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Highly sensitive colorimetric phosphorescent chemodosimeter for Hg^{2+} based iridium(III) complex with $(Ph_2PS)_2N$ auxiliary ligand

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ABSTRACT

A colorimetric phosphorescent iridium(III) complex chemodosimeter (**Ir1**) for Hg^{2+} has been prepared and confirmed by NMR, MS, and crystal data, which displays a high selectivity and antidisturbance for Hg^{2+} detection among relevant metal ions. Phosphorescent studies show that the luminescence intensity at 598 nm decreased to ca. 12%, while the luminescence intensity in 441 nm increased to ca. 195%. The ratio of **Ir1** responding to Hg^{2+} was determined to be 1:1 by UV–vis absorption and phosphorescent emission measurements. Further study demonstrates that the detection limit on phosphorescent response of the sensor to Hg^{2+} is down to 10^{-6} M range. The mechanism study shows that the interaction between the S atom of ancillary ligand and Hg^{2+} is responsible for the highly selective and sensitive phosphorescent senor for Hg^{2+} . © 2012 Elsevier B.V. All rights reserved.

Mercury(II) is one of the most toxic ions known that lack any vital or beneficial effects. Accumulation of Hg^{2+} over time in the bodies of humans and animals can lead to serious debilitating illnesses and central nervous system damages [1,2]. Therefore, the development of increasingly selective and sensitive methods for the detection of Hg^{2+} is currently receiving considerable attention [3–6]. Comparing to cold vapor atomic absorption spectroscopy or inductively coupled plasma mass spectroscopy, optical methods are more amenable to the on-site analysis of mercury with fewer resources [7]. Numerous fluorescent chemosensors and chemodosimeters have been reported in the literature [8,9]. Some of them were successfully applied to real samples and in biological settings with low concentrations of mercury ions [10–12].

A cyclometalated iridium(III) complex-based sensor is a promising alternative to detect Hg^{2+} for its excellent properties, such as their relatively short excited state lifetime, high photoluminescence efficiency and excellent color tuning [13]. Recently, Li et al. have exploited and demonstrated a series of iridium(III) complexes for the detection of heavy and transition metal ions. The sulfur atoms are introduced to these cyclometalated ligands by the "receptor-conjugated signaling unit approach" and the final iridium(III) complexes show a selective recognition for Hg^{2+} with multisignaling optical–electrochemical response [13–17]. A new sensory system based on the energy-transfer process between rhodamine and iridium complex has been used for the detection of Hg^{2+} [18]. A phosphorescent chemodosimeter for Hg^{2+} was also realized by an anionic iridium(III) complex containing the thiocyanate group [19]. However, there are still needs to develop simple and effective iridium(III) complex-based chemosensors with different methodologies.

In this article, a new iridium(III) bis-cyclometalated complex with bis(diphenylthiophosphoryl)amide auxiliary ligand has been synthesized and its application for mercury ion detection has been explored. Because mercury is a soft Lewis acid, the interaction of Hg^{2+} with the bis(diphenylthiophosphoryl)amide ancillary ligand can induce the dissociation of the ancillary ligand from the complex **Ir1**, which provides a new strategy for the detection of Hg^{2+} .

The neutral cyclometalated iridium(III) complex **Ir1** was readily prepared from the Ir^{III}- μ -chloro-bridged dimer and K[(Ph₂PS)₂N] at room temperature (Scheme 1). This complex was characterized by the MS and NMR spectroscopy. According to our previous research, the cyclometalated ligands hydrolyzed partially during the refluxing reaction of the ligands and IrCl₃·3H₂O [20].

The structure of **Ir1** has been further confirmed by X-ray crystallography. As shown in Fig. 2, the complex has distorted octahedral coordination geometry around iridium center by two cyclometalated ligands and one S,S-bidentate ligand with *cis*-C–C and *trans*-N–N dispositions. The Ir–C bond lengths – ranging from 2.019(6) to 2.029(6) Å – are close to the Ir–N bond distances spanning from 2.020(5) to 2.031(5) Å. The bond lengths between Ir center and the S,S-bidentate ligand are ranging from 2.4776(19) to 2.492(2) Å, which are longer than that between the Ir center and the cyclometalated ligands. It is because of stronger donating and back-bonding interactions between aryl groups and the iridium atom. The conformation of the six-membered IrS₂P₂N ring is described as a twisted boat imposed by the non-parallel orientation of the two P–S bonds [21]. Furthermore, the C–C and C–N bond lengths and angles are also within normal ranges and are in agreement

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Scheme 1. Synthesis route to iridium(III) complex Ir1.

with corresponding parameters described for similarly constituted complexes [22,23].

