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ARTICLE TYPE

Sulfur-free iridium(III) complex for highly selective and multi-signaling mercury(II)-chemosensor

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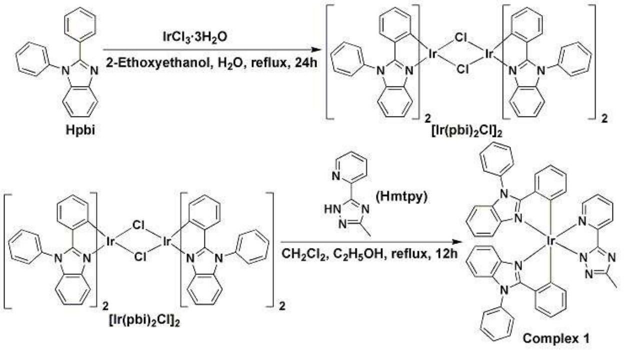
A sulfur-free iridium(III) complex $(pbi)_2Ir(mtpy)$ (**1**) was successfully prepared and adopted as a Hg(II)-chemosensor with high selectivity and sensitivity. Multi-signaling responses towards Hg(II) ions were observed by UV−vis absorption, phosphorescence and electrochemistry measurements. With addition of Hg(II) ions, complex **1** presented quenched emission in its phosphorescence spectrum and the detection limit was as low as 2.5×10^{-7} M. Additionally, its redox peak currents showed a broad linear relationships with the concentration of Hg(II) ions ranged from 0 to 500 μM, which was beneficial to the quantitative detection. Based on the ^{1}H NMR and ESI-MS analyses, the probing mechanism was tentatively supposed to be the Hg^{2+}-induced changes in local environment of complex **1**. Such response process was useful for achieving simple and effective detection of Hg(II) ions as well as developing more chemosensors.

Introduction

Mercury is considered to be a dangerous global pollutant that results in serious health and environmental problems even if its content is very low.[1] Hence, it is important to develop accurate method to detect trace amounts of Hg(II) ions. To date, a number of chemosensors in detecting Hg(II) ions have been achieved through utilizing chromogentic,[2] fluorogenic[3] and electrochemical behaviors.[4] Among these monitoring methods, fluorescent probes offer an intriguing future for rapid and facile detection due to their significant role in the signal processing and communication of a sensor network.[1b,5]

Up to now, many pure organic fluorophores as chemosensors to detect Hg(II) ions have been successfully reported.[6] In comparison with pure organic fluorophores, phosphorescent heavy-metal complexes possess some advantages such as relatively longer emission lifetimes for eliminating fluorescent backgrounds and larger Stoke's shifts for easy identification of emission spectra from excitation ones.[7] As a result, phosphorescent chemosensors based on heavy-metal complexes have aroused great interest. Among them, iridium(III) complexes are drawing more extensive attention due to their easy tunability of emission wavelength and high luminescence efficiencies.[7c,8] Many iridium(III) complexes are thus utilized as chemosensors for detection of Hg(II) ions. For instance, Li *et al.* adopted $Ir(btp)_2(acac)$ as the first example of neutral iridium complexes as phosphorescent chemosensor for Hg(II) ions.[9] Subsequently, more iridium complexes including ionic and polymeric species were developed as chemosensors in detecting Hg(II) ions.[1b,10] For example, Shi *et al.* used simple conjugated polymers based on iridium(III) complexes to successfully detect trace amounts of Hg(II) ions.[1b] The detection sensitivity of such polymer chemosensors was as low as 0.5 μg L^{-1} (ppb). Nevertheless, although these iridium(III) complexes-based chemosensors have been achieved, there remain several problems in developing phosphorescent chemosensors for detection of Hg(II) ions. Firstly, most reported Hg(II)-responding iridium(III) complexes mainly adopt thia-heterocycles in their cyclometallate ligands.[10b] This is due to the fact that the presence of a soft donor like sulfur atoms in chemosensors is commonly an appealing factor for the Hg(II)-induced optical response.[11] As a soft acid, Hg(II) ions may preferentially interact with sulfur atoms through coordinational bonding. However, in this sulfur-containing compound system, more attention should be paid to avoiding the pollution or damage when dealing with the sulfide crude material. In addition, developing sulfur-free iridium(III) complex can enrich the molecular structure of chemosensors. Secondly, the single detection method in chemosensors cannot provide high detection accuracy or sensitivity compared with that utilizing multiple signals.[12] Consequently, exploiting multisignaling chemosensors based on iridium(III) complexes that possess both optical and electrochemical sensing behaviors to Hg(II) ions is highly desirable.[10b,12a,13]

