Phosphorescent Azacrown Ether-appended Iridium (III) Complex for the Selective Detection of Hg^{2+} in Aqueous Acetonitrile

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A new phosphorescent cyclometalated heteroleptic iridium (III) complex with an ancillary ligand of 4-azacrown-picolinate was prepared and its metal ion selective phosphorescent chemosensing behavior was investigated. The new iridium (III) complex exhibits notable phosphorescence quenching for Hg^{2+} in aqueous 50% acetonitrile solution with respect to the selective phosphorescent detection of various metal ions including Li$^+$, Na$^+$, K$^+$, Cs$^+$, Mg^{2+}, Ca^{2+}, Ba^{2+}, Fe^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag$^+$, Pb^{2+}, Cd^{2+}, Cr^{2+}, Cr^{3+} and Hg^{2+}. The phosphorescence quenching for Hg^{2+} increased linearly with increasing concentration of Hg^{2+} in the range of 10 μM - 700 μM even in the presence of other metal ions, except for Cu^{2+}. Consequently, the new iridium (III) complex has the potential to be utilized for the determination of parts per million levels of Hg^{2+} in aqueous acetonitrile media.

Key Words: Iridium (III) complex, Azacrown ether, Phosphorescence quenching, Hg^{2+} detection, Phosphorescent chemosensor

Introduction

The mercuric ion (Hg^{2+}), which can be accumulated in the organs of human and animal bodies, is one of the most serious environmental and health threats originating from both natural and industrial sources.[1,2] Therefore, the development of highly sensitive sensors for the detection of Hg^{2+} is very important for environmental and/or biological applications. A large number of fluorescent chemosensors for Hg^{2+} have been developed because of their high sensitivity and selectivity. For example, rhodamine-based chemosensors,[3-7] nitrobezoxadiazole-based chemosensors,[8,9] fluorescein-based chemosensors[10,11] and other fluorophore-based chemosensors have been developed for the detection of Hg^{2+}.[12-17]

Phosphorescent chemosensors constitute another attractive method, because their emission may be discriminated readily from the scattered light and/or shorter-lived background fluorescence normally present in biological and clinical samples.[18] Among the various types of phosphors, cyclometalated iridium (III) complexes formed with three identical cyclometalated (C^N) ligands (homoleptic) or two cyclometalated (C^N) ligands and a bidentate ancillary ligand (LX) (heteroleptic) have been known to show high phosphorescence efficiency and micro-millisecond lifetimes and, consequently, they have been utilized as efficient phosphorescent dopants in organic light emitting diodes (OLEDs).[19-21] Such highly phosphorescent iridium (III) complexes have also been utilized as phosphorescent chemosensors for anions,[22-24] homocystein,[25] and cations.[26-29] Especially, iridium (III) complexes with sulfur containing C^N ligands have been used as phosphorescent chemosensors for Hg^{2+}.[30,31] The attractive interaction between Hg^{2+} and the sulfur atom of the C^N ligands is believed to alter the emission properties of the iridium (III) complexes. However, iridium (III) complexes without sulfur containing C^N ligands have not previously been utilized as phosphorescent chemosensors for Hg^{2+}.

In this paper, we present the synthesis of new azacrown ether-appended iridium (III) complex **1** and its application as a sensitive and selective phosphorescent chemosensor for the detection of Hg^{2+}. Crown ethers or azacrown ethers have occupied a special position as receptors for various cations because of their fairly high selectivity and accessibility and are widely used in the design of chemosensors by connecting them with signaling units.[32] In this instance, azacrown ether-appended iridium (III) complex **1** is expected to behave as a sensitive and selective phosphorescent chemosensor for cations.

