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Phosphorescent chemosensor for Hg^{2+} based on iridium(III) complex coordinated with 4-phenylquinazoline and carbazole dithiocarbamate

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A Highly selective and colorimetric phosphorescent turn-on chemosensor for Hg^{2+} based on iridium(III) complex $Ir(pqz)_2(cdc)$ (pqzH = 4-phenylquinazoline, Nacdc = sodium carbazole dithiocarbamate) was realized. The photograph of $Ir(pqz)_2(cdc)$ under ultraviolet light exhibited emitting color change from red to yellow without and with Hg^{2+} in acetonitrile(MeCN) solution, and it can also serve as a highly selective chemosensor for Hg^{2+} with naked-eye detection. Upon addition of tetrahydrofuran(THF) solution of Hg^{2+}, the dichloromethane (DCM) solution of $Ir(pqz)_2(cdc)$ gave a visual color change and significant luminescent quenching. When MeCN was added, a new emission peak at 562 nm emerged, which constituted a selective MeCN phosphorescent chemosensor.

Introduction

Highly effective chemsensors for quantitative or qualitative detection of heavy and transition metal ions in environmental and biological fields has received much attention over the past few years.[1] Among these metal ions, mercury is one of the most dangerous hazards to environment and biological systems due to its high affinity for thiol groups in proteins and enzymes.[2] Hence, the detection of Hg^{2+} is very important. Recent investigations have been devoted to design new and practical chemosensors for detecting Hg^{2+} by utilizing their chromogenic, electrochemical and fluorogenic properties.[3] Development of off–on fluorescent sensors for heavy and transition metal ions is more desirable than on–off fluorescent sensors in terms of improving selectivity and sensitivity.[3] However, it is known that many of these ions are typical fluorescence quenchers by reason of their paramagnetic nature and the heavy atom effect, and the development of off–on fluorescent probes for heavy and transition metal ions remains a significant challenge. [4]

Chemosensors based on heavy-metal complexes have attracted considerable interest because of their excellent photophysical properties, such as high thermal stability, relatively long lifetimes, and large Stokes shifts between absorption and emission.[5] Among the phosphorescent complexes, iridium (III) complexes have been considered to be one of the best phosphorescent materials due to their high luminescence efficiencies, relatively short excited-state lifetime and excellent color tuning capability through ligand structure control.[6] Some chemosensors based iridium(III) complexes for Hg^{2+} which show excellent performances have been reported. [7] They are used in several areas, such as sensors for metal cations, anions, pH, oxygen, volatile organic compounds and biomolecules.[8] Professor Li chooses the sulfur atom into the cyclometalated ligands and develops a kind of phosphorescent sensors for multisignaling detection of Hg^{2+} based on iridium(III) complexes.[9] Recently, we have reported a highly selective turn-on chemosensor for Hg^{2+} based on dithiocarbamate iridium(III) complex.[10] Herein, considering the importance of detection for Hg^{2+} and the advantages of phosphorescent iridium(III) complexes as probes, we are interested in developing a multisignaling sensor based on iridium(III) complexes that exhibits a significant naked-eye recognition effect upon addition of Hg^{2+} over other metal ions with different counterions.

Mercury(II) as soft acid can preferentially coordinate with sulfur as soft base according to the theory of hard and soft acids and bases.[11] When the auxiliary ligands of iridium(III) complexes contain specific metal-coordinating elements, dramatic change in the photophysica properties of complexes would be induced by coordination of mercury(II) and sulfur atom. A new iridium(III) complex $\mathbf{Ir(pqz)_2(cdc)}$ based on 4-phenylquinazoline as cyclometalated ligand and carbazole dithiocarbamate as auxiliary ligand has been synthesized in this paper. The new phosphorescent iridium (III) complex realizes highly sensitive and reversible change response for Hg^{2+} and MeCN with naked-eye detection. When addition of 2 equiv of various alkali, alkaline earth and transition-metal ions to a solution of $\mathbf{Ir(pqz)_2(cdc)}$ in DCM + MeCN showed a selective color

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† Electronic Supplementary Information (ESI) available: ^1H NMR, ^{13}C NMR, mass spectra and additional data for iridium (III) complex. Some titration experiment of iridium (III) complex and in the presence and absence of Hg^{2+} ions. See DOI: 10.1039/x0xx00000x

change from red to yellow only in the presence of Hg^{2+} (Figure 1). The response mechanisms for Hg^{2+} and MeCN have been analysed in detail. In addition, an AND logic gate with Hg^{2+} and MeCN as inputs has been developed with this complex.

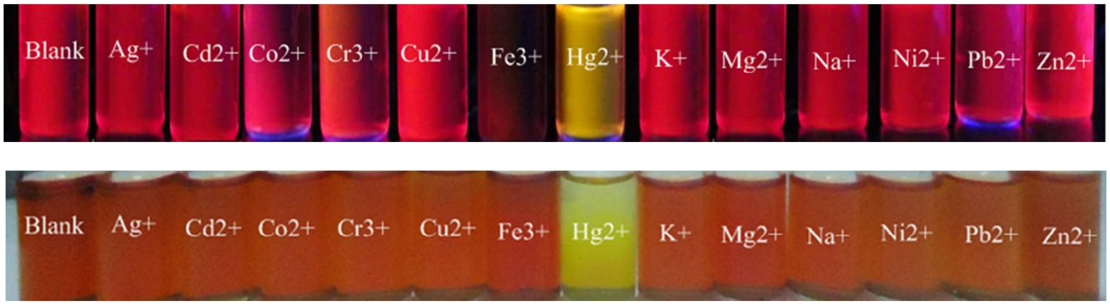


Fig.1 Changes in the color of **Ir(pqz)$_2$(cdc)** (c = 2.0×10^{-5} M) with 2 equiv of various metal ions in acetonitrile. Top: color changes by exciting at 360nm; bottom: color changes for “naked-eye”.

