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A highly selective chemosensor for mercury(II) cations based on cyclometalated iridium(III) complex

Bihai Tong [a,b], Qunbo Mei [c], Mangeng Lu [a,*]

[a] Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou 510650, PR China
[b] College of Metallurgy and Resources, Anhui University of Technology, Ma'anshan, Anhui 243002, PR China
[c] Key Laboratory for Organic Electronics & Information Displays (KLOEID), Institute of Advanced Materials (IAM), Nanjing University of Posts & Telecommunications (NUPT), Nanjing 210046, PR China

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ABSTRACT

A cyclometalated iridium(III) complex, Ir(dpci)$_2$(dtc) (**Ir1**, dpci = 3,4-diphenylcinnoline, dtcH = diethyl dithiocarbamic acid), was synthesized from the reaction of the iridium complex [Ir(dpci)$_2$(Cl)]$_2$ and dtcNa in methanol/CH$_2$Cl$_2$, and characterized by FT-IR, ^{1}H NMR and mass spectroscopies. The photoluminescence spectrum of **Ir1** shows emission maximum at 686 nm with a lifetime of 0.77 µs and PL quantum yields is ca. 0.021. Moreover, [Ir(dpci)$_2$(dtc)], containing a dithiocarbamate ancillary ligand, can serve as a highly selective turn-on chemodosimeter for Hg^{2+}, which is associated with the dissociation of the dithiocarbamate ancillary ligand from the complex.

1. Introduction

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 [1,2]. Therefore, the development of increasingly selective and sensitive methods for the detection of Hg^{2+} is currently receiving considerable attention [3–5]. Luminescent chemosensors for Hg^{2+} provide an effective and convenient approach [6–9]. The fluorescence enhancement (off–on signal) induced by complexation with heavy and transition metal ions is more desirable than fluorescence quenching (on–off signal) in terms of increased sensitivity and selectivity [10]. However, the development of off–on fluorescent probes for heavy and transition metal ions remains a significant challenge, because many of these ions are typical fluorescence quenchers by reason of their paramagnetic nature and the heavy atom effect [11].

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 [12]. Recently, Li and co-workers 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 [12–16]. A new sensory system based on the energy-transfer process between rhodamine and iridium complex has been used for the detection of Hg^{2+} [17]. A phosphorescent chemodosimeter for Hg^{2+} was also realized by an anionic iridium(III) complex containing the thiocyanate group [18]. However, the performance of these iridium(III) complex-based chemosensors is still limited to the "turn-off" response to Hg^{2+}. This issue necessitates the development of new cyclometalated iridium(III) complex sensor that can selectively respond to Hg^{2+} with "turn-on" phosphorescent signals.

Iridium(III) bis-cyclometalated complexes with dithionate ligands have been synthesized by several research groups, and also been applied as phosphors in organic light emitting diodes (OLEDs) [19–22], but their potential application for heavy and transition metal ions detection has never been explored. In our previous reports, iridium(III) complexes based on dpci ligand exhibited good photoluminescent and chemiluminescent properties [23,24]. Herein, we report on a "turn-on" phosphorescent chemosensor for Hg^{2+} based on a neutral iridium(III) complex, Ir(dpci)$_2$(dtc) (**Ir1**), containing dithiocarbamate ancillary ligands. The interaction of Hg^{2+} with the dithiocarbamate ancillary ligand can induce the dissociation of the ligand from the complex **Ir1**, which provides a new strategy for the detection of Hg^{2+}.

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* Corresponding author. Tel./fax: +86 20 85232978.
E-mail address: mglu@gic.ac.cn (M. Lu).

