Synthesis of Ru(II) complexes of N-Heterocyclic Carbenes and Their Promising Photoluminescence Properties in water

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Abstract

The potential use of Ru(bpy)$_3^{2+}$ and its derivatives as a chromophoric component in diverse areas of light emitting devices, artificial photosynthesis, light emitting sensors etc have received a considerable attention in recent times. The purpose of this study is to describe the synthesis of Ru(II) complexes of N-heterocyclic carbenes and to study their photoluminescence properties in water.

Two novel complexes of Ruthenium N-heterocyclic carbenes, which are analogous to Ru(bpy)$_3^{2+}$ and Ru(terpy)$_2^{2+}$ were synthesized. The complex, which is analogous to Ru(terpy)$_2^{2+}$ exhibited photoluminescence properties with long life time of 820 ns in acetonitrile and 3100 ns in water at room temperature respectively.
Introduction

Complex Ru(bpy)$_3^{2+}$ and its derivatives have received considerable attention as potential chromophoric components such diverse areas of research such as light emitting devices, artificial photosynthesis, light emitting sensors, etc.\textsuperscript{1} However, complexes of Ru(bpy)$_3^{2+}$ family are unsuitable for the construction of supramolecular systems, from geometric and synthetic view points.\textsuperscript{2} From purely structural and synthetic viewpoints, terpyridine-based ligands are particularly useful for the design of linear multimetallic component systems. However, in contrast to Ru(bpy)$_3^{2+}$, the complex Ru(terpy)$_2^{2+}$ has not attracted a great deal of attention as a result of its poor photochemical properties (in particular, very weak luminescence and short excited state life times at room temperature).

Recently, N-heterocyclic carbene (NHC) ligands have become universal ligands in organometallic and inorganic chemistry.\textsuperscript{3} Because of their specific coordination chemistry, N-heterocyclic ligands stabilizes and activate metal centers and, in some cases, and replace organophosphanes. Moreover, N-heterocyclic carbene ligands have a much higher trans effect than N- or P-donors and are more tightly bound to the metal.\textsuperscript{4} However, their photophysical and –chemical properties have been relatively less well studied.\textsuperscript{5} In the course of this study and of the use of N-heterocyclic carbene complexes,\textsuperscript{6} synthesis of complexes 1 and 2(PF$_6^-$), which are analogous to Ru(bpy)$_3^{2+}$ and Ru(terpy)$_2^{2+}$, respectively, as well as their photoochemical properties were studied. This paper presents the results of the synthesis and photochemical properties of complexes 1 and 2(PF$_6^-$) along with their relevance to Ru(bpy)$_3^{2+}$ and Ru(terpy)$_2^{2+}$. 
Synthesis

Complex 1 was synthesized in 75% yield by the complexation of RuCl₃ with ligand L₂ in a refluxing ethylene glycol solution. Complexes 2(PF₆⁻), 2(BPh₄⁻), and 2(Br⁻) was also synthesized by the complexation of RuCl₃ with ligand L₂ in refluxing ethylene glycol. The molecular structure of complex 2(BPh₄⁻) was confirmed by X-ray diffraction (Figure 1).⁷ The two ligands are mutually arranged about each metal center in an almost manner.

Scheme 1.
The resulting local environment around the Ru$^{2+}$ cation is therefore pseudo orthogonal (D$_{2d}$) with a conformational restriction imposed by the presence of methyl groups on ligand L2.$^7$

**Results and Discussion**

The photophysical properties of complex 1 and 2(PF$_6^-$), were investigated in order to make a comparison with those of Ru(bpy)$_3$$^{2+}$ and Ru(terpy)$_2$$^{2+}$. Complex 1, compared with Ru(bpy)$_3$$^{2+}$, shows a blue shifted $\lambda_{\text{max}}$ (368 nm) in the absorption spectrum presumably due to the electron rich property of NHC ligands (Figure 2 and Table 1).$^7$
Table 1. Spectroscopic Properties of Ru\(^{2+}\) Complexes

