the absorption spectrum showed little change, but the emission spectrum underwent a bathochromic shift and a progressive increase in intensity that was  $[\text{Zn}^{2+}]$  dependent (Figure 2). After complete complexation, the luminescence maximum had shifted from 636 to 658 nm. With added  $\text{Zn}^{2+}$ , the emission intensity rose to a maximum value of  $\varnothing/\varnothing_0 = 1.83$  at  $[\text{Zn}^{2+}] = 2.5 \times 10^{-4}$  M and then remained constant upon further increase in  $[\text{Zn}^{2+}]$ . Plotting the luminescence intensity changes as a function of  $\log[\text{Zn}^{2+}]$  reveals a single



**Figure 3.** Luminescence titration spectra of **Ru-2** ( $1 \times 10^{-5}$  M) with added  $\text{ZnCl}_2$  ( $0\text{--}3.2 \times 10^{-4}$  M) in MeOH at room temperature.

inflection point which is consistent with 1:1 binding and simple equilibrium.<sup>17</sup>

The luminescence titration could be analyzed according to eq 1 where  $\varnothing_0$  and  $\varnothing$  are the luminescence yields in the absence and presence of  $\text{Zn}^{2+}$ ,  $\varnothing_\infty$  is the final luminescence yield, and  $K$  is the binding constant for the formation of a 1:1 complex.<sup>17</sup> For  $\text{Zn}^{2+}$ , this binding constant was estimated to be  $17800 \text{ M}^{-1}$ . When  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$  were added to a solution of **Ru-3**, a similar luminescence enhancement was observed, and binding constants of  $18620 \text{ M}^{-1}$  for  $\text{Cd}^{2+}$  and  $162200 \text{ M}^{-1}$  for  $\text{Hg}^{2+}$  were measured.

$$\frac{\varnothing}{\varnothing_0} = \frac{1 + (\varnothing_\infty/\varnothing_0)K[\text{M}]}{1 + K[\text{M}]} \quad (1)$$

For comparison, the behavior of the analogous **Ru-1**, **Ru-2**, and **Ru-4** complexes was examined. When  $\text{Zn}^{2+}$  was added to a methanol solution **Ru-2** ( $1 \times 10^{-5}$  M), the emission band underwent a bathochromic shift from 641 to 657 nm and a progressive decrease in intensity to a minimum value of  $\varnothing/\varnothing_0 = 0.82$  at  $[\text{Zn}^{2+}] = 3.2 \times 10^{-4}$  M (Figure 3). Similarly, the addition of  $\text{Zn}^{2+}$  to a solution of **Ru-4** caused a bathochromic shift of 10 nm and a decrease in emission intensity to  $\varnothing/\varnothing_0 = 0.95$  at  $[\text{Zn}^{2+}] = 8.4 \times 10^{-4}$  M. The introduction of  $\text{Zn}^{2+}$  to a methanol solution of **Ru-1** had no significant effect on the emission, and only a slight increase in intensity was observed at high  $[\text{Zn}^{2+}]$ . The addition of  $\text{Zn}^{2+}$  had little effect on the absorption spectra of **Ru-1**, **Ru-2**, and **Ru-4**, but when added to ligand **3** (up to 64 equiv), it led to weak emissions at 640 and 760 nm.

From eq 1, the binding constants for **Ru-1**, **Ru-2**, and **Ru-4** with  $\text{Zn}^{2+}$  were estimated to be 620, 30200 and  $2750 \text{ M}^{-1}$ , respectively. The binding constant for **Ru-2** is considerably larger than the value for **Ru-3**, indicating that free rotation about the 3,3'-bond makes the unbound phen more accessible to added metal ion than in the bridged analogue **Ru-3**. The low binding constants of **Ru-1** and **Ru-4** imply that the

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vacant phen binding sites in these two complexes are less accessible to metal ions because of steric hindrance.

The emission of a methanol solution of **Ru-3** was monitored as other metal ions were added. Alkali and alkaline earth metal ions such as  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ba}^{2+}$  bind weakly to the vacant phen and barely perturb the photo-physical properties of **Ru-3**. The addition of transition metal ions such as  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Mn}^{2+}$  to **Ru-3** led to efficient luminescence quenching. Because these metal ions are easily reduced, it is reasonable to attribute the luminescence quenching to electron transfer from the triplet excited state of the Ru center to the added cation center.