Experimental Section

Reagents and Instruments. 2-Phenylpyridine, 2-ethoxyethanol, diethylene glycol dimethyl ether and 1-aza-18-crown-6 were purchased from Aldrich. 4-Chloropicolinic acid was purchased from TCI. Iridium (III) chloride trihydrate was purchased from Acros organics.
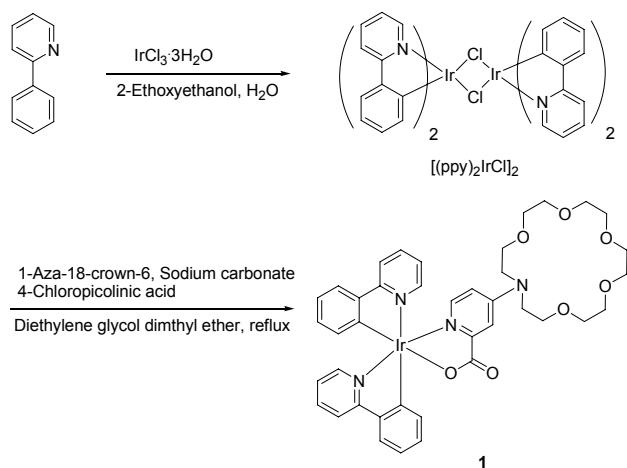
All glass ware, syringes and magnetic stirring bars were completely dried. The reactions were monitored by thin layer chromatography (TLC). Commercial TLC plates (Silica gel 60 F$_{254}$, Merck Co.) were developed and the spots were absorbed under UV light at a short wavelength of 254 nm and long wavelength of 365 nm. Silica column chromatography was performed with silica gel 60 G (particle size 0.063 ~ 0.200 mm, 70 ~ 230 mesh ASTM, Merck. Co.).

The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury Plus 300 MHz spectrometer. The high-resolution mass spectral data were obtained on a Jeol JMS 700 high resolution mass spectrometer at the Korea Basic Science Institute Daegu Center (HR-FAB Mass). The photoluminescentce (PL) spectra were measured in the range of 450 - 750 nm on a Jasco model FP-750 spectrofluorometer.

Synthesis of Azacrown Ether-appended Iridium (III) Complex 1. Azacrown ether-appended iridium (III) complex **1** was

prepared starting from 2-phenylpyridine, as shown in Scheme 1. 2-Phenylpyridine was converted to chloride bridged dimeric iridium complex, $[(ppy)_2IrCl]_2$ (ppy = 2-phenylpyridine), according to the reported procedure.[33] In a 50 mL one-necked round bottom flask equipped with a condenser were placed $[(ppy)_2IrCl]_2$ (0.30 g, 0.28 mmol), 4-chloropicolinic acid (0.11 g, 0.70 mmol), sodium carbonate (0.35 g, 4.20 mmol), 1-aza-18-crown-6 (0.18 g, 0.70 mmol) and diethylene glycol dimethyl ether (20 mL). The reaction mixture was refluxed for 24 hr under N_2 gas and then cooled to room temperature. The diethylene glycol dimethyl ether 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 light yellow residue was purified by chromatography over silica gel (ethyl acetate/*n*-hexane/methanol, 1/2/0.2, v/v/v). Additional purification of the product by recrystallization (dichloromethane, *n*-hexane) afforded azacrown ether-appended iridium (III) complex **1** as a light yellow solid. Yield: 0.20 g (40 %). ^{1}H NMR (300 MHz, Acetone-d_6) δ 8.72 (d, *J* = 6.6 Hz, 1H,), 8.12 (d, *J* = 8.2 Hz, 2H), 7.88 (t, *J* = 7.8 Hz, 2H), 7.80 (d, *J* = 6.6 Hz, 1H), 7.69-7.78 (m, 2H), 7.48 (d, *J* = 3.0 Hz, 1H), 7.34 (t, *J* = 6.6 Hz, 1H), 7.23-7.25 (m, 2H), 6.64-6.88 (m, 5H), 6.38 (d, *J* = 7.7 Hz, 1H), 6.22 (d, *J* = 7.7 Hz, 1H), 3.70-3.71 (m, 8H), 3.54-3.60 (m, 8H), 3.48-3.53 (m, 8H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 174.2, 169.7, 168.0, 153.9, 151.3, 151.0, 149.2, 148.6, 148.3, 147.9, 144.8, 144.3, 137.0, 136.8, 132.9, 132.7, 130.0, 129.6, 124.3, 124.2, 122.2, 122.0, 121.4, 120.7, 119.0, 118.4, 110.6, 109.9, 71.0, 70.9, 70.8, 70.7, 68.3, 51.1; HRFAB-MS *m/z* [M$^+$] calcd. for $C_{40}H_{43}IrN_4O_7$ 884.2761. Found: 884.2764; IR (KBr pellet) cm^{-1} 3448, 2859, 1603, 1470, 1359, 1125.