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2. Experimental

2.1. Materials and characterization

The solvents were purified by routine procedures and distilled under an atmosphere of dry nitrogen before use. All reagents, unless otherwise specified, were purchased from Aldrich and were used as received. 3,4-Diphenylcinnoline was prepared according to procedures described in the literature [25]. The infrared spectrum was recorded on a Digilab FTS-40 spectrophotometer with use of pressed KBr pellets. UV–Vis absorption spectra were recorded on a Shimadzu UV-2501 PC spectrophotometer. Positive-ion ESI mass spectra were recorded on a Perkin Elmer Sciex API 365 mass spectrometer. ^{1}H NMR spectra were recorded on a Varian Inova 300NB spectrometer using $CDCl_3$ as solvent. Photoluminescence (PL) spectra were measured with a Shimadzu RF-5301PC fluorescence spectrophotometer. Fluorescence quantum yield of the complexe was calculated using $[Ru(bpy)_3]Cl_2$ in aqueous solution ($\Phi = 0.042$) as a standard [26]. Luminescence lifetime was determined on an Edinburgh FL920 time-correlated pulsed single-photon-counting instrument with excitation at 405 nm and the emission was monitored at 686 nm.

2.2. Synthesis of $Ir(dpci)_2(dtc)$ (dpci = 3, 4-diphenylcinnoline, dtcH = diethyl dithiocarbamic acid) (**Ir1**)

The synthetic route to $Ir(dpci)_2(dtc)$ is given in Scheme 1.

To a round-bottomed flask (25 mL), 2-ethoxyethanol (9 mL), 3,4-diphenylcinnoline (0.5 g, 2.0 mmol), $IrCl_3 \cdot 3H_2O$ (0.2 g, 0.56 mmol) and water (3 mL) were added sequentially. The mixture was stirred under nitrogen at 120 °C for 24 h and cooled to room temperature. The precipitate was collected and washed with ethanol and acetone, and then dried in vacuum to give a dark red cyclometalated Ir^{III}-μ-chloro-bridged dimer (0.36 g, 81.3%).

In a round-bottomed flask, (0.08 g, 0.05 mmol) of dichloro-bridged iridium dimer and (0.03 g, 0.2 mmol) of sodium *N,N*-diethyl-dithiocarbamate (Nadtc) were mixed together in CH_2Cl_2/methanol (5:5 mL). The mixture was stirred at room temperature for 1 h. The product was precipitated from water and dried in desiccator. Dark red solid of $Ir(dpci)_2(dtc)$ (**Ir1**) was obtained from column chromatography on a silica column using CH_2Cl_2 and hexane (1:1) as eluent, 0.071 g, yield: 79%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.31 (t, $J = 7.1$ Hz, 6H), 3.28–3.35 (q, $J = 7.1$ Hz, 2H), 4.02–4.09 (q, $J = 6.8$ Hz, 2H), 6.34–6.40 (m, 6H), 6.55 (t, $J = 7.3$ Hz, 2H), 7.44 (d, $J = 6.9$ Hz, 2H), 7.49 (d, $J = 6.6$ Hz, 2H), 7.54–7.63 (m, 10H), 7.75 (t, $J = 7.3$ Hz, 2H), 8.48 (d, $J = 8.5$ Hz, 2H). *Anal.* Calc. for $C_{45}H_{36}N_5S_2Ir$: C, 59.84; H, 4.02; N, 7.75. Found: C, 59.74; H, 3.99; N, 7.81%. MS ((+)-ESI): $m/z = 904$ ($M+H^+$).