The  $\text{Zn}^{2+}$  cation-induced amplification of luminescence in **Ru-3** is interesting because it is most probably a reflection of increased electron delocalization over bridging ligand **3**. The binding of  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ , or  $\text{Hg}^{2+}$  to simple phen is known to raise the one-electron reduction potential of the ligand to ca.  $-1.01$  to  $-1.15$  V.<sup>18</sup> Presumably, the same effect takes place with **Ru-3** such that coordination of these ions at the vacant phen site raises  $E_{\text{red}}$  of this site closer to that of the Ru(II) coordinated phen ( $-1.20$  V), thus ensuring better blending of LUMOs located on the two phen components so that a more extended  $\pi^*$ -orbital becomes available for the promoted electron. This results in both a red shift and amplification of the **Ru-3** luminescence. This complex therefore possesses the potential for the spectrophotometric detection of  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Hg}^{2+}$  through cation-induced luminescence enhancement.<sup>19</sup> The introduction of further structural refinements might be expected to maximize the selectivity and sensitivity toward specific metal ions and thereby afford a new class of sensors for potential metallic environmental toxins.

## Experimental Section

Melting points were obtained on a Hoover capillary melting point apparatus and are uncorrected. Cyclic voltammograms were recorded using a BAS CV-27 voltammograph and a Houston Instruments model 100 X-Y recorder according to a procedure which has been previously described.<sup>20</sup> Absorption spectra were recorded with a Perkin-Elmer Lambda 3B spectrophotometer. Molar extinction coefficients are the average of at least two independent measurements and have expected error limits of  $\pm 5\%$ . Luminescence studies were carried out with  $1 \times 10^{-5}$  M solutions at room temperature using a Perkin-Elmer LS-50B spectrofluorometer. Absorption and emission maxima were reproducible to within 2 nm. NMR spectra were recorded on a General Electric QE-300 spectrometer at 300 MHz for  $^1\text{H}$  NMR and 75 MHz for  $^{13}\text{C}$  NMR. Elemental analyses were performed by National Chemical Consulting Inc., P.O. Box 99, Tenafly, NJ 07670. 8-Amino-7-quinolinecarbaldehyde (**8**),<sup>21</sup> 3-bromo-1,10-phenanthroline (**6**),<sup>6</sup> 2-chloro-1,10-phenanthroline (**5**),<sup>5</sup> and  $[\text{Ru}(\text{Me}_2\text{bpy})_2\text{Cl}_2]$ <sup>22</sup> were prepared according to reported procedures.

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**2,2'-Bi-1,10-phenanthroline (1)**. A solution of  $\text{NiCl}_2$  (152 mg, 1.19 mmol) and  $\text{PPh}_3$  (1.22 g) in DMF (10 mL) was heated at 50 °C with stirring under Ar for 0.5 h. The resulting blue suspension was treated with Zn dust (75 mg) to produce a red-brown suspension. After 0.5 h, a solution of 2-chloro-1,10-phenanthroline (248 mg, 1.16 mmol) in DMF (5 mL) was added and the mixture stirred overnight. After this period, the reaction mixture, containing a dark green precipitate, was evaporated to dryness. The residue was boiled with water (40 mL) for 2 h, after which the mixture was cooled and filtered. The pink filtrate was treated with  $\text{NH}_4\text{PF}_6$  (excess) to give a pink precipitate. After filtration, the solid was heated at reflux for 4 h with a solution of KCN (750 mg) in MeOH–H<sub>2</sub>O (19:1, 20 mL). After cooling, water (40 mL) was introduced. The precipitate was filtered, washed with H<sub>2</sub>O ( $3 \times 5$  mL), EtOH ( $2 \times 5$  mL), and ether ( $2 \times 5$  mL), and dried to afford a white solid (160 mg, 80%), mp  $> 300$  °C (lit.<sup>5</sup> mp 365–6 °C);  $^1\text{H}$  NMR (DMSO-*d*<sub>6</sub>)  $\delta$  9.25–9.22 (2 overlapping d, 4H), 8.79 (d, 2H), 8.56 (dd, 2H), 8.10 (AB quartet, 4H), 7.84 (dd, 2H);  $^{13}\text{C}$  NMR could not be obtained because of poor solubility; MS (*m/z*) 358.1 ( $\text{M}^+$ ).