Phosphorescent Spectra Measurements. The stock solutions of iridium (III) complex **1** and metal ions were prepared in 50% acetonitrile in water. For the phosphorescence measurements, the sample solutions were prepared by mixing a measured amount of the stock solution of iridium (III) complex **1** with a measured amount of the stock solution containing metal perchlorate and then diluting with 50% acetonitrile in water to achieve the desired concentrations of iridium (III) complex **1**

and metal ions. The phosphorescence measurements were carried out by exciting at 400 nm with an excitation band width of 5 nm and an emission band width of 10 nm.

Results and Discussion

The two-step synthetic pathway leading to the desired azacrown ether-appended iridium (III) complex **1** is depicted in Scheme 1. Azacrown ether-appended iridium (III) complex **1** was prepared simply by treating $[(ppy)_2IrCl]_2$ with 4-chloropicolinic acid and 1-aza-18-crown-6 in refluxing diethylene glycol dimethyl ether. By treating $[(ppy)_2IrCl]_2$ with 4-chloropicolinic acid first to form the iridium (III) complex containing 4-chloropicolinate as the ancillary ligand and then treating the resulting iridium (III) complex with 1-aza-18-crown-6 in refluxing diethylene glycol dimethyl ether, azacrown ether-appended iridium (III) complex **1** was obtained. From these results, the second step shown in Scheme 1 seems to involve the *in-situ* formation of the iridium (III) complex containing 4-chloropicolinate as the ancillary ligand and the subsequent substitution of the 4-chloro group of 4-chloropicolininate ancillary with 1-aza-18-crown-6. However, the treatment of 4-chloropicolinic acid with 1-aza-18-crown-6 in refluxing diethylene glycol dimethyl ether was found not to afford 4-azacrownpicolinic acid. Consequently, it is concluded that the formation of the iridium (III) complex containing 4-chloropicolinate as the ancillary ligand facilitates the substitution of the 4-chloro group of the 4-chloropicolininate ancillary ligand with 1-aza-18-crown-6.

The UV-vis and room temperature photoluminescence spectra of iridium (III) complex **1** in 50% acetonitrile in water are shown in Figure 1. The intense absorption bands at around 250 - 320 nm and the relatively weak absorption at 330 - 450 nm are thought to be due to the ligand-centered LC (π - π*) and spin-allowed metal-to-ligand charge transfer ([1]MLCT) transitions, respectively. In addition, according to the photophysical studies on related iridium (III) complexes, the weaker absorptions at wave-
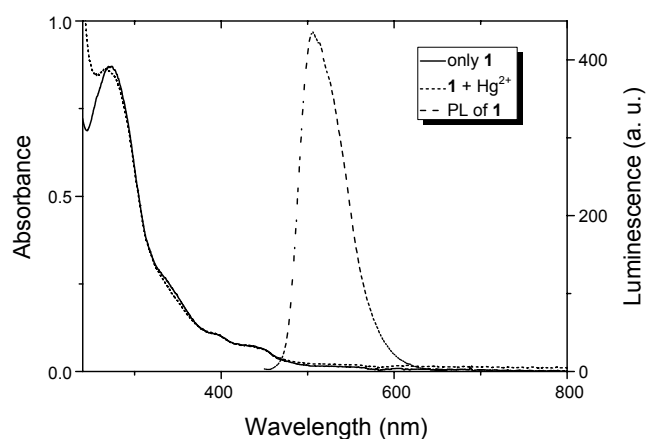
Figure 1. UV-vis and phosphorescence spectra of iridium (III) complex **1** (20 μM) in 50% acetonitrile in water. In the UV-vis spectra, the solid line was obtained with iridium (III) complex **1** only (20 μM) and the dotted line was obtained with iridium (III) complex **1** (20 μM) + Hg^{2+} (100 equiv.) The phosphorescence spectrum was obtained after excitation at 400 nm.

