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Highly sensitive and selective Hg^{2+}-chemosensor based on dithia-cyclic fluorescein for optical and visual-eye detections in aqueous buffer solution

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ABSTRACT

A new fluorescent sensor (**FC4**) based on fluorescein dithia-cyclic skeleton was designed and prepared as a fluoroionophore for the optical and visual-eye detections of Hg^{2+} in aqueous buffer solution. **FC4** was prepared *via* Kornblum oxidation, ester hydrolysis, alkylation, imine formation and imine reduction. The sensor provided highly sensitive and selective ON–OFF fluorescence sensing toward Hg^{2+} and was shown to discriminate various interfering metal ions, particularly Cu^{2+} and Pb^{2+} as well as Al^{3+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Fe^{3+}, K^+, Mg^{2+}, Mn^{2+}, Na^+ and Ni^{2+}. Sensor **FC4** also exhibited chromogenic change upon binding to Hg^{2+}, which served as a "visual-eye" indicator which could be observed as a noticeable change of the solution color from yellow to orange. The Hg^{2+} detection limit of the sensor was 7.38×10^{-9} or 1.48 ppb which was lower than a permissible concentration of Hg^{2+} in drinking water regulated by the United States Environmental Protection Agency (U.S. EPA).

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1. Introduction

Mercury is a highly toxic metal ion which is dangerous for the environment. Mercury contamination can be accumulated in the environment and biota [1–3]. In the marine system, inorganic mercury (Hg^{2+}) can be converted to methyl mercury by bacteria and then absorbed into biological membranes and entered into human food chain [2–5]. Human, as the final consumer, can collect more mercury which can lead DNA mutation, central nervous damage and endocrine system disorder as well as Minamata disease [4,6,7]. Considering the high toxicity of mercury, the United States Environmental Protection Agency (U.S. EPA) specifies a standard for the maximum allowed level of inorganic mercury in dietary sources, such as 0.55 ppm in edible fish and 2 ppb for Hg^{2+} in drinking water [8].

Fluorescent sensor was an interesting alternative technique for qualitative and quantitative analyses of many analytes, such as protons, small molecules, anions or cations, including Hg^{2+} [9–12]. This method was well-known for high sensitivity, high selectivity, inexpensive cost and rapid response, and could be applied for on-site detection of heavy metal ions [13–16]. Many fluorescent sensors have been reported for Hg^{2+} detection. All of these sensors utilized the ligands which responded and bound to Hg^{2+} to serve as the ionophores. These ligands included hydroxyquinolines [17,18], cyclens [19,20], cyclams [21–23], dioxocyclams [24], diazatetrathia crown ethers [25], azines [26], and calixarenes [27–29].

However, there was only few fluorescent sensors which could serve as "visual-eye" indicators and capable of Hg^{2+} detection in the aqueous or buffer solutions [30–32]. These properties are great advantages for the applications in the analysis of environmental sources and biological systems.

In order to provide the advantage of a fluorescent sensor for application in an environment, we have designed and developed a new aqueous fluorescent sensor, **FC4**, for Hg^{2+} detection, as a dithia-cyclic structure that has appropriate binding site to Hg^{2+}. The binding portion of the sensor was covalently connected to the fluorescein moiety which could serve as a signaling portion. We have chosen fluorescein as a fluorophore in this study due to its large

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molar extinction coefficient, high fluorescence quantum yield, relatively long absorption and emission wavelength (>490 nm) in the visible regions and structural flexibility for derivatization [33–36].

Furthermore, the compound in this study was designed based on an approach similar to host–guest supramolecular chemistry. The binding site of the sensor was preorganised by semi-rigid framework for the size to fit Hg^{2+}, and was also incorporated by sulfur and nitrogen atoms for strong and favorable interaction to Hg^{2+}. The preorganisation of a rigidly conformational host can enhance the affinity of sensor toward guest molecule by management of interactions and provides no additional energetic cost arising from host conformational rearrangement binding to a guest molecule. Therefore, we expected that our designed sensor, **FC4**, would be suitable for Hg^{2+} recognition which could contribute to strong and selective binding to Hg^{2+}.

Herein, we reported a new aqueous chemosensor (**FC4**) which was prepared from an assembly of 2-(4-(2-aminoethylthio) butylthio)ethanamine and fluorescein moiety for Hg^{2+} determination. Sensor **FC4** showed high sensitivity with low detection limit, high Hg^{2+}-selectivity in comparison with foreign ions in aqueous buffer solutions. Molecular modeling of the cyclic structure illustrated that **FC4** provided a semi-rigid framework and size fit for Hg^{2+}. In addition, **FC4** did not only exhibit fluorogenic response but also exhibited chromogenic change upon binding to Hg^{2+}, which could be observed by visual-eye as a color change of the solution from yellow to orange.