Herein, we synthesized sulfur-free iridium(III) complex $(pbi)_2Ir(mtpy)$ (**1**) with 1,2-diphenyl-1*H*-benzoimidazole (Hpbi) and 2-(5-methyl-2*H*-1,2,4-triazol-3-yl)pyridine (Hmtpy) as the cyclometalated ligand and ancillary ligand, respectively.[14] The Hg(II)-sensing experiments indicated that complex **1** showed a specific and sensitive multisignaling optical-electrochemical response to Hg(II) ions. The responded time was as short as 1 min with detectability as low as 2.5×10^{-7} M. Moreover, the redox peak currents presented good linear relationships with the amounts of Hg(II) ions over the range from 0 to 500 μM, which was beneficial to the quantitative analysis of Hg(II) ion concentrations. ^{1}H NMR titration and electrospray-ionization mass spectroscopy (ESI-MS) results revealed that the probing procedure was probably related to the Hg(II)-induced changes in local surroundings of complex **1**.



Scheme 1. Synthetic route and chemical structure of complex **1**.

Experimental section

General information

All experiments were performed under a nitrogen atmosphere by using commercially available anhydrous solvents or solvents that were well treated with an appropriate drying reagent. ^1H NMR spectra were measured on Bruker Avance 500 MHz spectrometer with tetramethylsilane as the internal standard. Synthetic routes and chemical structures of complex **1** iridium(III) [bis(1,2-diphenyl-1*H*-benzoimidazole) 2-(5-methyl-2*H*-1,2,4-triazol-3-yl)pyridine] have been shown in Scheme 1. Complex **1** was verified through using electrospray-ionization mass spectroscopy. Ultraviolet−visible (UV−vis) absorption spectra were recorded on a Hitachi U3030 spectrometer. The photoluminescent properties were measured on FLSP920 Edinburgh Fluorescence Spectrometer. The time- and pH-dependence experiments on the photoluminescence (PL) spectroscopy of complex **1** are performed using FL-4600 spectrophotometer. Deionized water was used to prepare all metal cation aqueous solutions.

Materials

$Hg(ClO_4)_2·3H_2O$, KNO_3, Na_2SO_4, $Zn(NO_3)_2·6H_2O$, $MgSO_4$, $Cd(NO_3)_2·4H_2O$, $Pb(NO_3)_2$, $Cu(NO_3)_2·3H_2O$, $Ni(NO_3)_2·6H_2O$, $Co(NO_3)_2·6H_2O$, $Cr(NO_3)_3·9H_2O$, $AgNO_3$, $Fe(SO_4)_2·7H_2O$ were purchased from China Pharmaceutical Co. Ltd. and used without further purification.

Mercury(II) titration and selectivity experiments

A stock solution of complex **1** (1 mM) was prepared in CH_3CN and then diluted to 20 μM with CH_3CN for titration and selectivity experiments. 2.5 mM stock aqueous solutions of Hg(II) perchlorate trihydrate and other metal ions (K^+, Na^+, Zn^{2+}, Mg^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Cr^{3+}, Ag^+, Fe^{2+}) were prepared in deionized water. The titration experiments were carried out by placing 2 mL of a solution of complex **1** (20 μM) in a quartz cuvette of 1 cm optical path length, and then adding the Hg(II) stock solution incrementally through a micropipet. The test samples for selectivity experiments were prepared by adding appropriate amounts of metal ion stock solutions to 2 mL of a solution of complex **1** (20 μM). The test solutions were stirred for 5 min, and then the UV-vis absorption, photoluminescence (PL) spectra and cyclic voltammograms (CV) were recorded. The PL spectra were collected from 400 to 750 nm. CV measurements were carried out on a BAS 100 W instrument with a scan rate of 100 mV s^{-1} in an argon-purged 50 μM anhydrous acetonitrile solution of complex **1** with tetra-butylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte. The CV system was constructed using a glassy carbon electrode, an aqueous saturated calomel electrode and a platinum wire as the working electrode, operating reference electrode and counter electrode, respectively.