2.3. Metal ions titration of **Ir1**

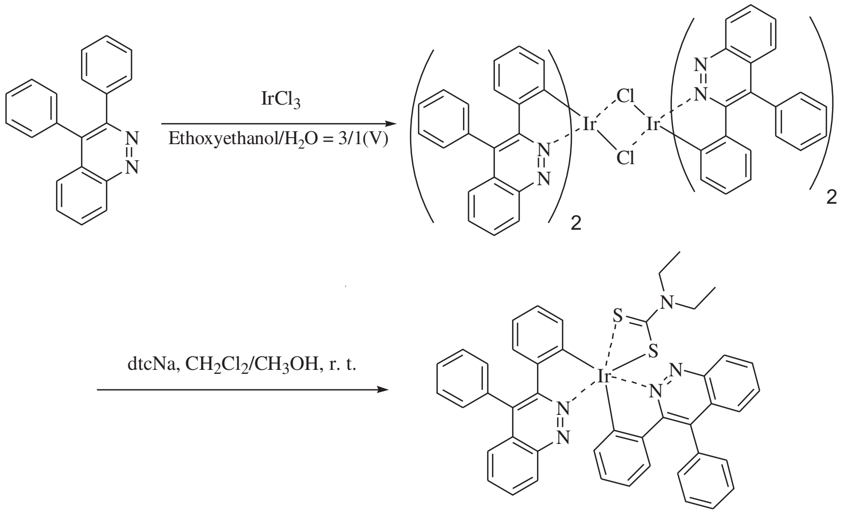
The UV–Vis absorption and luminescence emission spectrophotometric titrations were performed on 100 μM solutions of **Ir1** in DMF (*N,N*-dimethyl formamide). Typically, the aqueous solutions of fresh cations (Ag^+, Cu^{2+}, Co^{2+}, Cr^{3+}, Zn^{2+}, Mg^{2+}, Pb^{2+}, Ni^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Cd^{2+}) and THF solution of Hg^{2+} were used to evaluate the metal ion binding property and selectivity of **Ir1**. $Hg(ClO_4)_2$, $AgNO_3$, $FeSO_4$ and chlorides of the other cations were used as the cation source. The luminescence emission spectra were determined with excitation at 450 nm.

3. Results and discussion

3.1. Photophysical properties

UV–Vis absorption spectrum of the iridium(III) complex **Ir1** is shown in Fig. 1(a). The band around 294 nm is assigned to a typical spin-allowed $^1\pi$–π^* transition of the ligands, and band at 424 nm correspond likely to spin-allowed singlet metal-to-ligand charge-transfer (^{1}MLCT). On the other hand, the moderately intense absorptions at ca. 500–600 nm can be assigned to a spin-forbidden triplet metal-to-ligand charge-transfer (^{3}MLCT).

The room temperature photoluminescence spectra of the iridium(III) complex **Ir1** in CH_2Cl_2 solution are shown in Fig. 1(b and c). The excitation spectrum is dominated by a broad band centered at 373 nm, which is the absorption arising from the ^{1}MLCT and ^{3}MLCT states. The iridium(III) complex **Ir1** emit intense luminnescence with emission wavelength at 686 nm, corresponding to deep red light emitting. The excited state lifetime of the iridium(III) complex **Ir1** was determined to be 77 ns, remarkably shorter than those of $[Ir(Flpy)_3]$ (H(Flpy) = 2-(9,9-dimethylfluoren-2-yl)pyridine) (1.2 μs) [27] and most of the other reported neutral iridium complexes. The phosphorescence quantum efficiency in CH_2Cl_2



Ir1

Scheme 1. Synthetic route to $[Ir(dpci)_2(dtc)]$ (**Ir1**).

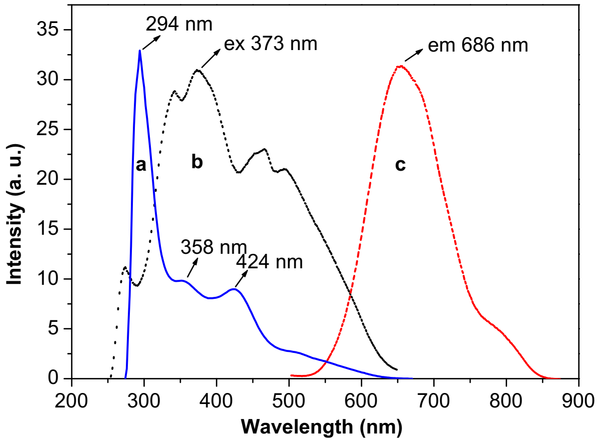


Fig. 1. UV–Vis absorption (a) and luminescence (b, ex.; c, em.) spectra of **Ir1** in CH_2Cl_2.

solution is ca. 0.021 used an aqueous solution of $[Ru(bpy)_3]Cl_2$ ($\Phi = 0.042$) as the standard solution [26].