Scheme 1. Synthesis of azacrown ether-appended iridium (III) complex **1**.

lengths > 500 nm are thought to be attributed to spin-forbidden ^{3}MLCT transitions.[25,27] The photoluminescence spectrum for iridium (III) complex **1** exhibits a maximum wavelength of 506 nm in 50 % acetonitrile in water upon its excitation at 400 nm.

The binding properties of iridium (III) complex **1** (20 μM) for various metal ions were studied by monitoring its phosphorescence changes upon the addition of perchlorate salts of various metal ions, including Li^+, Na^+, K^+, Cs^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Fe^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^+, Pb^{2+}, Cd^{2+}, Cr^{2+}, Cr^{3+} and Hg^{2+} (100 equiv.) in 50% acetonitrile in water, as shown in Figure 2. The phosphorescence emission intensities were shown to be significantly quenched upon the addition of Hg^{2+} and slightly quenched upon the addition of Cu^{2+} while almost no-quenching was absorbed upon the addition of the other metal ions. The phosphorescence quenching of iridium(III) complex **1** upon the addition of various metal ions is visually illustrated in Figure 3. While the addition of Hg^{2+} (100 equiv.) results in the significant phosphorescence quenching of iridium(III) complex **1**, it does not produce any significant change in its UV-vis absorption, as shown in Figure 1.

The selectivity of iridium (III) complex **1** for various metal ions was evaluated by determining the ratio, $I_{0(506)}/I_{(506)}$, where $I_{0(506)}$ and $I_{(506)}$ are the maximum emission intensities of complex **1** at the maximum wavelength of 506 nm in the absence and presence of the metal ions, respectively. The ratio $I_{0(506)}/I_{(506)}$ was 5.88 for Hg^{2+} and 1.37 for Cu^{2+}. The ratio $I_{0(506)}/I_{(506)}$ was in the range of 1.00 - 1.16 for the other metal ions. The selectivity of iridium (III) complex **1** for the metal ions is graphically presented in Figure 4. Iridium (III) complex **1** shows a pronounced
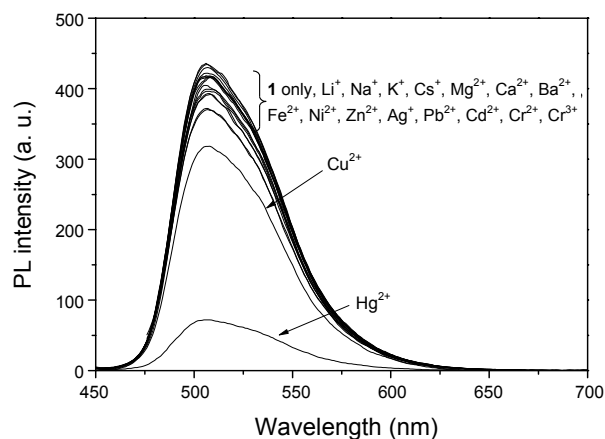
selectivity for Hg^{2+} (entry 18 in Figure 4) over the other metal ions. The presence of other metal ions was found not to interfere with the selectivity of iridium (III) complex **1** for Hg^{2+} (entries 19, 20, 21 and 22 in Figure 4).

The Job's plot experiment that was carried out by varying the concentration of both iridium (III) complex **1** and Hg^{2+} shows a maximum point at a mole fraction of 0.5, as shown in Figure 5. This result indicates the formation of the typical 1:1 (complex **1**: metal) complex.