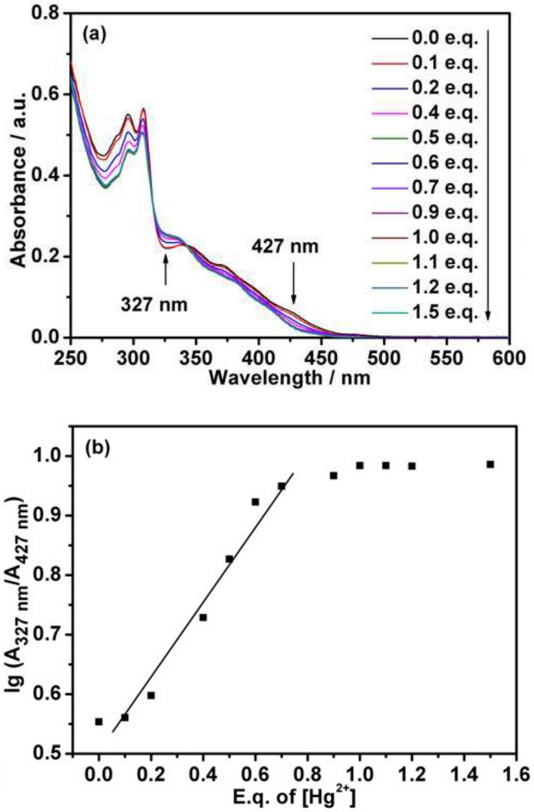


Fig. 1. Changes in the UV-vis absorption spectra of complex **1** (20 μM) in CH_3CN upon titration of Hg(II) ions (0–30 μM) and (b) titration curve of complex **1** with Hg(II) ions (absorbance ratio at 327 and 427 nm).

Results and discussion

Electronic absorption properties

Fig. 1a reveals that complex **1** displays high energy absorption bands below 380 nm, which are assigned to a ligand-centered $^1\pi$–π^* transition. The long tails absorption bands that occur in lower energy region (longer than 400 nm) may be associated with ^{1}MLCT (metal-to-ligand charge-transfer), ^{3}MLCT, ^{1}LLCT (ligand-to-ligand charge-transfer), ^{3}LLCT and ligand-centered $^3\pi$–π^* (^{3}LC) transitions.[15] Upon addition of Hg(II) ions, the absorbance of the transition bands at 340–510 nm and the band at 250–308 nm are gradually weakened. Conversely, the absorption bands around 327 nm are increasing progressively. The stoichiometry of complex **1** is given according to the variation of $\lg(A_{327\ nm}/A_{427\ nm})$ with respect to equivalents of Hg(II) ions added. The $\lg(A_{327\ nm}/A_{427\ nm})$ value increases continuously until addition of 1 e.q. of Hg(II) ions, indicating that the interaction between complex **1** and Hg(II) ions happens with a 1 : 1 mole ratio. This ratio is significant for achieving quantitative analysis.

Moreover, an approximate linear relationship between the lg($A_{327\ \mathrm{nm}}/A_{427\ \mathrm{nm}}$) value and the amounts of Hg(II) ions over the range from 2–14 μM is observed in Fig. 1b, which may be helpful to the detailed analysis of Hg(II) ion concentrations.

Photoluminescence properties

Complex **1** reveals bright green emission with a quantum yield of of 48% and an excited-state lifetime of 0.33 μs.[14] As known, the PL spectroscopy is more sensitive to small changes that affect the electronic properties of molecular receptors.[3a,10b,12a] Here, the response of complex **1** to Hg(II) ions is investigated *via* a PL measurement. Fig. 2a suggests that complex **1** exhibits green emission with two intense peaks at 502 and 530 nm. When Hg(II) ions are added into the CH_3CN solution of complex **1**, its PL intensity gradually decreases. After addition of 1 e.q. Hg(II) ions, it shows that the emission of complex **1** is greatly quenched and very weak luminescence is observed accompanying by two emission peaks. The time-dependence experiments indicate that complex **1** exhibits fast and sensitive detection of Hg(II) ions (Fig. S2, ESI†). The luminescence intensity at 502 nm is measured to monitor the sensing process of complex **1**. The titration curve in Fig. 2b suggests that there exists a 1 : 1 stoichiometry interaction between complex **1** and Hg(II) ions. This result is identical to its changes in the UV-vis absorption spectra. Fig. S1 presents the PL spectrum of complex **1** (20 μM) in CH_3CN upon titration of 0.0125 e.q. Hg(II) ions, which is obviously different from that without Hg(II) ions. Thus, the Hg(II) ions can be detected down to a concentration of 2.5×10^{-7} M, which is in the ppb range. Similar to the titration curve in UV-vis absorption spectra, it presents approximate linear relationship between the $I_{502\ \mathrm{nm}}$ value and the amounts of Hg(II) ions over the range from 2–14 μM.

