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Modulating the efficiency of Ru(II) luminescence *via* ion binding-induced conformational restriction of bipyridyl ligands

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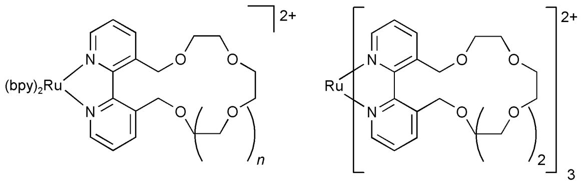
Conformational restriction imposed upon $Ru(bpy)_3^{2+}$ crown ether complexes by metal ion binding leads to enhanced luminescence.

We have recently shown that conformational restriction is a viable mechanism for transducing metal ion binding into enhanced fluorescence emission in organic fluorophores.[1] Although conformational control of internal conversion and intersystem crossing provide the necessary enhancement upon analyte binding, these systems suffer from such limitations as short excitation and emission wavelengths, short lifetimes, and susceptibility to heavy atom quenching. Herein we describe the extension of this conformational restriction-based signaling to Ru(II) complexes and show that these complexes have many advantages over their organic counterparts.

The photochemistry of ruthenium polypyridyl complexes is well-established.[2] In the context of chemosensor development, these complexes exhibit features that are well-suited to the fabrication of practical devices. They possess large extinction coefficients as well as excitation and emission at visible wavelengths. Further, the excited state lifetimes are long enough for biological applications but short enough to circumvent problems associated with intramolecular and environmental quenching. Perhaps most attractive, from a synthetic point of view, is a modular design which allows tuning of ground and excited state properties by variation of ligand(s) and coordination geometry.[3]

It might initially appear that the bipyridyl ligands in $Ru(bpy)_3^{2+}$ derivatives are not candidates for external conformational control owing to the rigid, pseudo-octahedral geometry about Ru(II). However, even small out-of-plane ligand distortions have been shown to have profound effects on both the photophysical and electrochemical properties of these complexes.[4] In particular, steric repulsion between substituents at the 3,3′-positions of a bipyridyl ligand produces a species that is much less emissive than the parent $Ru(bpy)_3^{2+}$. This reduced emission has been ascribed, at least in part, to distortion of the substituted bipyridyl.[5,6]

A series of $Ru(bpy)_3^{2+}$-based complexes with crown ether modified bipyridyl ligands was prepared, **1–4** (Fig. 1). These compounds were chosen for our initial study based on synthetic accessibility and homology to our previous work. The requisite bipyridine derivatives were prepared from 3,3′-dimethylol-2,2′-bipyridine by modification of literature procedures.[5,7] These compounds were converted to their corresponding ruthenium(II) complexes **1–3** by reaction with *cis*-dichlorobis(2,2′-bipyridine)ruthenium(II) and subsequent precipitation as hexafluorophosphate salts.[8] Compound **4** was prepared from ruthenium(III) trichloride hydrate and was also isolated as the hexafluorophosphate salt.[9] Complex **4** serves as an extreme case of distortion from pseudo-octahedral geometry and was, therefore, expected to show a more dramatic response to metal ions.



1 n=1 **2** n=2 **3** n=3 **4**

Fig. 1 $Ru(bpy)_3^{2+}$-crown ether conjugates.

Quantum yields for **1–3** were measured using $Ru(bpy)_3^{2+}$ as the standard (assumed 6.2% efficiency in CH_3CN).[2,5] They ranged from 0.9% to 1.3% in air, and from 1.3% to 1.6% in argon. This illustrates the impact of distortion from O_h geometry even in these minimally substituted cases.[6,9,10] Complex **4** exhibited no detectable emission at room temperature. Since a low baseline signal is desirable for sensing purposes, these complexes were well suited to evaluate the effect of conformational perturbations induced by metal ion binding.