The phosphorescence titration spectra of complex **1** upon the addition of various concentrations of anhydrous $Hg(ClO_4)_2$ in 50% acetonitrile in water was shown in Figure 6. Upon excitation at 400 nm, the phosphorescence maximum (506 nm) did not show any shift, and the emission intensity decreased continuously as the concentration of Hg^{2+} was increased. From the phosphorescence titration spectra shown in Figure 6, the association constant for Hg^{2+} was calculated to be 2.00×10^3 M^{-1} according to the Benesi-Hildebrand expression.[34,35]
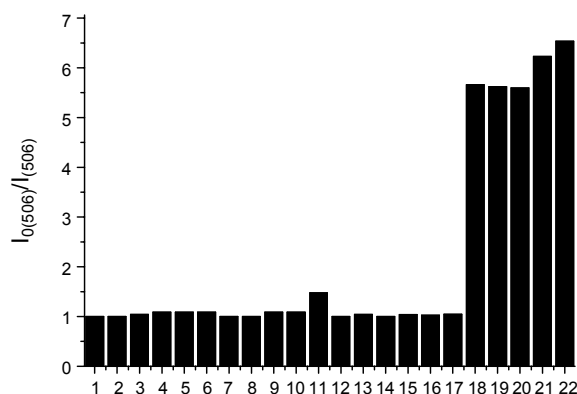
Figure 4. Relative emission intensities of iridium (III) complex **1** (20 μM), given as the ratio $I_{0(506)}/I_{(506)}$, upon the addition of different metal cations (100 equiv.) in 50 % acetonitrile in water: complex **1** only (1), Li^+ (2), Na^+ (3), K^+ (4), Cs^+ (5), Mg^{2+} (6), Ca^{2+} (7), Ba^{2+} (8), Fe^{2+} (9), Ni^{2+} (10), Cu^{2+} (11), Zn^{2+} (12), Ag^+ (13), Pb^{2+} (14), Cd^{2+} (15), Cr^{2+} (16), Cr^{3+} (17), Hg^{2+} (18), Hg^{2+} + X1 [K^+, Mg^{2+}, Ca^{2+}, Zn^{2+}, Ag^+, Fe^{2+}] (19), Hg^{2+} + X2 [Pb^{2+}, Li^+, Cs^+, Na^+, Ba^{2+}] (20), Hg^{2+} + 1 equiv. Cu^{2+} (21), Hg^{2+} + 10 equiv. Cu^{2+} (22).

Figure 2. Phosphorescence spectra of iridium (III) complex **1** (20 μM) upon addition of various metal ions (100 equiv.) in 50% acetonitrile in water (excitation: 400 nm).
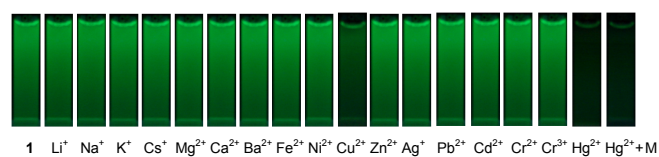

Figure 3. Visualized phosphorescent emission changes of iridium (III) complex **1** (20 M) upon addition of various metal ions (100 equiv.) in 50% acetonitrile in water. In the last entry (Hg^{2+} + M), M represents various other metal ions.
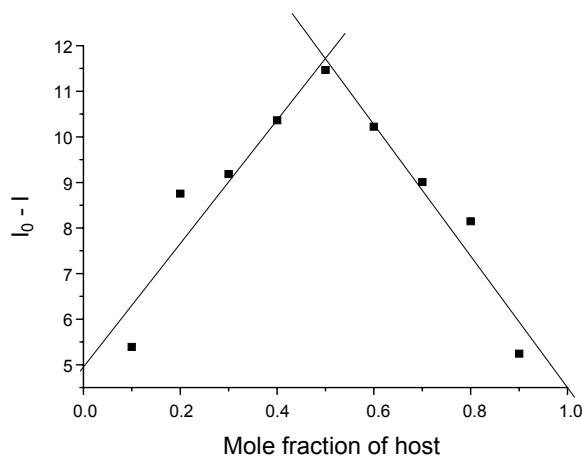

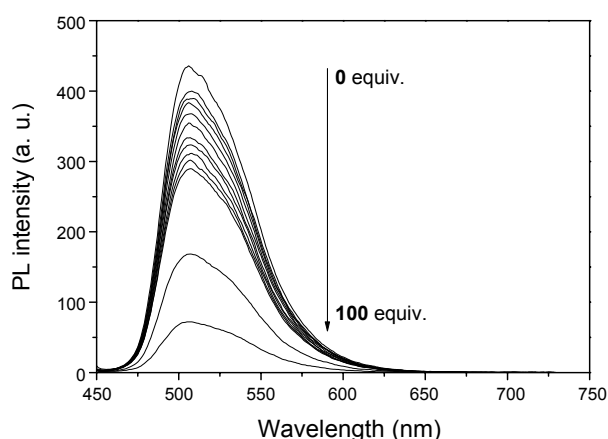**Figure 5.** Job's plot of complex **1** and Hg^{2+} in 50% acetonitrile in water.