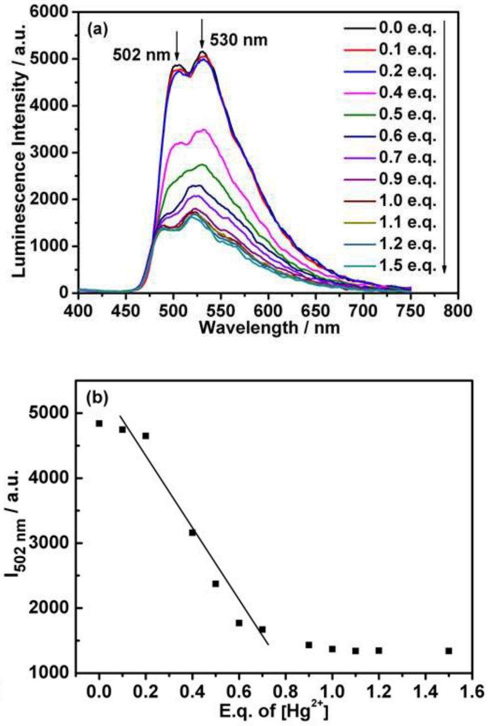


Fig. 2. (a) Changes in the PL spectra of complex **1** (20 μM) in CH_3CN upon titration of Hg(II) ions (0–30 μM) and (b) titration curve of complex **1** with Hg(II) ions (luminescence intensity at 502 nm).

Electrochemical properties

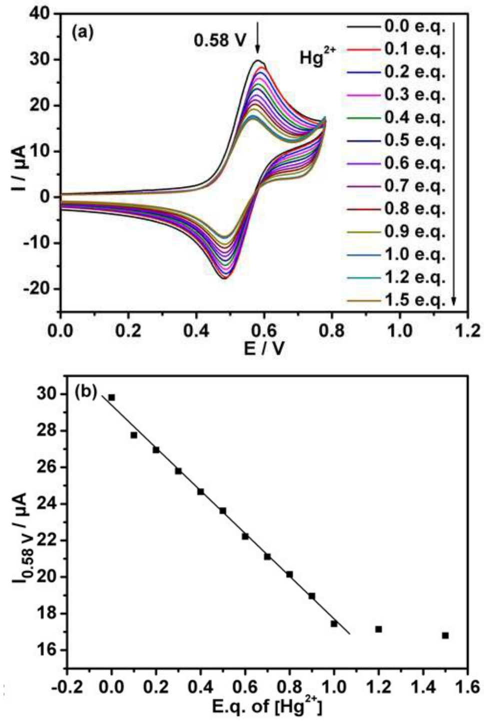


Fig. 3. (a) Changes in the cyclic voltammograms of complex **1** (500 μM) in CH_3CN upon titration of Hg(II) ions (0–750 μM) and (b) electrochemical titration of complex **1** with Hg(II) ions (current intensity at 0.58 V).

The CV behavior of complex **1** in the presence of mercury(II) ions is further investigated to estimate whether it can be used as an electrochemical sensor for Hg(II) ions. Fig. 3a suggests that complex **1** shows a reversible oxidation wave at 0.58 V, which is assigned to the oxidation of the iridium metal cationic site [Ir(III)→Ir(IV)].[16] Obvious changes in the CV are observed with of increasing amounts of Hg(II) ions to complex **1** in CH_3CN. It is found that the current intensity of the oxidation wave at 0.58 V decreases gradually. After addition of 1.0 e.q. of Hg(II) ions, no significant variation is observed in the oxidation waves, which can be viewed in Fig. 3b. This result indicates the stoichiometry of this interaction process is determined to be 1 : 1, which is in line with the optical titration results. In addition, Fig. 3b reveals that the redox peak currents show broad linear relationships with the amounts of Hg(II) ions over the range from 0–500 μM, which is beneficial to the quantitative analysis of Hg(II) ion concentrations. This appealing result is still rarely reported in iridium(III) complex-based chemosensors for Hg(II) ions.

