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A novel naphthalimide–glutathione chemosensor for fluorescent detection of Fe^{3+} and Hg^{2+} in aqueous medium and its application

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ABSTRACT

By rationally introducing glutathione functionalized 1, 8–naphthalimide, a novel fluorescent chemosensor (**NG**) was successfully synthesized. **NG** can high selectively and sensitively recognize Fe^{3+}/Hg^{2+} ions through quenching of fluorescence among all kinds of common metal ions in aqueous medium. The binding stoichiometry ratio of **NG**–$\mathbf{Fe^{3+}}$ is verified as 2:1and **NG**–$\mathbf{Hg^{2+}}$ as 1:2 confirmed by Job's plot method, FT-IR, ^{1}H NMR and ESI–MS spectrum, and the possible sensing mechanism were also proposed. The chemosensor **NG** toward Fe^{3+} and Hg^{2+} displays the excellent advantages of high selectivity and sensitivity, low detection limits (7.92×10^{-8} and 4.22×10^{-8} M), high association constants (3.37×10^{8} and 8.14×10^{4} M^{-2}), instataneous response (about 10s) and wide pH response range (3.0–8.0). Importantly, the chemosensor **NG** was successfully applied to determine Hg^{2+} in tap water. Meanwhile, the test strips based on **NG** were prepared, which could conveniently and efficiently detect Fe^{3+} and Hg^{2+}. Moreover, the complex of **NG** and Fe^{3+} (**NG**–$\mathbf{Fe^{3+}}$) showed high selectivity and sensitivity for $H_2PO_4^-$ over many other anions in the same medium.

1. Introduction

Amongst the various basic metal ions of the human body, Fe^{3+} is one of the most vital trace elements for lives. On one hand, excessive Fe^{3+} in body could result in cancers, Parkinson's disease and dysfunction of organs.[1] On the other hand, deficiency of Fe^{3+} will cause all kinds of disorders of living systems, and even premature death.[2] Unlike Fe^{3+}, Hg^{2+} is highly toxic and dangerous component for lives and the environment.[3] As the result of industrial processes, the release of Hg^{2+} can cause many health problems such as digestive, kidneys and neurological diseases.[4–6] Because of the above reasons, there is a great demand for detecting these metal ions.

Due to high sensitivity and selectivity, rapid response, low cost and easy performance, fluorescence sensors play an important role in medical, environmental and biological applications.[7–17] By far, a large number of fluorescent chemosensors for metal ions have been reported.[18–23] But only a few fluorescent sensors capable of the simultaneous detection of Fe^{3+} and Hg^{2+} have been reported.[24–26]

Owing to strong blue fluorescence and excellent photostability, 1, 8–naphthalimide derivatives are regularly used for fluorescence sensors, switchers and ion probes.[27–35] However, the application of naphthalimide sensors was limited due to poor solubility. Glutathione (GSH), which has multiple binding sites to cooperate with metals, is a most favorable oligopeptide. Moreover, the carboxyl of GSH has not only remarkable coordinate ability[36–42] but also excellent hydrophilic.

Based on these considerations above and continuing our researches interesting in ions recognition,[43–47] by rationally introducing glutathione functionalized 1, 8–naphthalimide, we designed and synthesized a novel, low–cost fluorescent chemosensor (**NG**) for simultaneously detecting Fe^{3+} and Hg^{2+} in aqueous medium. As expected, chemosensor **NG** displays highly selective fluorescent turn-off response toward Fe^{3+} and Hg^{2+} with no interference of other competing metal ions in aqueous medium. Excitingly, the complex **NG**–$\mathbf{Fe^{3+}}$ could detect $H_2PO_4^-$ with high sensitivity in same system.

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2. Experimental section

2.1. Materials and apparatus

All reagents and solvents in this work were commercially available and were used without further purification. Fresh double–distilled water in this work was used. ^{1}H NMR (400 MHz) spectra were acquired on a Mercury-400BB spectrometer. Tetramethylsilane (TMS) as an internal standard. UV–visible spectra measurements were performed on a Shimadzu UV–2550 spectrometer. Fluorescence spectra measurements were performed on a Shimadzu RF–5310. Melting point was measured on an X–4 digital melting–point apparatus. The infrared spectra were performed within the 4000–400 cm^{-1} region on a Digilab FTS–3000 FT–IR spectrophotometer. Mass spectra were performed on a Bruker Esquire 3000 plus mass spectrometer (Bruker–FranzenAnalytik GmbH Bremen, Germany) equipped with ESI interface and ion trap analyser.