Figure 6. Phosphorescence titration spectra of iridium (III) complex **1** (20 μM) upon addition of Hg^{2+} (20 μM, 40 μM, 60 μM, 80 μM, 100 μM, 120 μM, 140 μM, 160 μM, 180 μM, 200 μM, 1000 μM, 2000 μM) in 50% acetonitrile in water (excitation: 400 nm).
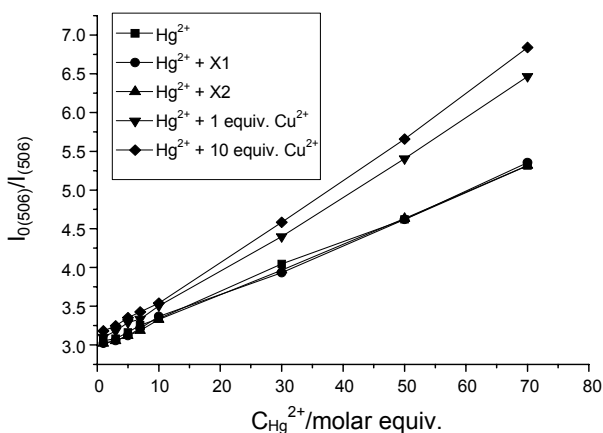

Figure 8. Phosphorescence spectra of complex **1** (20 μM) and complex **2** (20 μM) in the absence and presence of Hg^{2+} (100 equiv.) in 95% acetonitrile in water (excitation: 400 nm).

Figure 7. The linearity of the ratio I$_{0(506)}$/I$_{(506)}$ *vs.* the concentration of Hg^{2+} for the phosphorescence titration of Hg^{2+} with complex **1** (10 μM) in the absence (■), and presence of a mixture of K$^+$, Mg^{2+}, Ca^{2+}, Zn^{2+}, Ag$^+$, Fe^{2+} (X1, ●, 1.0 equiv. for each metal ion); in the presence of a mixture of Pb^{2+}, Li$^+$, Cs$^+$, Na$^+$, Ba^{2+} (X2, ▲, 1.0 equiv. for each metal ion); in the presence of 1.0 equiv. Cu^{2+} (▼); and in the presence of 10 equiv. Cu^{2+} (◆).

In the phosphorescence titration spectra of complex **1**, the ratio I$_{0(506)}$/I$_{(506)}$ was found to be linearly correlated with the concentration of Hg^{2+}, as shown in Figure 7. The addition of other metal ions, such as K$^+$, Mg^{2+}, Ca^{2+}, Zn^{2+}, Ag$^+$ and Fe^{2+} (X1) or Li$^+$, Cs$^+$, Na$^+$, Ba^{2+}, and Pb^{2+} (X2), was found to induce almost no changes in the linearity of the plot of the ratio I$_{0(506)}$/I$_{(506)}$ *vs.* the Hg^{2+} concentration. However, the addition of Cu^{2+} was found to enhance the ratio I$_{0(506)}$/I$_{(506)}$ slightly. These results indicate that other metal ions except for Cu^{2+} do not interfere with the determination of Hg^{2+} in aqueous acetonitrile media.