Experimental section

Materials

All manipulations involving air-sensitive reagent were performed in an atmosphere of dry argon atmosphere. Chromatographic pure acetonitrile was used directly without further drying and distillation. All other solvents and reagents were of analytical purity and used without further purification. $IrCl_3 \cdot 3H_2O$ was an industrial product and was used directly. The salts solutions of metal ions were $AgNO_3$, $Cd(NO_3)_2$•$4H_2O$, $Cd(ClO_4)_2$•$6H_2O$, $Co(NO_3)_2$•$6H_2O$, $Cr(NO_3)_3$•$9H_2O$, $Cu(NO_3)_2$•$3H_2O$, $Fe(NO_3)_3$•$9H_2O$, $Hg(ClO_4)_2$•$3H_2O$, KNO_3, $Mg(ClO_4)_2$, $NaNO_3$, $Ni(NO_3)_2$•$6H_2O$, $Pb(NO_3)_2$, $Zn(NO_3)_2$•$6H_2O$.

General experiment

^{1}H NMR spectra were recorded were recorded with a Bruker 400MHz spectrometer and used tetramethylsilane as the internal standard. Mass spectra were obtained on a Shimadzu GCMS-QP2010 instrument or a matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF-MS). UV-Vis absorption spectra were obtained on a Shimadzu UV-3600 spectrophotometer. Fluorescence spectra were determined with Shimadzu RF-5301PC luminescence spectrometer.

General procedures of spectra detection

Solutions of all metal ions were prepared in acetonitrile or THF. The solutions of **Ir(pqz)$_2$(cdc)** was prepared in DCM or acetonitrile. In titration experiments, each time a 3 mL solution of **Ir(pqz)$_2$(cdc)** was filled in a quartz cuvette with a path length of 1 cm, and quantitative mercury ion solution was added into quartz cuvette with a micro-pip-pet. Spectral data were recorded about 3 minutes after the addition of mercury ion.

Single-crystal X-ray diffraction measurement

The single crystal of **Ir(pqz)$_2$(cdc)** was grown by slow evaporation of a solution of **Ir(pqz)$_2$(cdc)** in a mixture of CH_2Cl_2 and hexane at room temperature, and then mounted on glass fibers. Diffraction data were obtained on a Bruker SMART Apex CCD X-ray diffractometer with MoKα radiation at 296 K using an ω scan mode.

Synthesis of 4-phenylquinazoline (pqzH)

4-Phenylquinazoline ligand was obtained from the condensation reaction of 2-aminobenzophenone and formamide, according to the literature method.[12] 2-Aminobenzophenone (2.0 g, 10 mmol), formamide (45.5 g, 40 ml, 1.06 mol), and formic acid (24.4 g, 20 ml, 0.54 mol) were heated to 150 °C about 3 hours. After cooled, the mixture was poured into cool water, and a large number of solid precipitation appeared. The solid was filtered off, washed with water, dried, and crystallized from ethanol as shining light yellow crystals of 4-phenylquinazoline (3.12 g, 75%), m.p. 95.0–97.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) d 9.40 (s, 1H), 8.14 (t, J =7.6, 2H), 7.94 (t, J =7.2, 1H), 7.79-7.81 (m, 2H), 7.64 (d, J =8.0, 1H), 7.59-7.60 (m, 3H).

Synthesis of sodium carbazole dithiocarbamate (Nacdc)

According to reference : [13] To the stirred solution of 3.34 g carbazole (20 mmol) in 40 mL anhydrous THF in round-bottom flask. Excess sodium was cut into many pieces, then was added to round-bottom flask. The mixture was refluxed gently at 80 °C with stirring for 5 hours. The reaction continued until the color of the solution turned blue. Continuous added the sodium wire into the solution until there were no gas bubbles visible in flask. The reaction was stirred and was continued for 4 hours. After cooled to room temperature, 1.67g (22mmol) carbon disulphide was added into the flask. Then the reaction mixture was continued at 40 °C with stirring for 3 hours until the color of the solution turned dull red. The resulting residue (**Nacdc**) was used in next step without further purification.