<table>
<thead>
<tr>
<th>complex</th>
<th>(\lambda_{\text{max}}^{\text{abs}}) (nm)</th>
<th>(\varepsilon\left(10^3 \text{ M}^{-1} \text{ cm}^{-1}\right))</th>
<th>(\lambda_{\text{max}}^{\text{em}}) (nm)</th>
<th>rel em int(^b)</th>
<th>decay time (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(bpy)(_3)^{2+}\</td>
<td>450</td>
<td>14.3</td>
<td>597</td>
<td>3.83</td>
<td>860(^c)</td>
</tr>
<tr>
<td>Ru(terpy)(_2)^{2+}\</td>
<td>474</td>
<td>17.2</td>
<td></td>
<td></td>
<td>0.25(^d)</td>
</tr>
<tr>
<td>1</td>
<td>368</td>
<td>11.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2(PF(_6^-))</td>
<td>343, 382</td>
<td>11.6, 15.2</td>
<td>532</td>
<td>1.04</td>
<td>820</td>
</tr>
<tr>
<td>2(BPh(_4^-))</td>
<td>343, 382</td>
<td>15.6, 20.1</td>
<td>532</td>
<td>0.39</td>
<td>490</td>
</tr>
<tr>
<td>2(Br(^-))</td>
<td>343, 382</td>
<td>13.0, 16.8</td>
<td>532</td>
<td>1.00</td>
<td>600</td>
</tr>
<tr>
<td>2(Br(^-))-H(_2)O</td>
<td>341, 381</td>
<td>13.8, 17.3</td>
<td>532</td>
<td>9.90</td>
<td>3100</td>
</tr>
</tbody>
</table>

Figure 2. Absorption and emission spectra, with excitation at 354 nm, of Ru\(^{2+}\) complexes in acetonitrile (if not specified) and water under argon.

The voltammetric oxidation of complexes 1 and 2(PF\(_6^-\)) occurred at a chemically reversible 1-electron process at a scan rate of 100 mV/s. As expected, \(E_{1/2}\) for 2\(^{2+}\)/2\(^{3+}\) was similar to that of 1\(^{2+}\)/1\(^{3+}\), but lower than those of Ru(bpy)\(_3\)^{2+} and Ru(terpy)\(_2\)^{2+} due to the electron-
The donating nature of NHC, which is consistent with the high energy for HOMO. The increase in the energy of the HOMO suggests a red shift in the absorption spectrum. However, experimental observation shows a blue shift in the absorption spectrum. It is possible that the NHC has a higher electron density than terpy, and a higher lying $\pi^*$ orbital. Therefore, it is expected that the increase in the LUMO energy in the complex $2(\text{PF}_6^-)$ is higher than that of Ru(terpy)$_2^{2+}$, which is consistent with DFT calculations. This would mean that the blue shift is essentially a LUMO effect.

Complex 1 was non emissive in acetonitrile at room temperature. However, complex $2(\text{PF}_6^-)$ showed a very significant photophysical properties. It shows a different absorption spectrum from that of Ru(terpy)$_2^{2+}$ (Figure 2 and Table 1). The complex $2(\text{PF}_6^-)$ showed two absorption peaks at 343 nm and 382 nm. Compared with those of Ru(bpy)$_3^{2+}$ and Ru(terpy)$_2^{2+}$, the two peaks were highly blue shifted. Using ab initio calculations, it was provisionally determined that the two blue-shifted peaks arose from the MLCT. In contrast to Ru(terpy)$_2^{2+}$, complex $2(\text{PF}_6^-)$ showed a very strong emission with a maximum at 523 nm.

The emission kinetics at 523 nm in Figure 3 shows a long lifetime of 820 ns in acetonitrile at room temperature, which is 3280 times larger than that (0.25 ns) of Ru(terpy)$_2^{2+}$. 
In artificial Photosynthesis, the lifetime of the chromophore in water is very important.\(^9\)
In order to measure its lifetime in water, complex 2(Br\(^-\)) was synthesized. The lifetimes of this complex was 600 ns in acetonitrile and 3100 ns in water, i.e., 12400 times larger than that of Ru(terpy)\(_2\)\(^{2+}\). This observation is quite unprecedented because MLCT chromophores generally show shorter lifetimes in water than in organic solvents.\(^{10}\) As shown in Table 1, the counter ions strongly influence the luminescence lifetimes of the chromophore.\(^{11}\)

**Conclusion**

In conclusion, complexes 1 and 2(PF\(_6\)\(^-\)) were synthesized on the basis of NHC. Complex 2(PF\(_6\)\(^-\)) showed a very significant photoluminescence in water, and it is expected that that
this complex can be a complement or substitute for Ru(bpy)$_3^{2+}$ in many fields. Complex 2(PF$_6^-$) represents an alternative molecular design that imparts a green photoluminescence into a synthetically facile system.

References