2. Experiment

2.1. Material and methods

2.1.1. Materials

The reagents and solvents were purchased from Sigma–Aldrich Corporation, Fluka Chemical Corporation while all of the metal salts (chloride salts) were purchased from Strem chemicals, Inc. 4′,5′-Bis(bromomethyl)fluorescein dibenzoate was obtained from Strem chemicals, Inc. All reagents, solvents, and metal salts were used as received.

2.1.2. Methods

NMR spectra in $CDCl_3$ and MeOD solutions were recorded using Bruker Avance 300 spectrometer operating at 300 MHz for ^1H and 75 MHz for ^{13}C. Melting points of the synthetic compounds were measured by Stuart Scientific Melting Point Apparatus SMP2. Absorption spectra were determined on a single beam Hewlett Packard 8453 spectrophotometer. Fluorescence spectra were measured using Perkin Elmer Luminescence spectrometer LS 50B. The excitation and emission slit widths used in fluorescence measurements were 5.0 nm with a scan rate of 300 nm/min. ThermoElectron LCQ-DECA-XP, ESI-Ion trap mass spectrometer was used to record mass spectra of the synthetic compounds. Molecular modeling was performed with the Discovery Studio 2.5 program package.

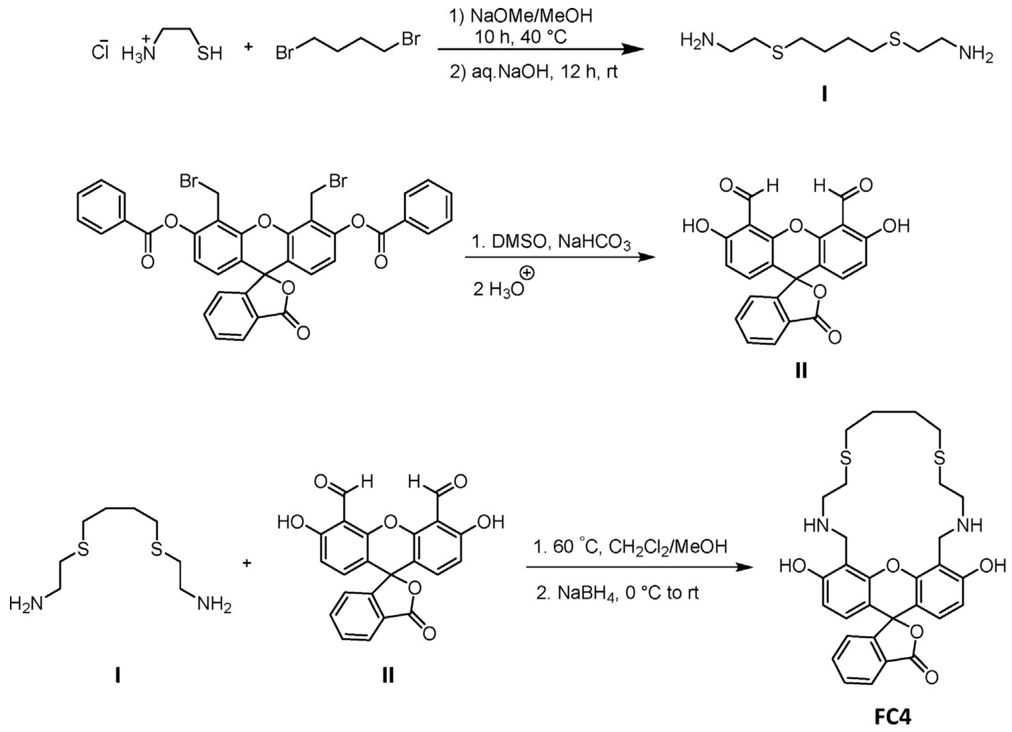
2.2. Syntheses

2.2.1. Synthesis of 2-(4-(2-aminoethylthio)butylthio) ethanamine (*I*)

The synthesis of the title compound was performed in the same manner as described previously [37] and the synthetic steps are outlined in Scheme 1.

2.2.2. Synthesis of 4′,5′-fluoresceindicarboxaldehyde (*II*)

Modified from a previous report [38], 4′,5′-bis(bromomethyl) fluorescein dibenzoate (0.40 g, 0.5 mmol) and $NaHCO_3$ (0.40 g, 4.8 mmol) were combined in 40 mL of DMSO and heated to 150 °C for 4 h. When the reaction mixture was cooled down to room temperature, it was slowly poured into 2 M hydrochloric solution (140 mL). The acid mixture was then stirred at room temperature for 2 h. The aqueous solution was extracted with CH_2Cl_2 (3×40 mL), and the organic portions were collected and removed to yield a dark orange liquid. Deionized water (60 mL) was added and the mixture kept at room temperature for 18 h, then the resulting orange precipitate was collected by vacuum filtration



Scheme 1. Synthesis of sensor **FC4**.

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