Synthesis of Ir(pqz)$_2$(cdc)

According to reference : [14] $IrCl_3 \cdot 3H_2O$ (0.70 g, 2 mmol) and 4-phenylquinazoline(1.03g, 5mmol) were added to a mixture of 2-ethoxyethanol/ water (16 mL, 3:1v/v), then the mixture was stirred at 125 °C for 24 hours under nitrogen. After cooled, the dark red precipitate was filtered and washed with ethanol. The dimeric iridium complex $[(pqz)_2Ir(\mu\text{-}Cl)]_2$ was obtained. After drying, the crude product was directly used for next step without further purification. A solution of $[(pqz)_2Ir(\mu\text{-}Cl)]_2$ (0.25g, 0.2 mmol) in dichloromethane (10 mL) and 5 equivalents of **Nacdc** in tetrahydrofuran (10 mL) were added in the round bottom flask. The solution was stirred at room temperature under a nitrogen atmosphere for 3 hours. The mixture was extracted with dichloromethane and washed with a lot of water. After dried with anhydrous $MgSO_4$, the extracted liquid was concentrate and the crude product was loaded onto silica gel. The desired complex **Ir(pqz)$_2$(cdc)** was obtained by silica gel column chromatography using dichloromethane/petroleum ether (V_{DCM}:V_{PE}=1:1) as the eluent. Yield = 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.28 (s, 2H), 9.30 (dd, *J* = 6.3, 3.2 Hz, 2H), 8.90 (d, *J* = 8.5 Hz, 2H), 8.39 (d, *J* = 8.1 Hz, 2H), 8.18 (d, *J* = 8.1 Hz, 2H), 7.93 (t, *J* = 7.0 Hz, 4H), 7.79 (t, *J* = 7.7 Hz, 2H), 7.36 (dd, *J* = 6.1, 3.2 Hz, 4H), 7.03 (t, *J* = 7.6 Hz, 2H), 6.83 (t, *J* = 7.4 Hz, 2H), 6.65 (d, *J* = 7.7 Hz, 2H). MADIL-TOF MS (m/z): 845.40 ($[M+H]^+$), calcd. 845.13 for [$C_{41}H_{26}IrN_5S_2$].

The X-ray crystallography of Ir(pqz)$_2$(cdc)

The structure correctness of **Ir(pqz)$_2$(cdc)** can be determined by the single crystal structure. The perspective view of the complex showed a distorted octahedral coordination geometry with *cis*-C-C and *trans*-N-N dispositions. Cyclometalated ligands 4-phenylquinazoline and ancillary ligand carbazole dithiocarbamate (**cdc**) revolved around the iridium center(Figure 2). The bond lengths of between the iridium atom and carbon atom (Ir-C) was about 2 Å changed from 1.994 to 2.010 Å, which were shorter than the Ir-N bond lengths ranging from 2.041 to 2.049 Å. This was because the electronegativity of the C atom was less than that of the N atom. The result led to the increase of the covalent component of the bonding atoms and there was a stronger trans influence of the phenyl group of the 4-phenylquinazoline.[15] The two coordinated S atoms of **cdc** ligands resided in the equatorial plane trans to the metalated C(**pqz**) atoms. The two Ir-S bonds ranged from 2.4474 to 2.4823 Å. Moreover, the C-C and C-N bond lengths and angles of **Ir(pqz)$_2$(cdc)** were consistent with the corresponding parameters of the similar complexes.[16] Crystallographic and experimental data of **Ir(pqz)$_2$(cdc)** were listed in Table S1. CCDC 874160 contained more comprehensive crystallographic data of **Ir(pqz)$_2$(cdc)**. If you visit the site of the Cambridge Crystallographic Data Centre(www.ccdc.cam.ac.uk/data_request/cif), you will get all of the above data.

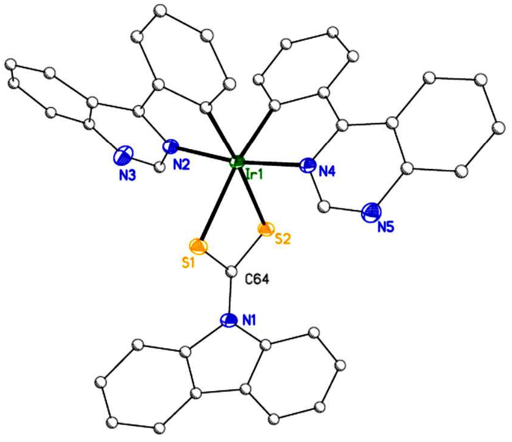
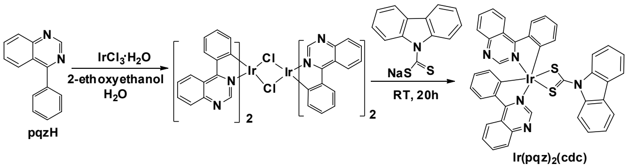


Figure 2. Perspective view of **Ir(pqz)$_2$(cdc)**. Thermal ellipsoids are shown at the 25% probability level.

Results and discussion

Synthesis and characterization



Scheme 1. Synthetic route for **Ir(pqz)$_2$(cdc)**

The synthetic route for **Ir(pqz)$_2$(cdc)** was shown in Scheme 1. The cyclometalated ligand 4-phenylquinazoline was synthesized from the condensation reaction of 2-aminobenzophenone and formamide, according to the literature method. **Ir(pqz)$_2$(cdc)** was synthesized in two steps using standard method in 62% yield. The detailed experimental procedures and ^{1}H NMR spectrum was explained in the supporting information.

