

3,9-Dithia-6-azaundecane-appended Iridium (III) Complex for the Selective Detection of Hg^{2+} in Aqueous Acetonitrile

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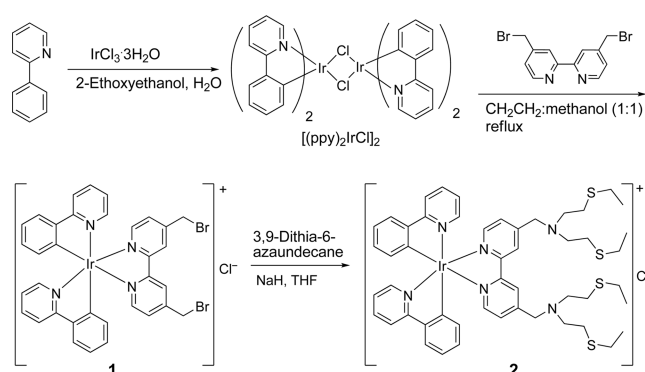
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Detection of mercuric ion (Hg^{2+}) originated from natural or industrial sources is very important because it is extremely toxic even at low levels and causes serious environmental and health problems.¹ Consequently, many efforts have been devoted to the development of sensitive chemosensors for the detection of Hg^{2+} . For example, various fluorescent chemosensors based on rhodamine,² nitrobenzoxadiazole,³ fluorescein,⁴ boradiazaindacene (BODIPY),⁵ dansyl,⁶ pyrene,⁷ or other fluorophores⁸ have been developed for the selective detection of Hg^{2+} .

While various fluorescent chemosensors for the selective detection of Hg^{2+} have been developed, phosphorescent chemosensors for the selective detection of Hg^{2+} are relatively rare. Among various phosphors, iridium (III) complexes with sulfur containing cyclometalated ligands have been used as phosphorescent chemosensors for the selective detection of Hg^{2+} .⁹ Azacrown ether-appended iridium (III) complex developed in our laboratory has also been utilized as a phosphorescent chemosensor for the selective detection of Hg^{2+} .¹⁰ As another iridium (III) complex-based phosphorescent chemosensors for the selective detection of Hg^{2+} , in this study, we wish to prepare iridium (III) complex containing two 3,9-dithia-6-azaundecane units as chelating ligands for metal ions. Some fluorophores containing 3,9-dithia-6-azaundecane unit have been successfully applied for the selective detection of Hg^{2+} .^{3c,4a,11} In this instance, iridium (III) complex containing two 3,9-dithia-6-azaundecane units is expected to be useful as a phosphorescent chemosensor for the selective detection of Hg^{2+} .

Iridium (III) complex containing two 3,9-dithia-6-azaundecane units was prepared starting from 2-phenylpyridine according to the procedure shown in Scheme 1. 2-Phenylpyridine was transformed into chloride bridged dimeric iridium complex, $[(\text{ppy})_2\text{IrCl}]_2$, via the reported procedure.¹² By treating $[(\text{ppy})_2\text{IrCl}]_2$ with 4,4'-bis(bromomethyl)-2,2'-bipyridine, which was prepared starting from 4,4'-dimethyl-2,2'-bipyridine according to the reported procedure,¹³ iridium (III) complex **1** was prepared. Finally iridium (III) complex **1** was treated with 3,9-dithia-6-azaundecane in the presence of NaH in tetrahydrofuran (THF) to afford iridium (III) complex **2** containing two 3,9-dithia-6-azaundecane units.



Scheme 1. Synthesis of iridium(III) complex **2**.