Selective cation-binding studies

The high selectivity is a matter of necessity for an excellent chemosensor. Therefore, further studies on selective cation-binding of complex **1** were then performed by absorption and PL spectroscopy. The related heavy, transition and main group metal ions mainly include K(I), Na(I), Zn(II), Mg(II), Cd(II), Pb(II), Cu(II), Ni(II), Co(II), Cr(III), Ag(I) and Fe(II) cations. As presented in Fig. 4a, the addition of these related metal ions only causes slight variations in $A_{427\ \mathrm{nm}}/A_{327\ \mathrm{nm}}$ value for the CH_3CN solution of complex **1**. However, significant changes in the absorption spectra are observed with the subsequent addition of

Hg(II) ions. Fig. S4 shows the absorption spectra of complex **1** in the presence of above metal cations, which suggests the slight variations in $A_{427\ \mathrm{nm}}/A_{327\ \mathrm{nm}}$ observed here. These results imply that complex **1** can be used as a highly selective Hg(II)-chemosensor.

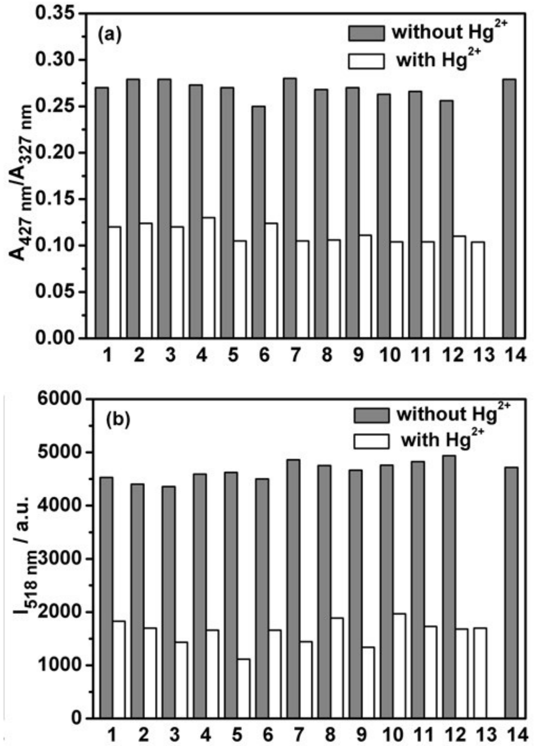


Fig. 4. The photophysical response of complex **1** (20 μM) with various metal cations (1.0 e.q.) in CH_3CN. (a) Absorption: bars represent the ratio ($A_{427\ \mathrm{nm}}/A_{327\ \mathrm{nm}}$) of absorbance intensity at 427 and 327 nm, while gray bars represent the addition of 1.0 e.q. of various metal cations to a 20 μM solution of complex **1** and white bars represent the addition of Hg(II) ions (1.0 e.q.) to the above solutions; (b) phosphorescence: bars represent the emission intensity ($I_{518\ \mathrm{nm}}$) at 518 nm, while gray bars represent the addition of 1.0 e.q. of various metal cations to a 20 μM solution of complex **1** and white bars represent the addition of Hg(II) ions (1.0 e.q.) to the above solutions. 1, K(I); 2, Na(I); 3, Zn(II); 4, Mg(II); 5, Cd(II); 6, Pb(II); 7, Cu(II); 8, Ni(II); 9, Co(II); 10, Cr(III); 11, Ag(I); 12, Fe(II); 13, Hg(II); 14, without metal cation.

Fig. 4b and Fig. S5 depict the PL response of complex **1** with various metal cations in CH_3CN. Considering the fact that complex **1** exhibits quenched and weak luminescence upon addition of Hg(II) ions, simultaneously possessing shifted emission peaks, we select the emission intensity at 518 nm ($I_{518\ \mathrm{nm}}$) to observe the response of complex **1** towards Hg(II) ions. We make this selection since it presents clear luminescence spectra changes to us, which is beneficial to better studying the selective cation-binding property. Similar to the absorption results, remarkable changes in the PL spectra are observed with addition of Hg(II) ions into above metal ions. This result indicates that complex **1** displays a high specificity toward Hg(II) ions, and thus can be utilized to detect Hg(II) ions in a complicated and competitive matrix. Other factor such as the effect of pH on the detection was also studied. The results indicate that complex **1** shows pH-dependent quenching behaviors toward Hg(II) ions, which may be due to the different coordination ability of Hg(II) ions in present of the acidity or basicity (Fig. S3, ESI†)

