

Synthesis of a Water-soluble Iridium(III) Complex with pH and Metal Cation Sensitive Photoluminescence

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A water-soluble iridium complex with bulky ligands was synthesized. Photoluminescence intensities of this iridium complex were stronger in basic aqueous solutions than that in organic solvents, and they were found to depend on pH and additive metal ions in its aqueous solution.

Iridium complexes have recently received much attention as photoluminescent materials¹ because of their long luminescence lifetime and strong phosphorescence intensity in organic solvents and on films. Such complexes with various kinds of ligands² and dendritic structures³ have been designed and reported. However, there are few examples of iridium complexes which can emit light efficiently at high brightness in water.⁴ When the iridium complexes can be dissolved in water, they have a potential to be used as a photoluminescent probe. We report here synthesis of a new water-soluble iridium complex and its photoluminescence property.

The water-soluble iridium complex with 3',5'-di(4-carboxyphenyl)-3-(2-pyridyl)biphenyl-4-yl ligands (**1**) was synthesized as shown Scheme 1. The ligand molecule was synthesized by Suzuki coupling reaction.⁵ We obtained the methyl ester derivative of the iridium complex by the reaction of the ligand with iridium chloride trihydrate. Finally, the methyl ester groups in the derivative were hydrolyzed to give the water-soluble iridium complex **1**. This complex was characterized by ¹H NMR, ¹³C NMR, FT-IR, MALDI-TOF MS, and elemental analysis. The details for the synthetic procedures of this complex were described in Supporting Information. This synthetic procedure could lead to *facial* and *meridional* isomers of complex **1**. The product was found to be the racemic mixture (Figure S1).

Complex **1** has three-dimensional blocking ligands around the iridium center. Therefore, photoluminescence quenching by self-assembling of these complexes can be inhibited. The solubility of this complex to water should be improved by introducing carboxyl groups to the ligands.

The UV-vis absorption spectrum of **1** can be divided into two regions; the metal-to-ligand charge-transfer (MLCT) band as shoulder peaks over 330 nm and the π - π^* transition of the bulky ligands at 270 nm. The difference of UV-vis spectra was not observed in basic aqueous solutions and DMF.

The photoluminescence intensity of the complex **1** was monitored in DMF or basic aqueous solution (Figure 1). We found that the photoluminescence intensities were stronger in

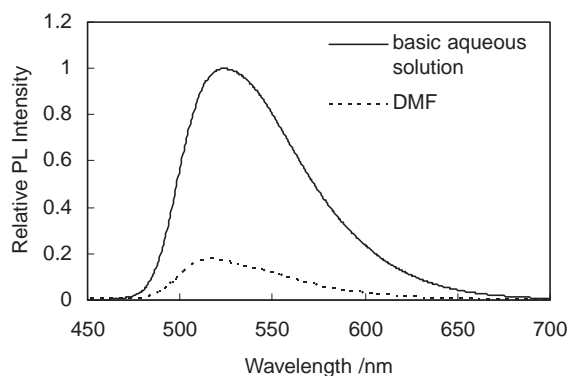
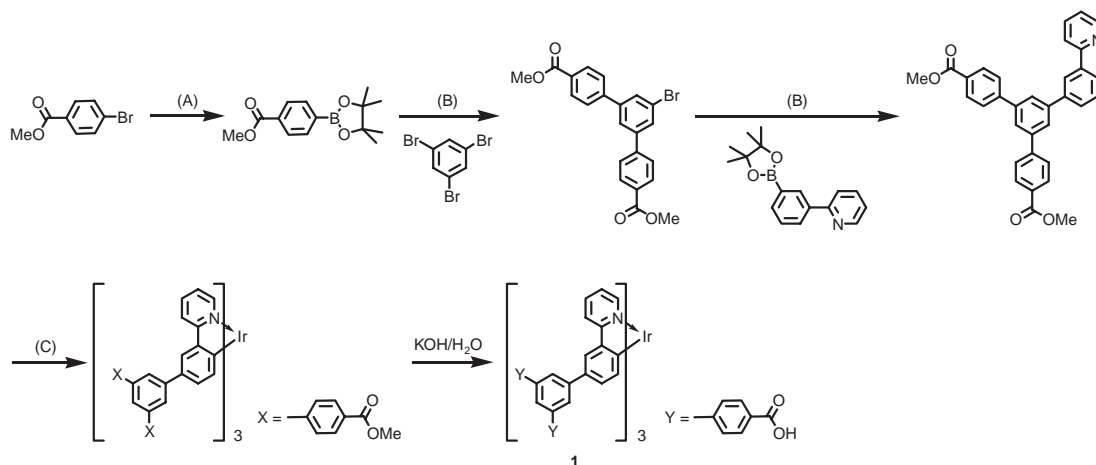


Figure 1. Solvent dependence of **1** on photoluminescence spectra in basic aqueous solution (pH = 10) and DMF. PL intensities were normalized by absorbance 0.31 at 360 nm ($[1] = 1.0 \times 10^{-5}$ M).



Scheme 1. (A) PdCl₂(dppf) (dppf = 1,1'-bis(diphenylphosphino)ferrocene), KOAc, bis(pinacolato)diboron, DMSO, 80 °C, Ar. (B) Tetrakis(triphenylphosphine)palladium(0), aqueous sodium carbonate, ethanol, toluene, reflux, Ar. (C) Iridium(III) chloride trihydrate, water, 2-ethoxyethanol, heat then silver trifluoromethanesulfonate, 130 °C, Ar.