Emissive response to the addition of metal ion was determined with solutions of **1–4** in CH_3CN. While **1** and **4** gave no response to metal addition, **2** and **3** exhibited significant (≈4-fold) increases in emission in the presence of Ca^{2+} and Pb^{2+} (Fig. 2). Complex **2** also responded to added Na^+ and **3** to Mg^{2+}, although these responses were smaller in magnitude and required much higher concentrations of added metal ion (Fig. 3).[11–13] At submillimolar concentrations of metal ion, **3** selectively signaled Ca^{2+} and Pb^{2+} in the presence of other analytes. Concomitant with significant increases in quantum yields, 15–20 nm bathochromic shifts were observed upon complexation.

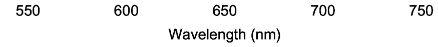


Fig. 2 Response of emission from **3** to added Pb(II).

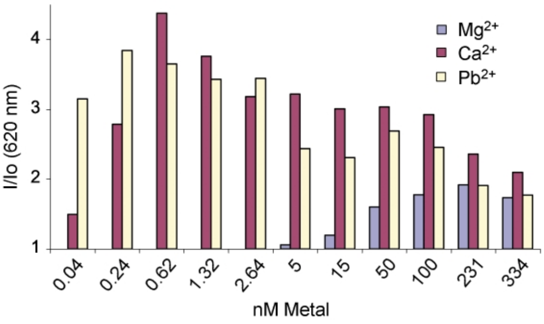


Fig. 3 Emission enhancement of **3** as a function of [metal].

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The observed enhancement induced by Pb^{2+} is noteworthy. One of the confines of organic fluorophores is that their fluorescence is typically quenched by heavy atoms. The coordination compounds described here appear to be free of this limitation, and this holds promise for the development of chemosensors for environmentally-relevant heavy metals.[14]

Although we do not yet have a definitive interpretation of the origins of the luminescence enhancement or red-shifts, we have several working hypotheses: (i) an increase in the energy of the metal e_g orbital manifold, (ii) a lowering of the ^{3}MLCT state, or (iii) an increase in the ground state energy of the complex. Little change is seen in the absorption spectra of **2** or **3** upon addition of metal ions, arguing against (iii).

Our attention is currently focused on the energetic separation between the ^{3}MLCT and d–d state. After photoexcitation, the initially populated ^{1}MLCT state decays efficiently and rapidly to the luminescent ^{3}MLCT.[4] However, a thermally activated transition to the metal-centered ligand field (LF) state is capable of depopulating the ^{3}MLCT. Promotion to this state leads to radiationless deactivation through ISC or photodecomposition. Therefore maximum emission is expected when the energy of the LF state lies well above that of the ^{3}MLCT, and increases in this energy separation should lead to enhanced emission.[2,15] A slight binding-induced lowering of the ^{3}MLCT band would explain both the enhanced emission and bathochromic shifts seen in the presence of certain metal ions. However, because the energy gap law precludes any large deviations in this direction without compromise of quantum efficiency,[16] we believe that binding-induced elevation of the energy of the ligand field state plays a more important role in the present case.

It is our contention that these energetics are influenced by the conformation of the crown ether-bipyridyl ligands which is, in turn, altered by the presence of a bound metal ion. Photophysical effects due to conformational restriction have now been observed for transition metal complexes as well as for organic fluorophores. This underscores the general importance of conformational effects in excited-state partitioning between radiative and non-radiative decay processes. Further measurements are in progress to determine the accessibility of the d–d state in the presence and absence of metals showing significant responses in our study.[17] These experiments are expected to provide a more detailed understanding of the nature of conformational control of photophysical parameters.

Notes and references

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11 As noted (reference 6), **2** has recently been reported by others. The results of our metal-titrations of **2** differ from those in the previous report in that we do not observe a response to added Li^+, and the magnitude of our Na^+-induced enhancement is smaller.

12 A typical metal titration consisted of successive additions of 2–300 mM metal perchlorates in acetonitrile to 10 mM solutions of ligand in aerated acetonitrile. Emission profiles were collected at 400 and 450 nm excitation with all monochromator slits at 5 nm.

13 The observed decrease in emission at higher metal ion concentrations may represent formation of less-emissive 2 : 1 M : L complexes. Efforts to confirm this supposition are ongoing.

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17 Crystallographic characterization of **1**–**3** with and without added metal ion will provide valuable ground-state structural information. Efforts to this end have not yet been fruitful.