The UV-vis absorption and photoluminescence spectra of iridium (III) complex **2** in 50% acetonitrile in water are shown in Figure 1. The UV-vis spectrum of iridium (III) complex **2** was found to be quite similar to that of azacrown ether-appended iridium (III) complex developed in our laboratory.¹⁰ The intense absorption bands at 250–290 nm is thought to be originated from the ligand-centered π - π^* transition. The relatively weak absorption bands at 300–350 nm might be originated from the metal-to-ligand charge transfer ($^1\text{MLCT}$) transition.^{10,14} In addition, the weak ab-

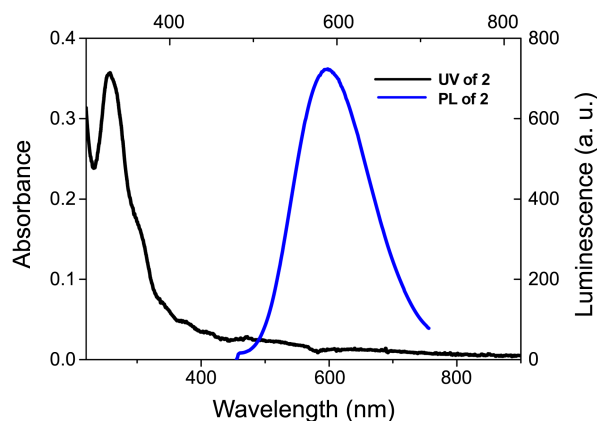


Figure 1. UV-vis and phosphorescence spectra of iridium (III) complex **2** (10 μM) in 50% acetonitrile in water. The phosphorescence spectrum was obtained after excitation at 370 nm.

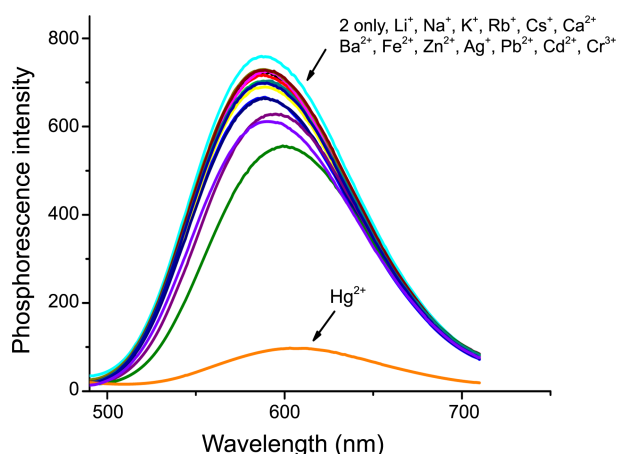


Figure 2. Phosphorescence spectra of iridium (III) complex **2** (10 μ M) upon addition of various metal ions (100 equiv) in 50% acetonitrile in water (excitation: 370 nm).

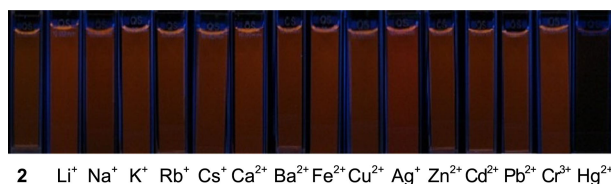


Figure 3. Phosphorescent emission changes of iridium (III) complex **2** (10 μ M) upon addition of various metal ions (100 equiv) in 50% acetonitrile in water.

sorption tail at > 450 nm might be due to the spin-forbidden $^3\text{MLCT}$ transition.^{10,14} The photoluminescence spectrum of iridium (III) complex **2** was found to show the maximum wavelength at 588 nm in 50% acetonitrile in water with the excitation at 370 nm.

The selectivity of iridium (III) complex **2** for various metal ions was investigated by monitoring its phosphorescence changes upon addition of perchlorate salts of various metal ions such as Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , Ca^{2+} , Ba^{2+} , Fe^{2+} , Cu^{2+} , Ag^+ , Zn^{2+} , Cd^{2+} , Pb^{2+} , Cr^{3+} and Hg^{2+} as shown in Figure 2.