Fig.5 gives the photographs of complex **1** in CH_3CN solution (500 μM) in the presence of different metal cations. With addition of 1.0 eq. of Hg(II) ions, complex **1** displays a color change from yellowish green to light-colored (Fig. 5a), which matches with the absorption intensities in the visible region of 400–510 nm. More encouragingly, Fig. 5b indicates that complex **1** presents remarkable quenching in its PL with addition of Hg(II) ions into above metal ions. The corresponding detecting process is fast and the quenching in PL is observed within 1 min. These results suggest that complex **1** is a Hg(II)-chemosensor with high selectivity, which can be adopted for potential real-time detection.

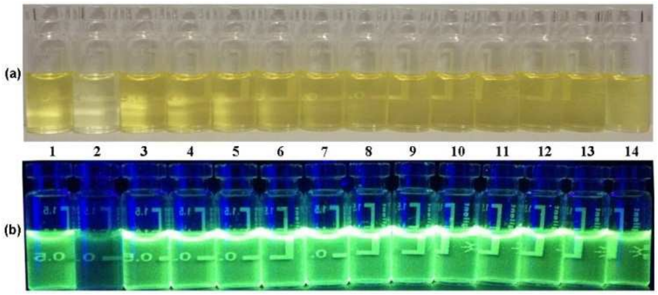


Fig. 5. Photographs of complex **1** in CH_3CN solution (500 μM) in the presence of different metal cations (1.0 eq.): (a) color; (b) phosphorescence. 1, blank; 2, Hg(II); 3, K(I); 4, Na(I); 5, Zn(II); 6, Mg(II); 7, Cd(II); 8, Pb(II); 9, Cu(II); 10, Ni(II); 11, Co(II); 12, Cr(III); 13, Ag(I); 14, Fe(II).

Probing sensing mechanism

Lu *et al.* developed a sulfur-free iridium(III) complex $Ir(pbi)_2(acac)$ as highly selective chemosensor for Hg(II) ions.[8a] They proposed that there existed some interaction between Hpbi and Hg(II) ions and assigned the sensing mechanism merely to the decomposition of the iridium chelate with the departure of the relatively weak Ir–O bond. Their work has enriched the research of Hg(II)-sensors based on iridium(III) complexes. However, developing more sulfur-free iridium(III) complexes for highly selective chemosensors toward Hg(II) ions is still limited. In the case of complex **1**, there exists no sulfur atom in the ligands. To better understand the response process of complex **1** to Hg(II) ions, the ^1H NMR and ESI-MS measurements are performed.

According to the reported literature,[10b] the ^1H NMR spectra measurement suggested that there was some coordinational bonding between the cyclometalated ligand Hpbi and Hg(II) ions. Here, the ^1H NMR spectra are just recorded for the ancillary ligand Hmtpy and complex **1**. Fig. 6a shows that, after addition of Hg(II) ions, most of the proton signals for Hmtpy shift to the downfield region, while the signal at 8.63 ppm shifts to 8.37 ppm. Moreover, the signal at 12.13 ppm for Hmtpy (-NH) disappears upon addition of 1.0 e.q. Hg(II) ions. These results imply that there exists obvious interaction between Hmtpy and Hg(II) ions. In respect of complex **1**, obvious changes in its ^1H NMR spectrum are observed with addition of Hg(II) ions. It is observed that, the spectrum of complex **1** + 1.0 e.q. Hg(II) ions differs significantly from those of complex **1** without Hg(II) ions, Hpbi and Hpbi + 1.0 e.q. Hg(II) ions.[8a] Thus, the mechanism of the decomposition of complex **1** together with the release of free Hpbi ligand followed by the formation of a pbi–Hg^{2+} complex is excluded. In addition, the spectrum of complex **1** + 1.0 e.q. Hg(II) ions is different from those of Hmtpy and Hmtpy + 1.0 e.q. Hg(II) ions. Therefore, the possibility of formation of the mtpy–Hg^{2+} complex with addition of Hg(II) ions is excluded.