**3,3'-Bi-1,10-phenanthroline (2)**. Following the procedure described for **1**, a solution of  $\text{NiCl}_2$  (152 mg, 1.19 mmol) and  $\text{PPh}_3$  (1.22 g, 4.65 mmol) in DMF (10 mL) was treated with Zn dust (75 mg, 1.15 mmol) followed by a solution of 3-bromo-1,10-phenanthroline (300 mg, 1.16 mmol) in DMF (5 mL) to provide **2** as a white solid (145 mg, 70%), mp  $> 300$  °C;  $^1\text{H}$  NMR (DMSO-*d*<sub>6</sub>)  $\delta$  9.66 (s, 2H), 9.09 (d, 4H,  $J = 9.9$  Hz), 8.49 (d, 2H,  $J = 7.2$  Hz), 8.08 (m, 4H), 7.78 (m, 2H);  $^{13}\text{C}$  NMR could not be obtained because of poor solubility; MS (*m/z*) 358.1 ( $\text{M}^+$ ).

**2,2'-Dimethylene-3,3'-bi-1,10-phenanthroline (3)**. A mixture of 8-amino-7-quinolinecarbaldehyde (**8**, 202 mg, 1.17 mmol), 1,4-cyclohexanedione (65 mg, 0.58 mmol), and freshly distilled piperidine (0.25 mL) in absolute ethanol (5 mL) was refluxed overnight, cooled, and filtered to provide **3** as a yellow solid (0.15 g, 67%), mp 300 °C;  $^1\text{H}$  NMR (PhNO<sub>2</sub>-*d*<sub>5</sub>)  $\delta$  9.26 (dd, 2H,  $J = 4.2$ , 1.5 Hz), 8.76 (s, 2H), 8.27 (dd, 2H,  $J = 8.1$ , 1.5 Hz), 7.88 (AB q, 4H), 7.66 (q, 2H), 3.8 (s, 4H);  $^{13}\text{C}$  NMR could not be obtained because of poor solubility. Anal. Calcd for C<sub>26</sub>H<sub>16</sub>N<sub>4</sub>: C, 81.25%; H, 4.17%; N, 14.58%. Found: C, 81.30%; H, 4.16%; N, 14.72%.

**5,6,7,8-Tetrahydro-[2,3-b]pyridoacrid-8-one (11)**. A mixture of **8** (43 mg, 0.25 mmol), 1,3-cyclohexanedione (28 mg, 0.25 mmol), and freshly distilled piperidine (0.25 mL) in absolute ethanol (5 mL) was refluxed overnight. The solvent was evaporated, and the residue was washed with ether ( $3 \times 10$  mL) to provide **11** as a yellow solid (58 mg, 94%), mp 239–241 °C;  $^1\text{H}$  NMR (CDCl<sub>3</sub>)  $\delta$  9.25 (dd, 1H,  $J = 4.2$ , 1.5 Hz), 8.91 (s, 1H), 8.28 (dd, 1H,  $J = 8.1$ , 1.5 Hz), 7.84 (AB q, 2H), 7.69 (q, 1H), 3.60 (t, 2H,  $J = 6.0$  Hz), 2.86 (t, 2H,  $J = 6.0$  Hz), 2.33 (m, 2H);  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>)  $\delta$  198.1, 163.1, 150.8, 150.6, 148.0, 145.5, 136.3, 136.2, 130.2, 127.6, 127.3, 126.7, 123.9, 39.1, 33.8, 22.0; MS (*m/z*) 248 ( $\text{M}^+$ ).

**2,3'-Dimethylene-3,2'-bi-1,10-phenanthroline (4)**. A mixture of **8** (42 mg, 0.24 mmol), **11** (58 mg, 0.23 mmol), and ethanolic KOH (0.5 mL) in absolute ethanol (5 mL) under Ar was refluxed for 5 h. After cooling, the solvent was evaporated. Water was added, and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> ( $3 \times 20$  mL). The combined organic layers were washed with water ( $3 \times 15$  mL) and dried over MgSO<sub>4</sub>. The solvent was evaporated, and the residue was washed with hexane ( $3 \times 15$  mL) to provide **4** as a yellow solid (0.07 g, 78%), mp 198–200 °C;  $^1\text{H}$  NMR (DMSO-*d*<sub>6</sub>)  $\delta$  9.65 (s, 1H), 9.15 (dd, 1H,  $J = 6.0$ , 3.0 Hz), 9.10 (dd, 1H,  $J = 6.0$ , 3.0 Hz), 8.49 (m, 2H), 8.44 (s, 1H), 8.19 (d, 1H,  $J = 9$  Hz), 7.99 (m, 3H), 7.80 (q, 1H), 7.77 (q, 1H), 3.48 (m, 2H), 3.41 (m, 2H);  $^{13}\text{C}$

NMR (DMSO- $d_6$ )  $\delta$  159.2, 150.6, 150.0, 149.8, 145.6, 145.3, 145.2, 144.6, 136.3, 136.2, 135.2, 132.6, 132.3, 129.6, 129.0, 128.53, 128.5, 127.9, 127.2, 127.0, 126.9, 126.3, 126.2, 123.3, 31.2, 27.0. Anal. Calcd For  $C_{26}H_{16}N_4 \cdot 1.5H_2O$ : C, 75.91; H, 4.62; N, 13.69. Found: C, 75.95; H, 4.54; N, 13.62. MS ( $m/z$ ) 383 ( $M^+ - 1$ ).