The phosphorescence emission of iridium (III) complex **2** was found to be quenched significantly upon addition of Hg^{2+} , but it remained almost no changes upon addition of other metal ions. The phosphorescence changes of iridium (III) complex **2** upon addition of various metal ions are visually illustrated in Figure 3. These results clearly indicate that iridium (III) complex **2** can be used as a phosphorescent chemosensor for the selective detection of Hg^{2+} .

The selectivity of iridium (III) complex **2** for various metal ions was evaluated by the relative emission intensities, I_0/I , where I_0 and I are the maximum emission intensity of iridium (III) complex **2** in the absence and presence of metal ion at 588 nm, respectively. The ratio, I_0/I , was 7.4 for Hg^{2+} while it was in the range of 0.95–1.30 for other metal ions, indicating the prominent selectivity for Hg^{2+} over the other metal ions as shown in Figure 4. The effective complexation of Hg^{2+} with the 3,9-dithia-6-azaundecane units of iridium (III) complex **2** might be responsible for the selective detection of Hg^{2+} .

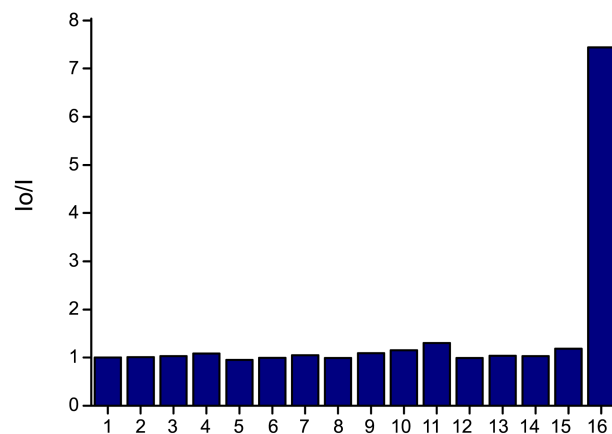


Figure 4. Relative emission intensities of iridium (III) complex **2** (10 μ M) upon addition of various metal ions (100 equiv) in 50% acetonitrile in water: complex **2** only (1), Li^+ (2), Na^+ (3), K^+ (4), Rb^+ (5), Cs^+ (6), Ca^{2+} (7), Ba^{2+} (8), Fe^{2+} (9), Cu^{2+} (10), Ag^+ (11), Zn^{2+} (12), Cd^{2+} (13), Pb^{2+} (14), Cr^{3+} (15), Hg^{2+} (16).

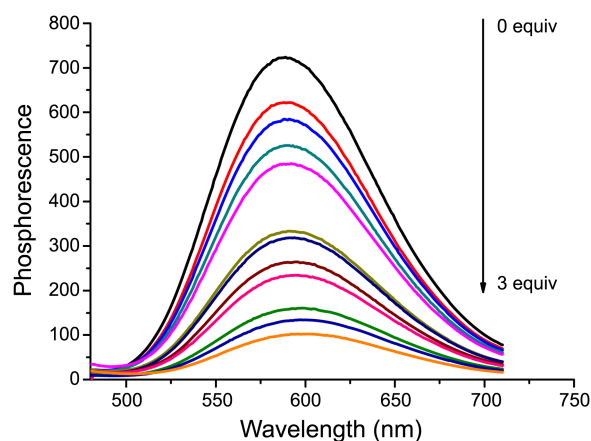


Figure 5. Phosphorescence titration spectra of iridium (III) complex **2** (10 μ M) upon addition of Hg^{2+} (2 μ M, 4 μ M, 6 μ M, 8 μ M, 10 μ M, 12 μ M, 14 μ M, 16 μ M, 18 μ M, 20 μ M, 30 μ M) in 50% acetonitrile in water (excitation: 370 nm).