3.2. The UV–Vis absorption spectroscopy response of **Ir1** to Hg^{2+} and other metal ions

To evaluate the metal ion-selective nature of **Ir1**, the influence of 2 equiv. of different metal cations (Hg^{2+}, Ag^+, Cu^{2+}, Fe^{2+}, Fe^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Mg^{2+}, Cr^{3+}, Pb^{2+} and Cd^{2+}) was investigated with UV–Vis absorption spectroscopy (Fig. 2(a)). As shown in Fig. 2(a), Hg^{2+} has a pronounced effect on the spectra of **Ir1**, the peak at 424 nm blue shifting to 400 nm. Except Ag^+ which has a week influence, resulting in a small blue shift, the other metal ions gave nearly no disturbance to the UV–Vis absorption spectra of **Ir1.** These results indicate **Ir1** has a high selectivity to Hg^{2+}.

In order to explore the quantitative interrelation of **Ir1** with Hg^{2+}, the changes in UV–Vis absorption spectra (Fig. 2(b)) were investigated by titration experiments. Upon addition of Hg^{2+} to **Ir1**, the absorption bands of **Ir1** at ca. 421–600 nm gradually decreased, and a new band centered at 400 nm start to develop with a distinct isosbestic point at 421 nm, indicating strong interactions between **Ir1** and the Hg^{2+}. The stoichiometry of **Ir1** is given by the variation of A_{450nm} with respect to equivalents of Hg^{2+} added (Fig. 2(b) inset). Effectively, A_{450nm} decreases continuously until the addition of 1 equiv. of Hg^{2+}. Further addition of Hg^{2+} induces only very minor changes in A_{450nm}, indicating that **Ir1** has a 1:1 interaction with Hg^{2+}.

3.3. The luminescence emission spectroscopy response of **Ir1** to Hg^{2+} and other metal ions

The luminescence emission spectroscopy is more sensitive to the interaction between chemosensor and analyte than absorption spectroscopy in general [11]. Photoluminescence responses of **Ir1** to two equivalent different metal cations (Hg^{2+}, Ag^+, Cu^{2+}, Fe^{2+},

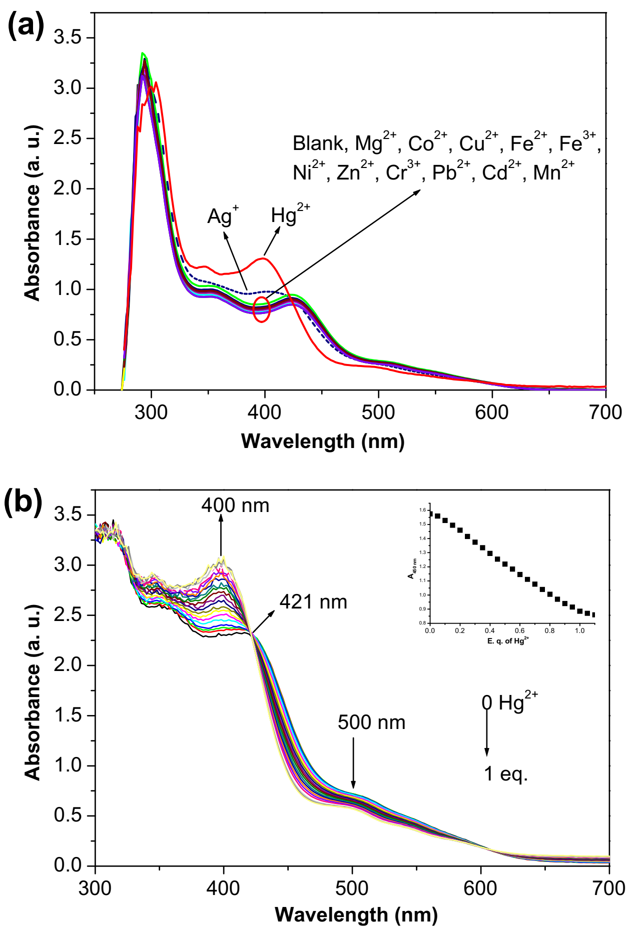


Fig. 2. UV–Vis absorption spectra of **Ir1** in the presence of 2 equiv. of different metal ions (a) and the changes in the UV–Vis absorption spectra of Ir1 with various amounts of Hg^{2+} (b).