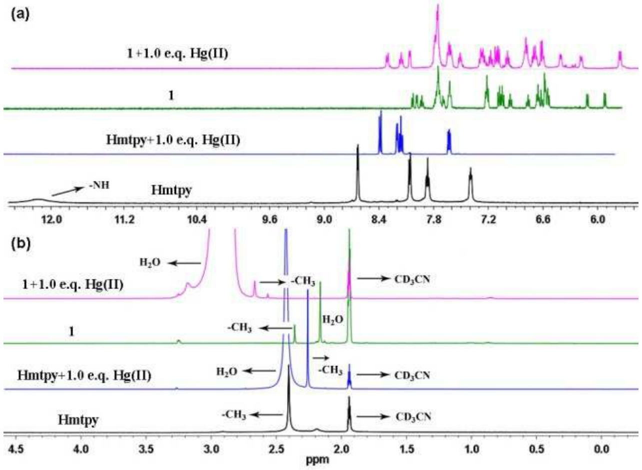


Fig. 6. Partial ^{1}H NMR spectral changes of complex **1** in CD_3CN in the presence of Hg(II) ions (0.0–1.0 e.q.): (a) 5.7–12.8 ppm; (b) 0.0–4.8 ppm.

In the ESI-MS spectra of complex **1** with 0.0 and 1.0 eq. Hg(II) ions (Fig. S6 and S7, respectively), obvious signals (m/z) at 891.2491 of $(pbi)_2Ir(mpty)$ (**1**) is observed, suggesting that complex **1** is not decomposed. This phenomenon is obviously different from that of the sulfur-free iridium(III) complex $Ir(pbi)_2(acac)$ developed by Lu *et al.* According to previous reports,[10b] the phosphorescent emission of heavy-metal complexes is sensitive to their local environment. If binding of heavy-metal complexes with analyte changes local surroundings, their phosphorescent emission will be probably altered and the detection can thus be realized. Considering the results from ^{1}H NMR and ESI-MS spectra, herein, we tentatively suppose that the probing mechanism of complex **1** towards Hg(II) ions may be assigned to the Hg^{2+}-induced changes in its local surroundings. This alteration probably leads to complicated energy transfer from complex **1** to the local environment or Hg(II) ions, which weakens its phosphorescent emission. The mechanism involved here is not the same as that of the early reported complex $Ir(pbi)_2(acac)$ with Hg(II) ions.[8a] Such response process is still useful for achieving simple and effective detection of Hg(II) ions.

Conclusions

In summary, we reported a highly selective and multisignaling optical-electrochemical chemosensor for Hg(II) ions adopting sulfur-free iridium(III) complex $(pbi)_2Ir(mtpy)$. This complex showed obvious naked-eye color and phosphorescence changes with Hg(II) ions in the presence of other metal cations. The corresponding response time is as short as 1 min with a low detection limit of 2.5×10^{-7} M. More importantly, its redox peak currents show broad linear relationships with the amounts of Hg(II) ions over the range from 0–500 μM, which helps to quantitatively detect Hg(II) ion concentrations. This appealing result is still rarely reported in many iridium(III) complex-based chemosensors for Hg(II) ions. With the ^{1}H NMR and ESI-MS analyses, we tentatively suppose that the probing mechanism of complex **1** towards Hg(II) ions may be assigned to the Hg^{2+}-induced changes in the local environment. This response process is useful for achieving simple and effective detection of Hg(II) ions as well as developing more chemosensors. It enlightens us to develop more chemosensors with enriched molecular structure to detect Hg(II) ions.

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Notes and references

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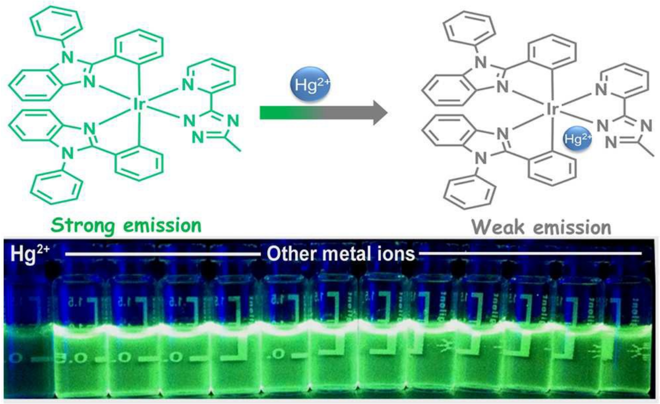

A sulfur-free iridium(III) complex adopting 1,2-diphenyl-1*H*-benzoimidazole ligand was successfully prepared, which showed high selectivity and sensitivity to Hg(II) ions through optical and electrochemical signals.