The phosphorescence titration spectra of iridium (III) complex **2** upon addition of Hg^{2+} in 50% acetonitrile in water are shown in Figure 5. As the concentration of Hg^{2+} was increased from 0 to 3 equiv, the emission intensity decreased continuously and the emission maximum was slightly shifted from 588 to 600 nm. Based on the phosphorescence titration spectra, the association constant of iridium (III) complex **2** for Hg^{2+} was calculated to be $2.3 \times 10^4 \text{ M}^{-1}$ according to the Benesi-Hildebrand expression.¹⁵

Iridium (III) complex **2** contains two 3,9-dithia-6-azaundecane units and each 3,9-dithia-6-azaundecane unit is expected to be utilized for the complexation with Hg^{2+} . Consequently, iridium (III) complex **2** was expected to form 1:2 complex with Hg^{2+} as shown in Figure 6(a). However, the Job's plot experiment shown in Figure 7 demonstrates the formation of 1:1 complex between iridium (III) complex **2** and Hg^{2+} . The two 3,9-dithia-6-azaundecane units of iridium (III) complex **2** might be close enough to chelate Hg^{2+} together, forming 1:1 complex as shown in Figure 6(b).

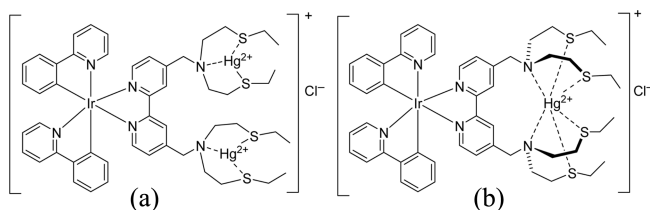


Figure 6. Proposed model for the formation of (a) 1:2 and (b) 1:1 complex between iridium (III) complex **2** and Hg^{2+} .

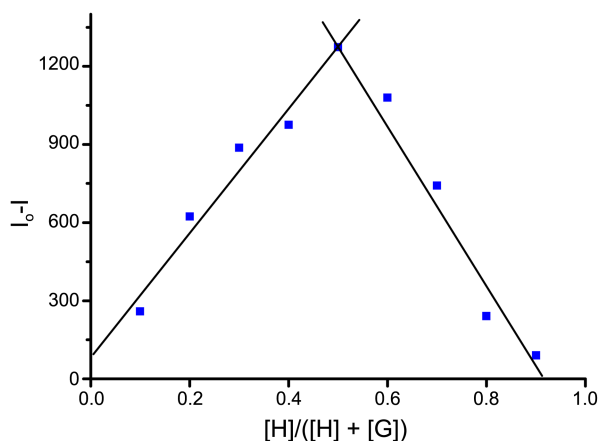


Figure 7. Job's plot for the complex formation between iridium (III) complex **2** and Hg^{2+} .

In summary, iridium (III) complex **2** containing two 3,9-dithia-6-azaundecane units was prepared and applied successfully for the selective detection of Hg^{2+} with the association constant of $2.3 \times 10^4 \text{ M}^{-1}$.

Experimental

^1H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury Plus 300 MHz spectrometer. High-resolution mass spectral data were obtained from the Korea Basic Science Institute Daegu Center (HR-FAB Mass) on a Jeol JMS 700 high resolution mass spectrometer. Photoluminescence (PL) spectra were measured on a HITACHI F-7000 fluorescence spectrophotometer. Phosphorescence measurements were performed by exciting at 370 nm with an excitation band width of 10 nm and an emission band width of 10 nm. The stock solution of iridium (III) complex **2** ($1 \times 10^{-4} \text{ M}$) and metal ions ($1 \times 10^{-2} \text{ M}$) were prepared in 50% acetonitrile in water. For phosphorescence measurements, sample solutions were prepared by mixing a measured amount of the stock solution of iridium (III) complex **2** with a measured amount of the stock solution of metal ion and then diluting the mixed solution with 50% acetonitrile in water to obtain the desired concentrations of iridium (III) complex **2** and metal ion.