Fig. 1 shows the absorption and photoluminescence spectra of the iridium(III) complex **Ir1** in CH₃CN solution at room temperature. The strong absorption bands between 220 nm and 330 nm in the ultraviolet region areas are assigned to the spin-allowed π - π * transition of the ligands, and the broad absorption bands spanning from 330 nm to 570 nm can be attributed to the typical spin-allowed and spin-forbidden metal-to-ligand charge transfer bands (MLCT).

On irradiation with 385 nm light, the PL spectrum of **Ir1** exhibits an orange emission band at 600 nm and a weak blue emission at 441 nm. The orange emission can be assigned to the emission of cyclometalated iridium(III) center and the blue emission to ancillary ligand. This implies that energy transfer from the ancillary ligand to the cyclometalated iridium(III) center is not complete.

3.3. The UV-vis absorption spectroscopy response of $\mathbf{lr1}$ to Hg^{2+} and other metal ions.

To evaluate the metal ion-selective nature of **Ir1**, the influence of 2 equivalents of different metal cations $(Hg^{2+}, Ag^+, Cu^{2+}, Fe^{3+}, Co^{2+},$



Fig. 1. Perspective view of Ir1 with selected displacement ellipsoids drawn at the 25% probability level. H atoms omitted.

Ni²⁺, Zn²⁺, Mg²⁺, Cr³⁺, Pb²⁺ and Cd²⁺) was investigated with UVvis absorption spectroscopy (Fig. 3(a)). As shown in Fig. 3(a), Hg²⁺ has a pronounced effect on the spectra of **Ir1**, the peak at 357 nm blue shifting to 334 nm. The other metal ions gave inconsiderable disturbance to the UV-vis absorption spectra of **Ir1**. These results indicate that **Ir1** has a high selectivity to Hg²⁺. At the same time, the color of the solution changed from orange to light yellow (Fig. 3(a) inset) as soon as Hg²⁺ was added, but no change occurred in the presence of other metal ions, indicating that **Ir1** can serve as a sensitive "naked-eye" indicator for Hg²⁺.

In order to explore the quantitative interrelation of **Ir1** with Hg²⁺, the changes in UV–vis absorption spectra (Fig. 3(b)) were investigated by titration experiments. Upon addition of Hg²⁺ to **Ir1**, the absorption bands of **Ir1** at longer than 355 nm gradually decreased, and a new band centered at 334 nm starts to develop with a distinct isosbestic point at 355 nm, indicating strong interactions between **Ir1** and the Hg²⁺. The stoichiometry of **Ir1** is given by the variation of $A_{390 nm}$ with respect to equivalents of Hg²⁺ added (Fig. 3(b) inset). Effectively, $A_{390 nm}$ decreases continuously until the addition of 1 equivalent of Hg²⁺. Further addition of Hg²⁺ induces only very minor changes in $A_{390 nm}$, indicating that **Ir1** has a 1:1 interaction with Hg²⁺.

The luminescence emission spectroscopy is more sensitive to the interaction between chemodosimeter and analyte than absorption spectroscopy in general [11]. Photoluminescence responses of **Ir1** to two equivalent different metal cations (Hg^{2+} , Ag^+ , Cu^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Mg^{2+} , Cr^{3+} , Pb^{2+} and Cd^{2+}) show that Hg^{2+} induces the strongest emission changes (Fig. 4(a)), and the luminescence intensity in 598 nm decreased to ca. 12%, while the luminescence intensity in 441 nm increased to ca. 195%. However, no discernible change is observed for all other metal ions, i.e., Ag^+ , Cu^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Mg^{2+} , Cr^{3+} , Pb^{2+} and Cd^{2+} . The photoluminescence responses of **Ir1** upon addition indicate a fairly high selectivity and sensitivity chemodosimeter for Hg^{2+} .