Selectivity and competition of Ir(pqz)$_2$(cdc) to various metal ions

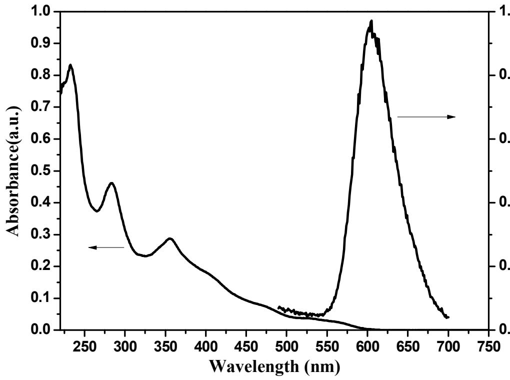


Figure 3. UV-vis and fluorescence spectra (λ_{ex} = 360 nm) of **Ir(pqz)$_2$(cdc)** in DCM+ MeCN (V_{DCM}:V_{MeCN}=10:1, *c* = 2.0×10^{-5} M)

The UV-Vis absorption spectrum and fluorescence spectrum of **Ir(pqz)$_2$(cdc)** in DCM solution in the presence of MeCN were tested. As shown in Figure 3, the complex diplayed strong absorption bands around 250-325 nm, which were assigned to the spin-allowed intra-ligand (π-π*) transitions. The weak absorption bans at 325-600 nm were due to the mixed singlet and triplet metal-to-ligand charge-transfer (MLCT). Upon excitation at 360 nm, **Ir(pqz)$_2$(cdc)** showed moderate red fluorescence emission at 606 nm in DCM+MeCN at room temperature.

Selectivity was the very important parameter to evaluate the performance of a probe. Detailed optical tests were carried out and used to investigate the anti-interference ability of probe **Ir(pqz)$_2$(cdc)** toward Hg^{2+} in the presence of acetonitrile. The binding behaviors of compound **Ir(pqz)$_2$(cdc)** toward different cations (Ag^+, Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{3+}, Hg^{2+}, K^+, Mg^{2+}, Na^+, Ni^{2+}, Pb^{2+}, Zn^{2+}) were investigated by UV-vis and fluorescence spectroscopy (Figure 4 and Figure 5(a)). The UV-Vis absorption change of **Ir(pqz)$_2$(cdc)** in the presence of 2 equiv of different metal ions (Ag^+, Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{3+}, Hg^{2+}, K^+, Mg^{2+}, Na^+, Ni^{2+}, Pb^{2+}, Zn^{2+}) indicated that only Hg^{2+} arose an apparent response and a visual color change from red to yellow (Figure 4). Upon addition of Fe^{3+}, the peak of **Ir(pqz)$_2$(cdc)** at 282 nm and 355 nm showed slight change in UV-vis spectra was observed, it was because of the fluorescence self-absorption of Fe^{3+}. The solution of **Ir(pqz)$_2$(cdc)** in DCM + MeCN exhibited a moderate emission at 606 nm. As shown in Figure 5(a), **Ir(pqz)$_2$(cdc)** displayed extraordinarily selective luminescence enhancement at 562 nm in the presence of Hg^{2+}, while almost no changes were observed at 562 nm after adding the other metal ions. And the relative fluorescence intensity at 562 nm, namely I/I_0 (562 nm), were found to be 70 fold in the presence of Hg^{2+}(Figure5(b)). The phosphorescent chemosensor **Ir(pqz)$_2$(cdc)** displayed sensitive UV-Vis absorption change and luminescence change by N-carbazolylcarbodithioate chelating with Hg^{2+}.

Anti-interference ability was another important parameter to evaluate the performance of a probe. The effects of coexisting metal ions (Ag^+, Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{3+}, Hg^{2+}, K^+, Mg^{2+}, Na^+, Ni^{2+}, Pb^{2+}, Zn^{2+}) on Hg^{2+} determination were also investigated by competition experiments, as demonstrated by UV-vis absorption(Figure S4 and Figure S5) and fluorescence emission (Figure 5(b) and Figure S6). When **Ir(pqz)$_2$(cdc)** was treated with 2.0 equiv. of Hg^{2+} and 2.0 equiv. of other metal ions, similar spectra change and color change was also observed. The effect was almost the same as the addition of Hg^{2+}. The results showed that there was no interference to the detection of Hg^{2+} in the presence of other competing metal ions. Thus, the phosphorescent complex **Ir(pqz)$_2$(cdc)** can be used as a selective, colorimetric and fluorescent sensor for Hg^{2+}. In order to eliminate the interference of counter ion, we have tested the contrast experiment about another perchlorate salt($Cd(ClO_4)_2{\cdot}6H_2O$), and it was a soft transition metal ion with similar properties to mercury(II)(Figure S7). We chose many main group metal salt and transition metal salt with different anions. As the Figure S7 showed, the UV-Vis absorption and the fluorescence emission change of Ir(pqz)2(cdc) in the presence of 2 equiv of different counter ions indicated that the counter ion had no significance in the mechanism of the sensing response. We could eliminate other possible mechanism and to confirm that the sensor was indeed responding with specificity to mercury. All results of these selective and interference tests indicated that probe **Ir(pqz)$_2$(cdc)** had high selectivity and strong interaction toward Hg^{2+} and could meet the highly selective requirements for environmental or biological applications.