Synthesis of Iridium (III) Complex 1. Iridium (III) complex **1** was prepared starting from 2-phenylpyridine as shown in Scheme 1. 2-Phenylpyridine was converted to dimeric iridium complex, $[(\text{ppy})_2\text{IrCl}]_2$, according to the reported procedure.¹² Iridium complex, $[(\text{ppy})_2\text{IrCl}]_2$ (1.0 g, 0.94 mmol) and 4,4'-bis(bromomethyl)-2,2'-bipyridine (0.64 g,

1.87 mmol) were dissolved in 1:1 mixture (70 mL, v/v) of dichloromethane and methanol. The reaction mixture was refluxed for 12 hr under an Ar atmosphere and then cooled to room temperature. The solvent was removed by rotary evaporation. The residue was dissolved in dichloromethane. The organic solution was washed with brine and then dried over Na_2SO_4 . The solvent was removed by a rotary evaporator. The residue was purified by chromatography on silica gel (eluent:methylene chloride/methanol, 1/1, v/v) to afford iridium (III) complex **1**. Yield: 1.5 g (95 %). mp $> 350^\circ\text{C}$; ^1H NMR (300 MHz, CDCl_3) δ 4.83-5.04 (m, 4H), 6.28 (d, 2H), 6.90 (t, 2H), 7.03 (t, 4H), 7.47-7.57 (m, 4H), 7.67 (d, 2H), 7.77 (t, 2H), 7.83-7.92 (m, 4H), 9.87 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 43.9, 119.9, 122.9, 123.7, 125.0, 131.0, 131.9, 132.0, 138.3, 143.6, 143.8, 150.0, 150.2, 150.3, 150.4, 150.5, 168.0; HRFAB-MS m/z [M^+] calcd. for $\text{C}_{34}\text{H}_{26}\text{Br}_2\text{IrN}_4$ 841.0153. Found: 841.0156. IR (KBr pellet) cm^{-1} 3385, 1607, 1477.

Synthesis of Iridium (III) Complex 2. In a 50 mL round bottom flask were placed 3,9-dithia-6-azaundecane (0.23 g, 1.20 mmol), which was prepared from bis(2-chloroethyl)-amine hydrochloride and ethanethiol *via* the reported procedure,¹⁶ and THF (10 mL). The solution was transferred into a solution of NaH (0.032 g, 1.33 mmol) dissolved in THF (10 mL). The mixed solution was stirred for 1 hr under an Ar atmosphere and then transferred into a solution of iridium (III) complex **1** (0.51 g, 0.60 mmol) dissolved in THF (10 mL) through a cannula. The whole mixture was stirred for 12 hr and then 20 mL water was added. The mixture was extracted with diethyl ether (50 mL) twice. The combined ether solution was dried over anhydrous Na_2SO_4 and then evaporated. The residue was purified by chromatography on silica gel (eluent:methylene chloride/methanol, 1/1, v/v) to afford iridium (III) complex **2** as deep orange solid. Yield: 0.35 g (55%). mp 248°C ; ^1H NMR (300 MHz, CDCl_3) δ 1.16 (t, 12H), 2.46 (q, 8H), 2.62 (t, 8H), 2.75 (t, 8H), 4.04 (s, 4H), 6.27 (d, 2H), 6.85 (t, 2H), 7.01-7.04 (m, 4H), 7.44-7.59 (m, 4H), 7.64-7.91 (m, 8H), 9.38 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 15.1, 26.5, 30.0, 54.1, 56.9, 119.8, 122.7, 123.4, 125.0, 125.8, 127.6, 131.0, 131.9, 138.2, 143.7, 148.7, 149.0, 151.0, 155.0, 155.8, 168.2; HRFAB-MS m/z [M^+] calcd. for $\text{C}_{50}\text{H}_{62}\text{IrN}_6\text{S}_4$ 1067.3548. Found: 1067.3546. IR (KBr pellet) cm^{-1} 3428, 1606, 1477.

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