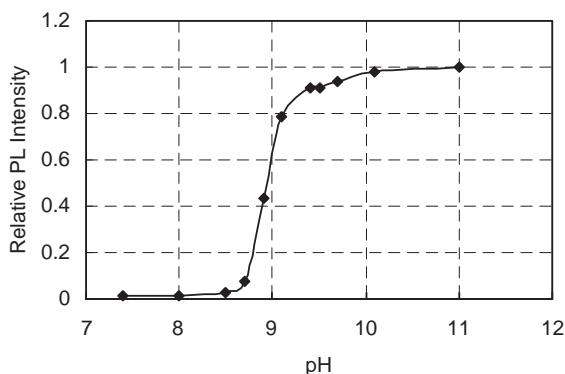


Figure 2. Correlation between pH and photoluminescence intensities of **1** in 0.13 M phosphate buffer [$\text{KH}_2\text{PO}_4(\text{aq})/\text{Na}_2\text{-HPO}_4(\text{aq})$, pH 7–9] and 0.13 M carbonate buffer [$\text{Na}_2\text{CO}_3(\text{aq})/\text{NaHCO}_3(\text{aq})$, pH 9–11] ($[\mathbf{1}] = 1.0 \times 10^{-5}$ M). PL intensities were respectively normalized by absorbance at 360 nm.

basic aqueous solution ($\Phi = 0.11$) than that in DMF ($\Phi = 0.028$).⁶ The photoluminescence lifetime of complex **1** was 0.82 μs in basic aqueous solution. It was found to be 4.5 times longer than that in DMF solution (0.18 μs). These results indicate that the chromophores are isolated each other by electrostatic repulsion due to the dissociation of protons from carboxylic acids in the ligands at higher pH.

The pH dependence of **1** on photoluminescence spectra was studied. The correlation between pH and the photoluminescence intensity of **1** was shown in Figure 2. The emission intensity increased with an increase in pH. The drastic change of the intensity occurred around pH 9. It was suggested that the change of the emission intensity of complex **1** was in accord with the degree of ionization of carboxylic acid in the ligand (Figure S2).

Photoluminescence spectra of **1** in the presence of various kinds of metal chlorides were measured. As shown in Figure 3, the photoluminescence intensity of **1** was quenched by adding metal ions. The degrees of quenching by the addition of divalent metal cations (Mg^{2+} , Cu^{2+} , and Hg^{2+}) were larger than that of monovalent alkali metal cations (Li^+ , Na^+ , K^+ , Rb^+ , and Cs^+). In the case of monovalent metal ions, it was suggested that the photoluminescence of **1** was quenched by the exchanges between protons of carboxylic acids and metal ions. While, the chelate formation could be considered in the case of divalent metal ions to give a larger photoluminescence quenching.

In conclusion, a water-soluble iridium complex was synthesized, and its photophysical properties were investigated. We found that photoluminescence intensities of the iridium complex **1** were stronger in basic aqueous solution than that in organic solvents, and they depend on pH and additive metal ions in aqueous solutions. The luminescent probe based on **1** can be applied for sensing toxic heavy metal ions such as lead, cadmium, and mercury.

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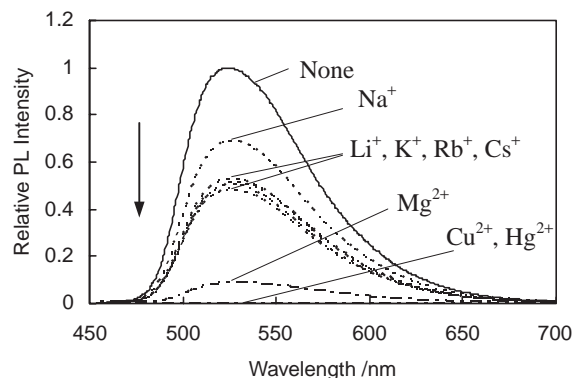


Figure 3. Changes of photoluminescence intensities of **1** by adding various metal chlorides in 0.13 M carbonate buffer [$\text{Na}_2\text{CO}_3(\text{aq})/\text{NaHCO}_3(\text{aq})$] including 0.27 M metal ion ($[\mathbf{1}] = 1.0 \times 10^{-5}$ M). PL intensities were normalized by absorbance 0.31 at 360 nm. In these measurements, pH was constant at 10.

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References and Notes

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- 6 Photoluminescence quantum yields were measured by a relative method using quinine sulfate in 0.1 M sulfuric acid, which has a photoluminescence quantum yield of 0.55, as a standard. The quantum yield (Φ_{Ir}) of the iridium complex was calculated by the following equation: $\Phi_{\text{Ir}} = \Phi_{\text{std}}(A_{\text{std}}P_{\text{Ir}}/A_{\text{Ir}}P_{\text{std}})(n_{\text{Dir}}/n_{\text{Dst}})^2$, where A_{std} and A_{Ir} are the absorbance of the standard and the iridium complex, respectively. P_{std} and P_{Ir} are the corresponding relative integrated photoluminescence intensities, and n is the refractive index of the solvent.