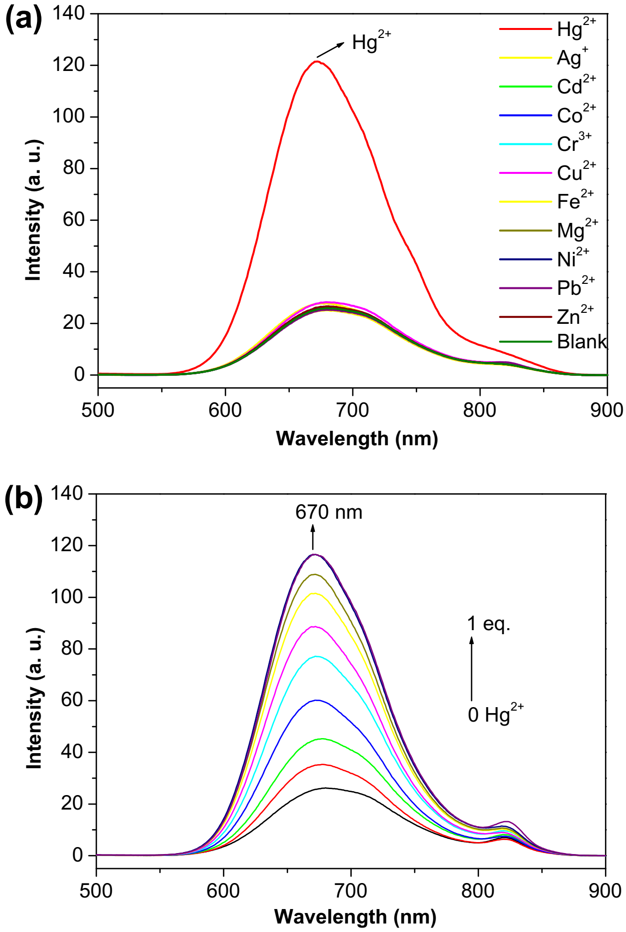


Fig. 3. Luminescence emission spectra of Ir1 in the presence of 2 equiv. of different metal ions (a) and the changes in the emission spectra of **Ir1** with various amounts of Hg^{2+} (b).

Co^{2+}, Ni^{2+}, Zn^{2+}, Mg^{2+}, Cr^{3+}, Pb^{2+} and Cd^{2+}) show that Hg^{2+} induce the strongest emission changes, and the luminescence intensity in 686 nm of **Ir1** increased to ca. 474%, and the max emission wavelength blue shift to 670 nm. But no discernible change is observed for all other metal ions, i.e. Ag^{+}, Cu^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Mg^{2+}, Cr^{3+}, Pb^{2+} and Cd^{2+} (Fig. 3(a)). The photoluminescence responses of **Ir1** upon addition indicate a fairly high selectivity and sensitivity for Hg^{2+}.

The emission spectra titration of **Ir1** with Hg^{2+} was also measured. It can be seen from Fig. 3(b) that the emission increases continuously until the addition of 1 equiv. of Hg^{2+} and the luminnescence intensity in 686 nm of **Ir1** increased to ca. 474%, and the maximum emission wavelength blue shift to 670 nm. Further addition induces only very minor change, which is consistent with the UV–Vis absorption result. The linear response of the fluorescence emission intensity toward $[Hg^{2+}]$ was obtained in Hg^{2+} concentration range of 0 to 10×10^{-5} M, indicating the probe **Ir1** can detect quantitatively relevant concentrations of Hg^{2+}. The linear equation was found to be $y = 0.84x + 25.92$ ($R = -0.988$), where y is the fluorescence at 686 nm measured at a given Hg^{2+} concentration (μM) 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 1.6 μM, which was close to the reported values of iridium complex probe (10^{-7} M) [12]. In addition, the reaction was fairly fast and the emission intensity was changeless within 3 min. Generally, cyclometalated iridium(III) complexes have the character of lower cytotoxicity [28], so this probe is potentially suitable for the real-time tracking of Hg^{2+} in organisms.