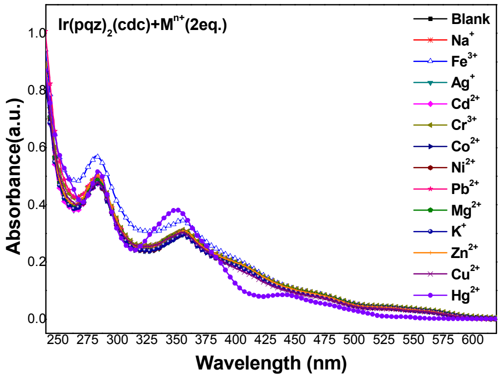
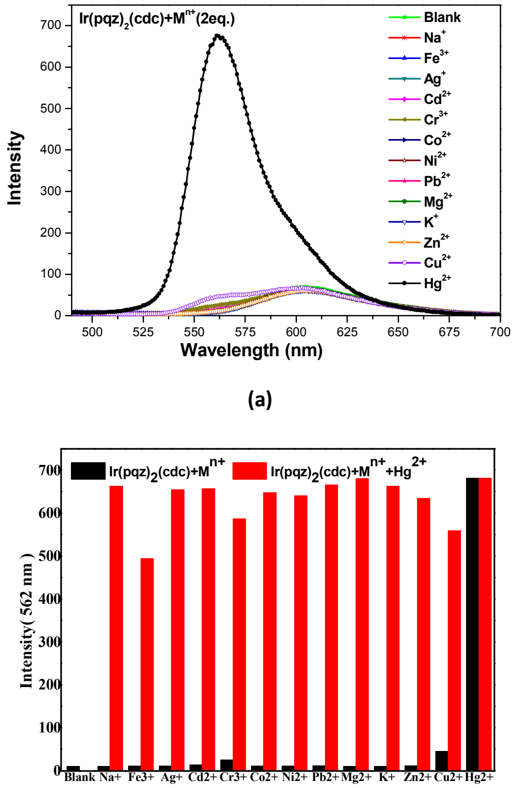


Figure 4. UV-vis spectra of **Ir(pqz)$_2$(cdc)** (c = $2.0{\times}10^{-5}$ M) in the presence of metal ions (2.0 equiv) in DCM+ MeCN(V_{DCM}:V_{MeCN}=10:1). Na^+, Fe^{3+}, Ag^+, Cd^{2+}, Cr^{3+}, Co^{2+}, Ni^{2+}, Pb^{2+}, Mg^{2+}, K^+, Zn^{2+} and Cu^{2+} were added, respectively.



(a)

(b)

Figure 5. (a) Emission spectra of **Ir(pqz)$_2$(cdc)** (c = $2.0{\times}10^{-5}$ M) in the presence of 2 equiv of metal ions in DCM+ MeCN(V_{DCM}:V_{MeCN}=10:1). Na^+, Fe^{3+}, Ag^+, Cd^{2+}, Cr^{3+}, Co^{2+}, Ni^{2+}, Pb^{2+}, Mg^{2+}, K^+, Zn^{2+} and Cu^{2+} were added, respectively. (b) Fluorescence responses of **Ir(pqz)$_2$(cdc)** in DCM+ MeCN (V_{DCM}:V_{MeCN}=10:1, $2.0{\times}10^{-5}$ M) to various 2 equiv of metal ions. Bars represent the final (I_{562nm}) emission intensity. The black bars represent the free **Ir(pqz)$_2$(cdc)** solution and the addition of various metal ions (2 equiv) to a solution of **Ir(pqz)$_2$(cdc)**. The red bars represent I_{562nm} after addition of 2 equiv of Hg^{2+} to the above solution.

Optical response and mechanism of Ir(pqz)$_2$(cdc) to Hg^{2+} in DCM + MeCN

The UV-vis spectra of **Ir(pqz)$_2$(cdc)** in DCM + THF (c = $2.0{\times}10^{-5}$ M) in the presence of increasing amount of $Hg(ClO_4)_2$ predissolved in THF was shown in Figure S2. There was a slight change of absorption band at 360 nm while the absorption bands at 550 and 450 nm disappeared completely. The color of the solution changed from red to colorless. Figure 6 showed the absorption spectral changes of **Ir(pqz)$_2$(cdc)** in the presence of increasing amount of Hg^{2+}(dissolved in MeCN). Upon addition of Hg^{2+} to **Ir(pqz)$_2$(cdc)** in DCM+ MeCN (c =

2.0×10^{-5} M), new absorption bands at 350 nm appeared and the absorption bands at 550 nm disappeared completely. Compared with Figure S2, the absorption band at 450 nm did not disappear completely which meant a new compound appeared. Meanwhile, the well-defined isosbestic points at 321 nm and 385 nm clearly indicated the presence of **Ir(pqz)$_2$(cdc)** in equilibrium with the new compound. The UV-Vis absorption spectra remained unchanged after more than 1 equiv. of Hg^{2+} was added, which made it possible to ratiometrically detect Hg^{2+}. The new absorption spectral band blue shifted, which was responsible for the change of color from red to yellow(inset of Figure 6).

