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# Spectroscopic study of the recognition of 2-quinolinone derivative on mercury ion

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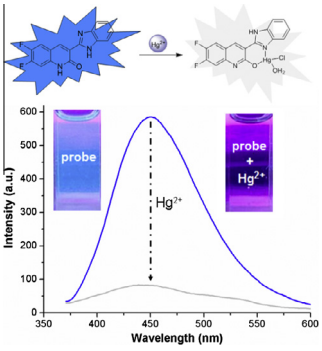
## HIGHLIGHTS

- A new compound, 2-quinolinone derivative was designed, synthesized and characterized.
- Its selective recognition ability on $Hg^{2+}$ was firstly studied by fluorescence and UV–vis spectroscopies.
- The detection mechanism was explored by ESI-MS and $^1H$ NMR analysis.

## GRAPHICAL ABSTRACT

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## ABSTRACT

A new compound based on 2-quinolinone derivative with very little side effects on organisms, 3-(1*H*-benzo[*d*]imidazol-2-yl)-6,7-difluoroquinolin-2(1*H*)-one, has been designed, synthesized and characterized. And its recognition ability was firstly studied by spectroscopy. The result indicated that the compound shows high selectivity for $Hg^{2+}$ over other metal ions with detectable fluorescent signals in aqueous-methanol media. The proposed mechanism is that the fluorescence of the probe was quenched due to the effect from spin–orbit coupling of $Hg^{2+}$ after the probe coordinated with $Hg^{2+}$, and was proved by ESI-MS and $^1H$ NMR analysis.



## Introduction

Mercury is one of the most prevalent toxic metals in the environment and is widespread in air, water and soil due to various sources, such as coal and gold mining, solid waste incineration, wood pulping, fossil fuel combustion, and chemical manufacturing [1–3]. Once absorbed in the human body, even at a very low concentration, the mercury ion ($Hg^{2+}$) can cause brain damage, kidney failure, serious cognitive and motion disorders, and Minamata disease [4–6]. Thus, $Hg^{2+}$ detection has attracted considerable attention and a variety of detection strategies have been developed for $Hg^{2+}$, such as atomic absorption spectrometry (AAS), atomic fluorescence spectrometry (AFS) and inductively coupled plasma mass spectrometry (ICP-MS) [7–9]. However, these methods are time-consuming, require highly trained personnel and sophisticated instrumentation, especially not suitable to real-time monitoring.

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All these disadvantages considerably prevent these conventional methods to be effectively applied for the quick detection of $Hg^{2+}$. Therefore, a simple and an inexpensive method to detect $Hg^{2+}$ is desirable for real-time monitoring of environmental, biological, and industrial samples. Compared with other methods, fluorescent detection is the most efficient method for $Hg^{2+}$ detection because of its operational simplicity, low cost, real time monitoring and high sensitivity [10,11]. To date, considerable efforts have been devoted to develop fluorescent probes for $Hg^{2+}$ over the last few decades [12–22]. Among various fluorescent probes, the fluorophores employed as signal reporters of fluorescent probes mainly focused on coumarin [23–27], pyrene [28–30], 1,8-naphthalimide [16], xanthenes [12,14,15,17,21,31–34], squaraine [35–37], boron dipyrromethene difluoride (BODIPY) [18–21], etc. Quinolines and their oxo derivatives were rarely reported as the fluorescent probes for $Hg^{2+}$ detection except for 8-hydroxyquinoline derivatives [38,39]. However, quinolines and their oxo derivatives are widely present in the structure of various natural compounds that have biological activities [40,41]. It is assumed that quinolines and their oxo derivatives are employed as the fluorescent probes to detect $Hg^{2+}$ in living creature, they will produce very little side effects on organisms, thus it is more advantageous to achieve their applications in living creature.

In fact, we designed and synthesized a kind of 2-quinolinone derivative, 3-(1*H*-benzo[*d*]imidazol-2-yl)-6,7-difluoroquinolin-2(1*H*)-one (**1**) in this work. And the recognition ability of **1** on various metal ions was studied by fluorescence and UV–vis spectroscopies firstly. The result showed that **1** was a high selective fluorescence probe for mercury ion over other metal ions and the detection mechanism of **1** to $Hg^{2+}$ was also demonstrated by ESI-MS and $^1H$ NMR analysis.

## Materials and methods

### *Materials*

4-(2-Hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) was purchased from Sigma–Aldrich (St. Louis, MO). Sodium hydroxide solution (0.1 mol/L) was added to aqueous HEPES (10 mmol/L) to adjust the pH to 7.0. Metal salts were purchased from Shanghai Experiment Reagent Co., Ltd. (Shanghai, China). 2-chloro-6, 7-difluoro-3-quinolinecarboxaldehyde (**2**) was prepared by the literature method [42]. All other chemicals used were of analytical grade.

### *Instruments*

A pH meter (Mettler Toledo, Switzerland) was used to determine the pH. Ultraviolet–visible (UV–vis) spectra were recorded on a Cary 50 Bio UV–visible spectrophotometer. Fluorescence spectra were measured on Cary Eclipse fluorescence spectrophotometer. A PO-120 quartz cuvette (10 mm) was purchased from Shanghai Huamei Experiment Instrument Plant, China. $^1H$ NMR and $^{13}C$ NMR spectra were recorded on a Bruker DRX-300 MHz NMR spectrometer (Bruker, Billerica, MA). Elemental analyses were performed on a Vario EL-III instrument. Melting points were taken on an electrothermal apparatus and were uncorrected. ESI was measured with an LTQ-MS (Thermo) instrument.