**Ru-1.** A mixture of  $[Ru(Me_2bpy)_2Cl_2]$  (48 mg, 0.083 mmol) and **1** (30 mg, 0.083 mmol) in ethylene glycol (4 mL) was heated in a microwave oven for 30 min. After cooling, water (30 mL) was introduced, and a saturated  $NH_4PF_6$  aqueous solution was added until no further precipitation occurred. The precipitate was collected by filtration, washed with water (5 mL), EtOH (5 mL), and ether (5 mL), and dried. The solid was first purified by chromatography on  $Al_2O_3$  eluting with toluene- $CH_3CN$  (3:2). After evaporation of the solvent, the residue was further purified by chromatography on silica gel eluting with  $CH_2Cl_2$ -MeOH (20:1). **Ru-1** was obtained as a red solid (15 mg, 16%);  $^1H$  NMR ( $CD_3CN$ , mixture of two isomers in a ratio of ~2:1)  $\delta$  9.08 (dd), 9.03 (d), 8.94 (dd), 8.80 (d), 8.73 (d), 8.62 (d), 8.45 (m), 8.34 (m), 8.29 (s), 8.17 (d), 7.95 (d), 7.91 (s), 7.85 (m), 7.77 (m), 7.67 (m), 7.53 (m), 7.21 (d), 6.96-7.14 (m), 6.66 (s), 6.64 (s), 6.19 (t), 5.20 (dd), 2.57 (s), 2.56 (s), 2.50 (s), 2.49 (s), 2.41 (s), 2.40 (s), 2.08 (s), 1.59 (s); MALDI-TOF MS  $m/z$  972.83  $[M - PF_6]^+$ , 826.76  $[M - 2PF_6]^+$ . Anal. Calcd for  $C_{48}H_{38}N_8RuP_2F_{12}$ : C, 51.57; H, 3.40; N, 10.03. Found: C, 51.25; H, 3.44; N, 9.36.

**Ru-2.**  $[Ru(Me_2bpy)_2Cl_2]$  (64 mg, 0.11 mmol) in EtOH (10 mL) was added dropwise to a refluxing solution of **2** (40 mg, 0.11 mmol) in EtOH- $H_2O$  (3:1, 40 mL) under Ar over 2 h. After addition, the solution was refluxed overnight. The solvent was evaporated, and the residue was dissolved in  $H_2O$ -EtOH (2:1, 20 mL). Saturated  $NH_4PF_6$  solution was added to precipitate the product. After filtration, the yellow solid was purified by chromatography on silica gel eluting with  $CH_2Cl_2$ -MeOH (20:1). **Ru-2** was obtained as a red solid (25 mg, 20%);  $^1H$  NMR ( $CD_3CN$ )  $\delta$  9.24 (d, 1H), 9.10 (dd, 1H), 9.01 (d, 1H), 8.63 (dd, 1H), 8.60 (d, 1H), 8.46 (dd, 1H), 8.42 (d, 1H), 8.40 (s, 1H), 8.38 (s, 1H), 8.36 (s, 1H), 8.33 (s, 2H), 8.32 (s, 1H), 8.12 (dd, 1H), 8.00 (m, 2H), 7.74-7.80 (m, 3H), 7.65 (d, 1H), 7.56 (d, 1H), 7.37 (d, 1H), 7.29 (m, 2H), 7.08 (m, 2H), 2.58 (s, 3H), 2.54 (s, 3H), 2.48 (s, 3H), 2.46 (s, 3H); MALDI-TOF MS  $m/z$  973.55  $[M - PF_6 + H]^+$ , 828.34  $[M - 2PF_6 + H]^+$ . Anal. Calcd for  $C_{48}H_{38}N_8RuP_2F_{12}$ : C, 51.57; H, 3.40; N, 10.03. Found: C, 51.85; H, 3.52; N, 9.39.