To explore practical applicability of **Ir1** as a Hg^{2+} selective chemosensor, a competition experiment was done. As shown in Fig. 4 (Bars represent the final luminescence intensity at 686 nm. White bars represent the addition of 15 equiv. of metal ions (Ag^{+}, Fe^{2+}, Co^{2+}, Cd^{2+}, Cr^{3+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Ni^{2+}, Mg^{2+} and blank) to the **Ir1** solution. Black bars represent the subsequent addition of 2 equiv. of Hg^{2+} to the solution.), in the absence and in the presence of competitive cations, **Ir1** showed similar luminescence changes to Hg^{2+} ions, but the large excessive of Ag^{+} had also increased the luminescence intensity of **Ir1** to ca. 225%. All these results indicate that the selectivity of **Ir1** for Hg^{2+} over other cations was high.

The proposed mechanism for the selective and sensitive response of **Ir1** to Hg^{2+} is shown in Scheme 2. In the presence of heavy atom substituted quenchers, the internal heavy atom effects (due to the presence of S atom in the **Ir1**) are responsible for the weak luminescence intensity. Therefore the distinct emission enhancement of iridium(III) complex **Ir1** after the addition of Hg^{2+} can be deduced that a desulfurization reaction have occured. This phenomenon could be explained by the properties that Hg^{2+}

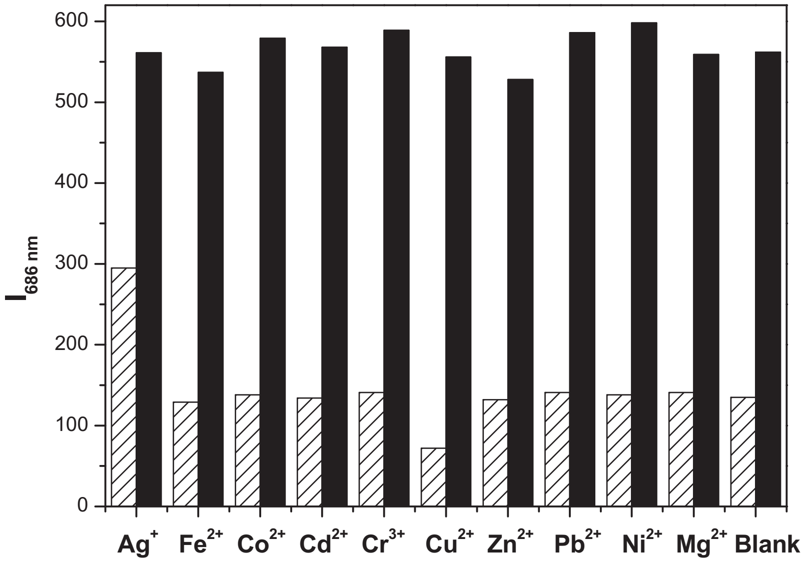
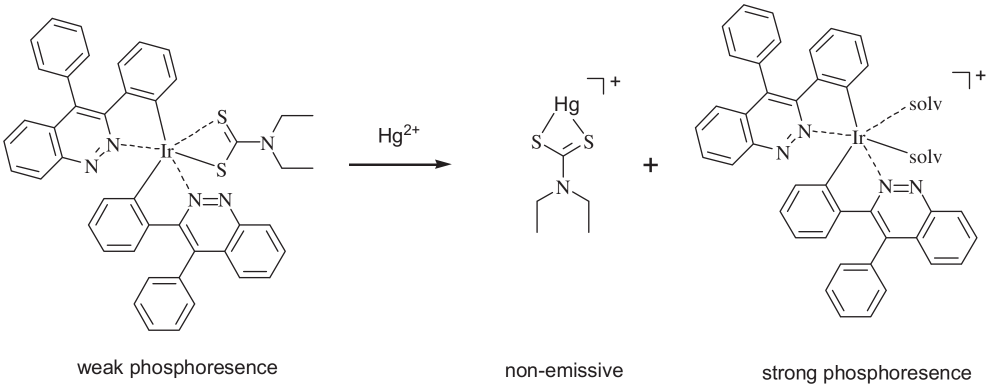


Fig. 4. Luminescence responses of **Ir1** to various metal ions in DMF solution (λ_{ex} = 450 nm).



Scheme 2. Proposed mechanism of the sensing reaction.