### *Synthesis of probe **1***

The synthesis of probe **1** was summarized in Scheme 1. As shown in Scheme 1, 6,7-difluoro-2-oxo-quinoline-3-carbaldehyde (**3**) was easily prepared from 2-chloro-6, 7-difluoro-3-quinolinecarboxaldehyde (**2**) according to a similar procedure reported in the literature [43]. A suspension of **2** (2.275 g, 10 mmol) in 70% aqueous acetic acid (25 mL) was heated under reflux for 6 h. After cooling the reaction mixture, a solid product was filtered and washed well with water and dried to provide **3** (1.71 g, 81.8% yield) as a white solid: mp > 300 °C; $^1H$ NMR (300 MHz, $\delta$ ppm, DMSO-$d_6$): 7.25 (t, $J$ = 10.5, 1H), 8.06 (t, $J$ = 9.9, 1H), 8.45 (s, 1H), 10.18 (s, 1H), 12.33 (br, 1H).

To a mixture of **3** (209 mg, 1 mmol) and o-phenylenediamine (108 mg, 1 mmol) in ethanol (5 mL) was added one to two drops of glacial acetic acid. The resulting mixture was stirred at reflux for 5 h. After cooling the reaction mixture, the resulting precipitate was collected and recrystallized with acetone to give **1** (193 mg, 65% yield) as a pale yellow solid: mp > 300 °C; $^1H$ NMR (300 MHz, $\delta$ ppm, DMSO-$d_6$): 7.20 (s, 2H), 7.33 (t, $J$ = 11.1 Hz, 1H), 7.64 (s, 1H), 7.71 (s, 1H), 8.10 (t, $J$ = 9.9 Hz, 1H), 9.09 (s, 1H), 12.57 (br, 1H), 12.62 (br, 1H); $^{13}C$ NMR (75 MHz, $\delta$ ppm, DMSO-$d_6$): 102.66 (d, $J$ = 21.0 Hz), 112.17, 115.17 (t, $J$ = 19.0 Hz), 117.65, 118.66, 119.75, 121.29, 133.81, 135.23, 137.24, 142.03, 143.20, 146.53, 149.22, 152.54, 159.83. Elemental analysis (calcd.%) for $C_{16}H_9F_2N_3O$: C, 64.65; H, 3.05; N, 14.14. Found: C, 64.78; H, 3.04; N, 14.10. Electrospray ionization mass spectra (ESI-MS) $m/z$ 298.08, $[M+H]^+$ (Fig. S1).

### *General UV–vis and fluorescence spectra measurements*

Stock solutions of probe were prepared in methanol. UV–vis and fluorescence spectra were obtained in methanol: water (1:1 (v/v), HEPES buffer, pH 7.0) solutions. Fluorescence measurements were carried out with a slit width of 5 nm ($\lambda_{ex}$ = 340 nm). The solutions of $Hg^{2+}$, $Zn^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Cu^{+}$, $Mn^{2+}$, $Ru^{3+}$, $Cd^{2+}$, $Pb^{2+}$, $La^{3+}$, $Ce^{4+}$, $Er^{3+}$, $Mg^{2+}$, $Sn^{2+}$, $Al^{3+}$, $Nd^{3+}$, $K^{+}$, $Sm^{3+}$, $Fe^{2+}$, $Fe^{3+}$, $Eu^{3+}$, $Cr^{3+}$, $Zr^{4+}$ and $Co^{2+}$ were prepared from their chloride salts. The solutions of $Ag^{+}$ and $Bi^{3+}$ were prepared from their nitrate salts. The solution of $VO^{2+}$ was prepared from its sulfate salt.

### *Detection range*

Fluorescence spectra were measured from 350 to 600 nm with excitation at 340 nm, and the sensitivity for $Hg^{2+}$ was $10^{-7}$–$10^{-5}$ mol/L. The main band in the UV–vis spectrum was centered at about 375 nm. The detection threshold for $Hg^{2+}$ was $10^{-5}$–$10^{-4}$ mol/L.

## Results and discussion

### *Selectivity over metal ions*

The fluorescence spectrum of probe **1** exhibited a strong emission at 450 nm in 10 mmol/L HEPES buffer, pH 7.0/$CH_3OH$ (v/v, 1:1) when excited at 340 nm. No obvious fluorescence intensity changes were observed in emission spectra of probe **1** after addition of a wide range of environmentally and physiologically active metal ions, such as $Zn^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Cu^{+}$, $Mn^{2+}$, $Ru^{3+}$, $Cd^{2+}$, $Pb^{2+}$, $La^{3+}$, $Ce^{4+}$, $Er^{3+}$, $Mg^{2+}$, $Sn^{2+}$, $Al^{3+}$, $Nd^{3+}$, $K^{+}$, $Sm^{3+}$, $Fe^{2+}$, $Fe^{3+}$, $Eu^{3+}$, $Ag^{+}$, $VO^{2+}$, $Cr^{3+}$, $Zr^{4+}$, $Bi^{3+}$ and $Co^{2+}$ (100 equiv.), except for quenched by $Hg^{2+}$. Fig. 1 shows fluorescence optical density of probe **1** at 450 nm when various metal ions are added.

High selectivity toward the target analyte over the other potentially competitive species is a very important parameter to evaluate the performance of a probe. Therefore, the competition experiments in the presence of potentially competitive metal ions were also conducted by monitoring the change in fluorescence intensity at 450 nm upon addition of $Hg^{2+}$ ion to a solution of probe **1** and different metal ions in 10 mmol/L HEPES buffer, pH 7.0/$CH_3OH$ (v/v, 1:1). As shown in Fig. 2, it can be observed that none of the