In order to elucidate the role of the appended azacrown ether moiety of iridium (III) complex **1**, iridium (III) complex **2** (Figure 8) was prepared by simply treating [(ppy)$_2$IrCl]$_2$ with picolinic acid and sodium carbonate in refluxing 2-ethoxyethanol *via* the previously reported procedure[36] and the spectroscopic behavior of iridium (III) complex **2** was compared to that of iridium (III) complex **1**. The UV-vis spectrum of iridium (III)
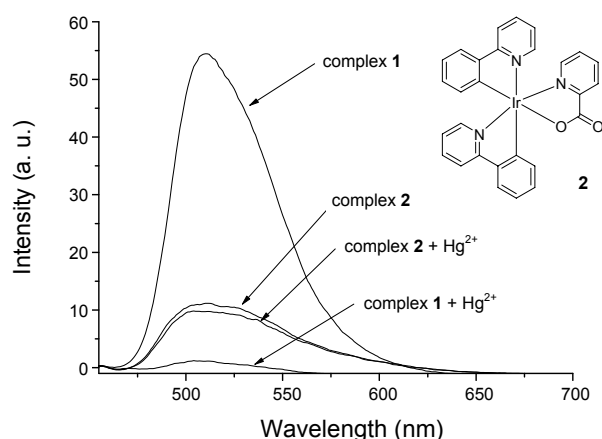
complex **2** in 50% acetonitrile in water was very similar to that of iridium (III) complex **1** and we attempted to obtain the phosphorescent emission of iridium (III) complex **2** in 50% acetonitrile in water with excitation at 400 nm. However, the phosphorescent emission of iridium (III) complex **2** with excitation at 400 nm was too weak to observe in 50% acetonitrile in water. However, when the acetonitrile content in water was increased, the emission of iridium (III) complex **2** became strong enough to be observable. The phosphorescent emission intensity of the azacrown appended iridium (III) complex **1** is shown to be about 5.5 times stronger than that of iridium (III) complex **2**, as seen in their emission spectra (Figure 8). The phosphorescence quenching behavior of iridium (III) complex **1** and iridium (III) complex **2** upon the addition of Hg^{2+} (100 equiv.) in 95% acetonitrile in water was investigated. As shown in Figure 8, iridium (III) complex **1** shows the significant quenching of its phosphorescence upon the addition of Hg^{2+} and the emission almost disappeared when 100 equiv. of Hg^{2+} was present in the solution. In contrast, iridium (III) complex **2** shows little or no quenching of its phosphorescence in the presence of 100 equiv. of Hg^{2+}. These observations indicate that the azacrown ether moiety in iridium (III) complex **1** enhances its phosphorescence emission efficiency in a significant manner and also plays an important role in the phosphorescence quenching of iridium (III) complex **1** by Hg^{2+} in aqueous acetonitrile media. The electron donating ability of the tertiary amino group of the azacrown ether moiety in iridium (III) complex **1** seems to be responsible for the enhancement of its phosphorescence intensity in aqueous acetonitrile media. The dramatic decrease in the phosphorescence emission of iridium (III) complex **1** in the presence of Hg^{2+} is thought to be due to both the decreased electron donating ability of the amino group of the azacrown ether through the effective complexation of Hg^{2+} with the azacrown ether ring and the possible heavy atom effect exerted by the resulting complexed Hg^{2+}. In this case, the enhancement of the intersystem crossing rate by the heavy atom effect seems to be greater in the thermal decay process of the phosphorescent triplet state to the ground state than its phosphorescent emissive decay to the ground state and intersystem crossing from the singlet excited state to the

triplet excited state. Both effects are lacking in the case of iridium (III) complex **2** without the tertiary amino containing azacrown ring and heavy metal ion Hg^{2+} complexation.

In summary, a new azacrown ether-appended iridium (III) complex (**1**) was prepared and its metal ion-selective phosphorescent chemosensing behavior was investigated. The new azacrown ether-appended iridium (III) complex (**1**) was found to show selective phosphorescence quenching for Hg^{2+} in 50% acetonitrile in water. The selective phosphorescence quenching for Hg^{2+} in 50% acetonitrile in water was linearly correlated with the concentration of Hg^{2+} in the range of 10 μM - 700 μM, even in the presence of other metal ions, except for Cu^{2+}. Consequently, the new azacrown ether-appended iridium (III) complex could be utilized for the detection of Hg^{2+} in aqueous acetonitrile media.

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