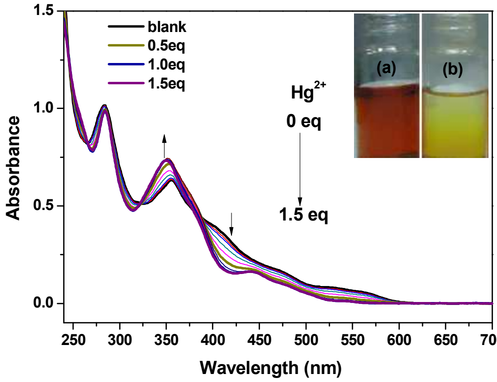


Figure 6. Changes in UV-vis spectra of **Ir(pqz)$_2$(cdc)** in DCM+ MeCN (V_{DCM}:V_{MeCN}=10:1, *c* = 2.0×10^{-5} M) with various amounts of $Hg(ClO_4)_2$ (0-1.5 equiv) predissolved in acetonitrile. Inset: Change in the color of **Ir(pqz)$_2$(cdc)** after addition of 1.5 equiv of $Hg(ClO_4)_2$, **Ir(pqz)$_2$(cdc)** in DCM+ MeCN (a) and **Ir(pqz)$_2$(cdc)** plus 1.5 equiv of $Hg(ClO_4)_2$ in DCM+ MeCN (b).

To examine the sensitivity of **Ir(pqz)$_2$(cdc)**, luminescence emission spectra of **Ir(pqz)$_2$(cdc)** in DCM+ THF (*c* = 2.0×10^{-5} M) in the presence of increasing amount of $Hg(ClO_4)_2$ predissolved in THF was shown in Figure S3, while luminescence emission spectra of **Ir(pqz)$_2$(cdc)** in DCM+ MeCN (2.0×10^{-5} M) in the presence of increasing amount of Hg^{2+} (0-1.5 equiv.) predissolved in acetonitrile were recorded and shown in Figure 7. As shown in Figure S3, the emission intensity at 606 nm had an obvious decrease and quenched almost completely after addition of 1.0 equiv. of Hg^{2+}(dissolved in THF) No change happened when more Hg^{2+} was added. As shown in Figure 7, upon addition of Hg^{2+}, there was an obvious "turn on" process with the appearance and enhancement of a new luminescence at about 562 nm. A “off-on” fluorescence changes of **Ir(pqz)$_2$(cdc)** to Hg^{2+}(dissolved in MeCN) were observed. The fluorescence titration profile of **Ir(pqz)$_2$(cdc)** versus Hg^{2+} revealed that the maximum of the emission from **Ir(pqz)$_2$(cdc)** was obtained when 1.0 equiv Hg^{2+} was added to the solution (Figure 7, Inset (a)). As a result, an obvious change in fluorescent color from red to yellow was observed (Figure 7, Inset (b)). The sensitivity curve indicated that the probe **Ir(pqz)$_2$(cdc)** maintained the linear response at Hg^{2+} concentration range of 6×10^{-6} M to 24×10^{-6} M (Figure S1), indicating the probe **Ir(pqz)$_2$(cdc)** can be used for the analysis of micromolar concentrations of Hg^{2+}. The linear equation obtained by fitting curve was y=31.438x-106.557(R=0.998), where y was the fluorescent intensity data at 562 nm and x represented the concentration of Hg^{2+} added. So the detection limit for Hg^{2+} was 25 nM,[17] indicating that probe **Ir(pqz)$_2$(cdc)** was potentially useful for the quantitative determination of Hg^{2+} concentration.

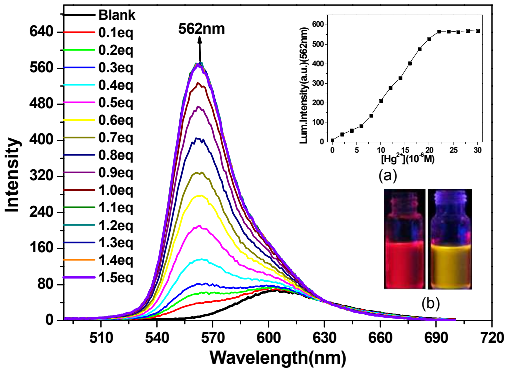


Figure 7. Luminescence emission spectra of **Ir(pqz)$_2$(cdc)** in DCM + MeCN (V_{DCM}:V_{MeCN}=10:1, 2.0×10^{-5} M) in the presence of increasing amount of Hg^{2+} (0-1.5 equiv) predissolved in acetonitrile. Inset: Fluorescence intensity of a solution of **Ir(pqz)$_2$(cdc)** contained different concentrations of Hg^{2+} at λ_{em} = 562 nm.

The luminescent response of Ir(pqz)$_2$(cdc) to Hg^{2+} in various solvents

The luminescence response behaviors of **Ir(pqz)$_2$(cdc)** to Hg^{2+} on various solvents have also been investigated in Figure 8 and Figure S9. The emission band centered at 606 nm had no change in these solvents such as acetone, DCM, toluene, ethyl acetate, THF, diethyl ether and n-hexane, and while ethanol, methanol, N, N-dimethyl formamide, dimethyl sulfoxide and pyridine caused luminescence enhancing under the same condition. However in MeCN solution, the emission peak blue shifted to 562 nm and the emission intense increased 286 times for contrast in dichloromethane (Table S3), which meaned that only MeCN arose an apparent response and this system showed high solvent selectivity. Moreover, a competition experiment for MeCN with other different solvents was done. Additionally, the effects of coexisting metal ions on MeCN determination were also investigated by competition experiments, as demonstrated in Figure S10 and Figure S11. The interference for the detection of MeCN was not observed in the presence of most of solvents, only dimethyl sulfoxide and pyridine effected the detection result. So it can be used as a luminescence-enhanced chemosensor for MeCN.