**Ru-3.** A mixture of **3** (42 mg, 0.12 mmol) and  $[Ru(Me_2bpy)_2Cl_2]$  (65 mg, 0.12 mmol) in absolute EtOH (7 mL) was refluxed under Ar for 6 h. After cooling,  $NH_4PF_6$  (47 mg) was added to precipitate

the complex. The precipitate was then collected and purified by chromatography on  $Al_2O_3$ , eluting with acetonitrile-toluene (2:3). Recrystallization from acetonitrile-ether provided **Ru-3** as a red solid (30%);  $^1H$  NMR ( $CD_3CN$ )  $\delta$  9.15 (s, 1H), 9.00 (dd, 1H,  $J = 1.5, 4.2$  Hz), 8.88 (s, 1H), 8.59 (dd, 1H,  $J = 8.1, 0.9$  Hz), 8.42 (d, 1H,  $J = 1.2$  Hz), 8.40 (d, 1H,  $J = 1.2$  Hz), 8.35 (s, 2H), 8.25 (m, 3H), 7.97 (m, 3H), 7.90 (dd, 1H,  $J = 4.5, 0.9$  Hz), 7.85 (d, 1H,  $J = 5.7$  Hz), 7.70 (dd, 1H,  $J = 4.2, 8.1$  Hz), 7.65 (dd, 1H,  $J = 8.1, 5.1$  Hz), 7.43 (d, 1H,  $J = 5.7$  Hz), 7.30 (d, 1H,  $J = 5.7$  Hz), 7.21 (d, 1H,  $J = 5.7$  Hz), 7.14 (d, 1H,  $J = 6.3$  Hz), 6.99 (m, 2H), 3.30 (m, 2H), 3.14 (m, 1H), 2.62 (m, 1H), 2.56 (s, 3H), 2.53 (s, 3H), 2.49 (s, 3H), 2.40 (s, 3H). Anal. Calcd for  $C_{50}H_{40}N_8RuP_2F_{12}$ : C, 52.49; H, 3.50; N, 9.80. Found: C, 52.47; H, 3.58; N, 9.60.

**Ru-4.** The same procedure as described for **Ru-3** was followed, using a mixture **4** (51 mg, 0.146 mmol) and  $[Ru(Me_2bpy)_2Cl_2]$  (80 mg, 0.146 mmol) in absolute EtOH (7 mL), to provide **Ru-4** as a red solid (81 mg, 51%);  $^1H$  NMR ( $CD_3CN$ )  $\delta$  9.74 (s, 1H), 9.14 (dd, 1H,  $J = 3.0, 1.2$  Hz), 8.58 (d, 1H,  $J = 8.1$  Hz), 8.43 (m, 2H), 8.39 (m, 2H), 8.29 (s, 1H), 8.25 (m, 2H), 8.20 (m, 2H), 7.90 (m, 3H), 7.74 (m, 2H), 7.64 (dd, 1H,  $J = 8.1, 5.1$  Hz), 7.42 (d, 1H,  $J = 5.7$  Hz), 7.22 (m, 2H), 7.14 (m, 1H), 7.05 (m, 1H), 6.96 (m, 1H), 3.16 (m, 2H), 2.95 (m, 2H), 2.55 (s, 3H), 2.514 (s, 3H), 2.511 (s, 3H), 2.40 (s, 3H). Anal. Calcd for  $C_{50}H_{40}N_8RuP_2F_{12}$ : C, 52.49; H, 3.50; N, 9.80. Found: C, 52.43; H, 3.56; N, 9.72.

**Titrations.** Into a 1  $cm^2$  cuvette was placed 2 mL of a  $10^{-5}$  M MeOH solution of the Ru(II) complex, and the absorbance was measured. To this solution were added increments of ( $5 \times 10^{-6}$ )-( $4 \times 10^{-5}$ ) M MeOH solutions of the following metal salts:  $Zn(OAc)_2 \cdot 2H_2O$ ,  $Cd(OAc)_2 \cdot 2H_2O$ ,  $Hg(NO_3)_2 \cdot H_2O$ ,  $LiClO_4$ ,  $KClO_4$ ,  $NaClO_4$ ,  $Ba(OAc)_2$ ,  $Mg(OAc)_2 \cdot 4H_2O$ ,  $Cu(OAc)_2 \cdot H_2O$ ,  $Cu(CH_3CN)_4PF_6$ ,  $Ni(OAc)_2 \cdot 4H_2O$ ,  $Mn(OAc)_2 \cdot 4H_2O$ , and  $CoCl_2 \cdot 6H_2O$ , and the absorbances were recorded.

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**Supporting Information Available:** Titration profiles (Figures S1-S6) for Ru complexes showing the relative luminescence quantum yield as a function of  $-\log[M^{2+}]$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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