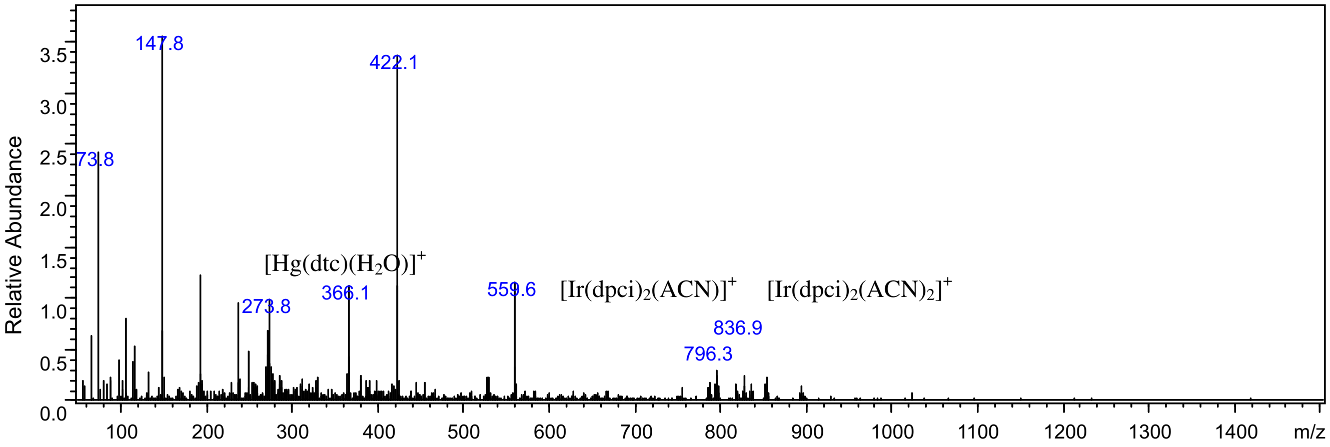


Fig. 5. ESI mass spectra of the mixture of **Ir1** and $Hg(ClO_4)_2$ in ACN solution.

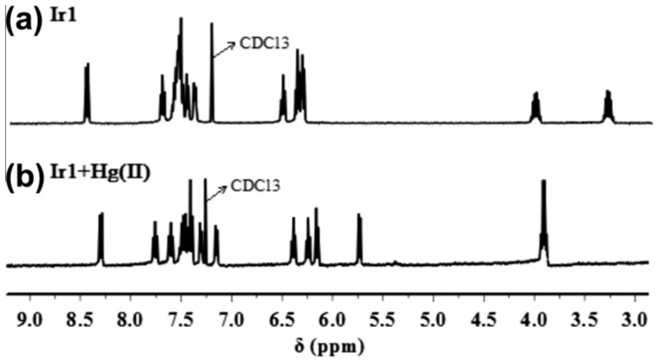


Fig. 6. ^1H NMR spectra (in $CDCl_3$) of **Ir1** and the mixture of **Ir1** and $Hg(ClO_4)_2$ in ACN solution.

(soft acid) can preferentially interact with sulfur (soft base) according to Pearson's hard and soft acids and bases theory [29]. This mechanism was proved by the ESI-MS spectrum of the mixture of **Ir1** and $Hg(ClO_4)_2$ in ACN solution (Fig. 5). The peak of **Ir1** (904) disappeared, and the peaks of $[Ir(dpci)_2(ACN)_2]^+$ (837), $[Ir(ddp)_2(ACN)]^+$ (796) and $[Hg(dtc)(H_2O)]^+$ (366) appeared. ^1H NMR titration experiment was also carried to confirm the detection mechanism (Fig. 6). The reaction between Hg^{2+} and **Ir1** led to a significant change of the optical signals.

4. Conclusions

In conclusion, we have demonstrated for the first time that a neutral cyclometalated iridium(III) complex, $Ir(dpci)_2(dtc)$, containing dithiocarbamate ligand can serve as a highly selective "turn on" chemosensor for Hg^{2+}. The interaction between the S atom of dithiocarbamate 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 with specific leaving ability. This work would be very useful to the design of novel phosphorescent probes based on iridium(III) complexes.

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