The emission spectra titration of Ir1 with Hg^{2+} was also measured. It can be seen from Fig. 4(b) that the emission increases continuously until the addition of 1 equivalent of Hg²⁺ and the luminescence intensity in 598 nm decreased to ca. 12%, while the luminescence intensity in 441 nm increased to ca. 195%. Further addition induces only very minor change, which is consistent with the UV-vis absorption result. The linear response of the fluorescence emission intensity in 598 nm toward $[Hg^{2+}]$ was obtained in Hg^{2+} concentration range of 0 to 100 μ M, indicating that the probe Ir1 can detect quantitatively relevant concentrations of Hg²⁺. The linear equation was found to be y = -8.79x + 989(R = -0.988), where y is the fluorescence at 598 nm measured at a given Hg^{2+} concentration (μ M) and x is the concentration of Hg^{2+} added. The limit of detection defined here as the concentration equivalent to a signal of blank plus three times the standard deviation of the blank was calculated to be 1.2 µM, which was close to the reported values of iridium complex probe (10^{-7} M) [13]. In addition, the reaction was fairly fast and the emission intensity was changeless within 2 min.



Fig. 2. UV-vis absorption and photoluminescence spectra of the complex Ir1.

To explore practical applicability of **Ir1** as an Hg^{2+} selective chemodosimeter, a competition experiment was done. As shown in Fig. 5, in the absence and in the presence of competitive cations, **Ir1** showed similar luminescence changes to Hg^{2+} ions except that the existence of Ni²⁺ slightly increased the last luminescence intensity ratio of 441 nm to 598 nm to ca. 130% than blank and the existence of Cu^{2+} slightly decreased the ratio to ca. 80%. As a whole, these results indicate that the selectivity of **Ir1** for Hg^{2+} over other cations was high and **Ir1** had the potential capacity in application.

The proposed mechanism for the selective and sensitive response of **Ir1** to Hg^{2+} is shown in Scheme 2. The distinct orange emission decrease and the blue emission enhancement of **Ir1** after the addition of Hg^{2+} can be deduced that ligand exchange reactions have occurred. This phenomenon could be explained by the properties that Hg^{2+} (soft acid) can preferentially interact with sulfur (soft base) according to Pearson's hard and soft acid and base theory [24]. This mechanism was proved by the ESI-MS spectrum of the mixture of **Ir1** and $Hg(ClO_4)_2$ in ACN solutions (Fig. S1). The peak of **Ir1** (1187) disappeared, and the peaks of [Ir(ppa)(dmppa)]⁺ (739) and [Hg((Ph_2PS)_2)N]⁺ (650) appeared. The reaction between Hg^{2+} and **Ir1** led to a significant change of the optical signals.

In conclusion, we have demonstrated that a neutral cyclometalated iridium(III) complex, Ir(ppa)(dmppa)((Ph₂PS)₂N), containing bis(diphenylthiophosphoryl)amide ligand can serve as a highly selective chemodosimeter for Hg^{2+} . The interaction between the S atom of bis(diphenylthiophosphoryl)amide leaving group and Hg^{2+} is responsible for the highly selective and sensitive phosphorescent senor for Hg^{2+} . This work showed that new phosphorescent probes based on iridium(III) complexes could be realized by using the auxiliary ligand containing S atoms. This work would be very useful to the design of novel phosphorescent probes based on iridium(III) complexes.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2012.11.014.

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Fig. 3. The UV-vis absorption spectra of Ir1 in the presence of 2 equivalents of different metal ions (a) and changes on addition of Hg²⁺ (b).

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Fig. 4. Luminescence emission spectra of Ir1 (λ_{ex} = 385 nm) in the presence of 2 equivalents of different metal ions (a) and the changes in the emission spectra of Ir1 with various amounts of Hg²⁺ (b).



Fig. 5. Luminescence responses of **Ir1** to various metal ions in DMF solution (λ_{ex} = 385 nm). Bars represent the final luminescence intensity at 598 nm. White bars represent the addition of 2 equivalents of metal ions (Ag⁺, Fe²⁺, Co²⁺, Cd²⁺, Cr³⁺, Cu²⁺, Zn²⁺, Pb²⁺, Ni²⁺, Mg²⁺ and blank) to the **Ir1** solution. Black bars represent the subsequent addition of 2 equivalents of Hg²⁺ to the solution.



Scheme 2. Proposed mechanism of the sensing reaction.