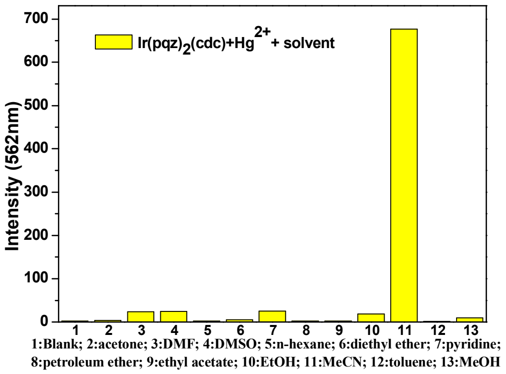


Figure 8. Fluorescence responses of **Ir(pqz)$_2$(cdc)** (2.0×10^{-5} M) in the presence of 2 equiv of Hg^{2+} in 2 mL DCM in the presence of various solvents(10 μL). The yellow bars represent the final ($I_{562\ nm}$) emission intensity.

Logic gate based on Ir(pqz)$_2$(cdc)

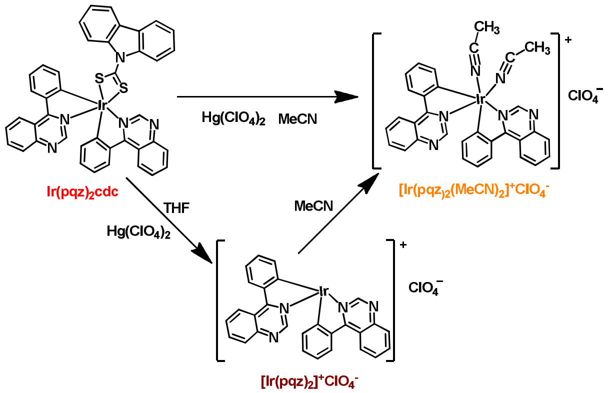
To acquire a molecular logic gate based on the fluorescence behavior of **Ir(pqz)$_2$(cdc)**, the response of iridium(III) complex **Ir(pqz)$_2$(cdc)** to Hg^{2+} and MeCN have also been used to develop AND logic gates by luminescence analysis (Table 1 and Figure S12). The addition of Hg^{2+} totally quenched the emission of **Ir(pqz)$_2$(cdc)** without MeCN. However, upon addition of both Hg^{2+} and MeCN, the emission blue shifted and resulted in an intensive emission band centered at 562 nm. The phosphorescent chemosensor **Ir(pqz)$_2$(cdc)** for selective detection of Hg^{2+} generated AND logic gate by taking the luminescent emission signals as outputs.

Table 1. The truth table of AND gate.

Input		output	
Hg^{2+}	MeCN	Intensity (562 nm)^{a}	AND
0	0	Low(8.72)	0
1	0	Low(1.94)	0
0	1	Low(8.72)	0
1	1	High(569.55)	1

[a] Fluorescence output of Ir(pqz)$_2$(cdc) (2.0×10^{-5} M) in the presence of chemical inputs (Hg^{2+} (1.5 equiv) and MeCN (1 μL)

Mechanism of Ir(pqz)$_2$(cdc) in sensing Hg^{2+} and MeCN



Scheme 2. The possible binding mechanism of **Ir(pqz)$_2$(cdc)** with Hg^{2+}

In order to study the detection mechanism of probe **Ir(pqz)$_2$(cdc)** to Hg^{2+}, a comparison experiment of ^{1}H NMR titration of **Ir(pqz)$_2$(cdc)** with different concentrations of Hg^{2+} was carried out. Figure 10(b) showed the results of ^{1}H NMR titration of **Ir(pqz)$_2$(cdc)** with Hg^{2+} in CDCl$_3$. Treatment of 1.0 equiv. of Hg^{2+} resulted in very large upfield shift of H$_a$ in the quinazoline group of **Ir(pqz)$_2$(cdc)** (δ= 10.28 ppm) by Δδ= 0.64 ppm. Similarly, H$_f$ in the benzene ring of **Ir(pqz)$_2$(cdc)** shifted Δδ= 0.46 ppm from δ= 6.66 ppm to δ= 6.20 ppm. The chemical shifts of **Ir(pqz)$_2$(cdc)** in the range of 6.81−10.28 ppm shifted to downfield obviously upon addition of 1.0 equiv of Hg^{2+}, which may be ascribed to the interaction of Hg^{2+} with **Ir(pqz)$_2$(cdc)**. The proton signal of H$_b$, H$_c$, H$_d$ and H$_e$ in the carbazole ring disappeared completely. The prospective structure was **[Ir(pqz)$_2$]$^+$ClO$_4^-$**, which was proved by the ^{1}H NMR of **Ir(pqz)$_2$(cdc)** with excessive Hg^{2+} (Figure S15). At the same time, when addition of Hg^{2+} in **Ir(pqz)$_2$(cdc)**, the fragment ion peak at 603 of MALDI-TOF mass spectrum indicated the formation of **[Ir(pqz)$_2$]$^+$**. Moreover, another new fragment ion peak at 443 and 441 was the complex **Hg^{2+}-cdc**(Figure S17). The interaction between Hg^{2+} and **Ir(pqz)$_2$(cdc)** was responsible for the significant variation in optical signals. Upon addition of excessive Hg^{2+}, the ^{1}H NMR spectra were almost no changes compared to the spectra in presence of 1.0 equiv. of Hg^{2+} in **Ir(pqz)$_2$(cdc)** solution. These spectral changes might be suggested that **Ir(pqz)$_2$(cdc)** associated with Hg^{2+} led to the formation of **[Ir(pqz)$_2$]$^+$ClO$_4^-$,** yet in the same breath formed another new complex **Hg^{2+}-cdc** between the sulfur atom of carbazole dithiocarbamate and Hg^{2+}. Based on the result of the ^{1}H NMR titration experiments, the possible binding mechanism of **Ir(pqz)$_2$(cdc)** with Hg^{2+} was schematically depicted in Scheme 2. When Hg^{2+} was bound by the sulfur atom of **Ir(pqz)$_2$(cdc)** in THF, the conjugation length of new iridium(III) complex **[Ir(pqz)$_2$]$^+$** was shorter than that of **Ir(pqz)$_2$(cdc)**, and resulted in shorter wavelength absorption band and emission band in UV-vis spectra and fluorescence emission spectra respectively. **Ir(pqz)$_2$(cdc)** in MeCN exhibited intensive red fluorescence and selectively sensed Hg^{2+} upon reaction in MeCN, which led to form new complexes **[Ir(pqz)$_2$(MeCN)$_2$]$^+$** with yellow fluorescence emission.

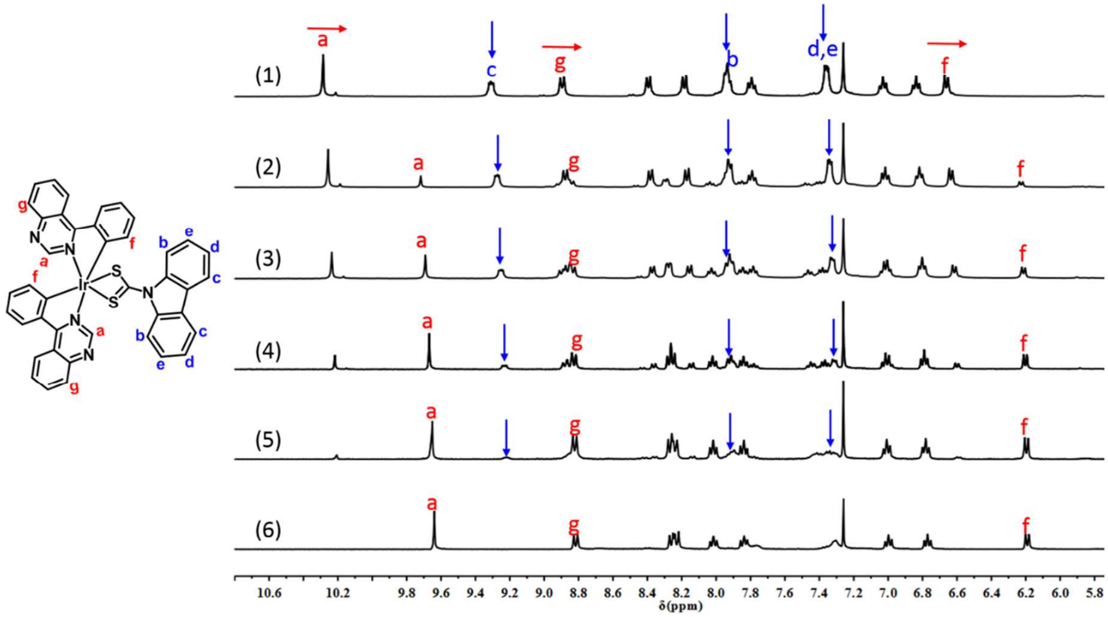


Figure 10. Molecular structure formulas of **Ir(pqz)$_2$(cdc** and change in partial ^{1}H NMR (CDCl$_3$) spectra of **Ir(pqz)$_2$(cdc)** upon addition of (1) 0, (2) 0.2, (3) 0.5, (4) 0.8, (5) 1.0 and (6) 2.0 equiv of Hg^{2+}. The black bars represent the free **Ir(pqz)$_2$(cdc)** solution and the addition of various metal ions (2 equiv) to a solution of **Ir(pqz)$_2$(cdc)**. The red solid arrows represent that the chemical shift of hydrogen proton have changed. The blue solid arrows represent that the signal of hydrogen proton gradually weakened until completely disappeared.

Conclusions

In summary, we have developed a novel phosphorescent turn-on chemosensor for Hg^{2+} with naked-eye detection based on **Ir(pqz)$_2$(cdc)** with high sensitivity and selectivity. The photograph exhibits intensive emitting color change of **Ir(pqz)$_2$(cdc)** from red to yellow without and with Hg^{2+} in MeCN, which blue shift of wavelength about 44 nm in fluorescence emission spectra. It can be used as a colorimetric and fluorometric chemosensor. Based on the results of MADIL-TOF mass spectrum and the ^{1}H NMR experiments, the Hg^{2+} and MeCN sensing mechanisms of **Ir(pqz)$_2$(cdc)** have been analysed in detail. Moreover, a AND logic gate can be used as a potential candidates for a molecular logic circuit.

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