2.2. Synthesis of the chemosensor NG

Glutathione (1.38 g, 4.0 mmol) and 1, 8-naphthalic anhydride (0.79 g, 4.0 mmol) were mixed in hot absolute DMF (50 mL), and the mixture was stirred under reflux conditions for 10 h. The resulting solution was cooled to room temperature, and added 20 ml distilled water in it, after stewing 24 h, the dark brown precipitate appeared, afterwards filtrated, washed with absolute ethanol three times, and then recrystallized with DMF to give a the dark brown powder product **NG**. As shown in Scheme 1 (m.p: 216–217 °C). The chemosensor **NG** has been characterized by ^{1}H NMR, ^{13}C NMR, IR and ESI–MS. ^{1}H NMR (DMSO-d_6, 400 MHz) (Fig. S1): δ 12.72 (s, 1H), δ 8.52 (m, 5H), δ 8.20 (m, 2H), 7.90 (m, 2H), 5.56 (d, J = 6.0 Hz, 1H), 3.69 (t, J = 6.0 Hz, 2H), 3.01 (m, 2H), 2.76 (m, 1H), 2.24 (m, 5H)·^{13}C NMR (DMSO-d_6, 151 MHz) (Fig. S2) δ(ppm) 171.97, 171.27, 170.73, 163.67, 161.14, 135.82, 135.18, 132.90, 131.82, 130.17, 127.90, 52.91, 41.19, 36.22, 32.27, 29.03, 24.61. IR (KBr, cm^{-1}) v: 3329 (w), 2473 (w), 1659 (s), 1506 (m), 1216 (s), 1046 (m). ESI–MS *m/z*: calcd for $C_{22}H_{22}N_3O_8S$, $[NG+H]^+$ = 488.1128, found $[NG+H]^+$ = 488.1112 (Fig. S3).

2.3. General procedure for UV–vis experiments

All UV–vis spectra were recorded on a Shimadzu UV–2550 spectrometer after the addition of perchlorate metal salts in DMSO, while keeping the ligand concentration constant (20 μM) in DMSO/H_2O (1/4, v/v, pH = 7.20) buffer solution.

2.4. General procedure for fluorescence spectra experiments

All fluorescence spectra were recorded on a Shimadzu RF–5301 fluorescence spectrometer after the addition of perchlorate metal salts in DMSO and sodium salt of anion in water, while keeping the ligand concentration constant (20 μM) in DMSO/H_2O (1/4, v/v, pH = 7.20) buffer solution. The excitation wavelength was 335 nm. The excitation slit widths were 5 nm and emission slit widths were 5 nm, respectively.

2.5. Testing and calculating methods

The stock solutions of metal salts were first prepared with 4.0 mM in DMSO. The stock solutions of anions were first prepared with 10 mM in deionized water. **NG** was dissolved in DMSO to get the stock solution (2.0×10^{-4} M), which diluted to a concentration of 20 μM as the determined solution (DMSO/H_2O, 1/4, v/v, pH = 7.20). The wide pH range solutions were prepared by adjustment of HEPES (1 mM, pH 7.20) solution with 1 M $HClO_4$ or 1 M TBAOH.

The detection limit (DL) was calculated on the basis of the fluorescence titrations by 3σ/S, in which σ is the standard deviation of twenty times blank measurement, S is the slope of the fit line in titration experiment.

The binding constant Ka was calculated by Benesi-Hildebrand Eq. (1). Where F is the fluorescence intensity of **NG** at 480 nm at any given Fe^{3+}/Hg^{2+} concentration, F_0 is the fluorescence intensity at 480 nm in the absence of Fe^{3+}/Hg^{2+}, and Fmax is the maxima fluorescence intensity at 480 nm in the presence of Fe^{3+}/Hg^{2+} in DMSO/H_2O (1/4, v/v, pH = 7.20) buffer solution. $[M^{m+}]$ is the concentration of Fe^{3+} or Hg^{2+}.

$$1/(F - F_0) = 1/(F_{max} - F_0)\left\{\left(Ka\left[M^{m+}\right] + 1\right)\right\} \quad (1)$$

2.6. General procedure for ^{1}H NMR experiments

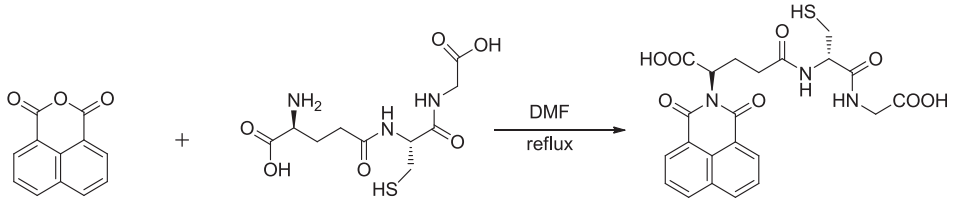
For ^{1}H NMR titrations, sensor **NG** was prepared in DMSO- d_6 and Hg^{2+} was prepared in D_2O. First of all, only sensor **NG** in DMSO- d_6 was added into the NMR tube, and then Hg^{2+} was added at 0.1, 0.5, 1.0, 2.0 and 4.0 equiv. sequentially. All solutions were mixed directly in the NMR tube.

2.7. Practical samples analysis

For practical sample analysis, the tested tap water samples were prepared by adding known amounts of Hg^{2+}. The fluorescence spectrum of each sample was tested for three times, and the found concentration of Hg^{2+} was measured according to the developed calibration curve.

2.8. Preparation of the test strips

The test strips were carried out by submersing filter papers in DMSO/H_2O (1/4, v/v) solution of **NG** (2.0×10^{-4} M) and then dried them in air. The Fe^{3+}/Hg^{2+} and competitive anions water solution (4.0×10^{-3} M) were dropped on the test strips. After drying, the images were recorded by a digital camera unde UV lamp. The same procedures were done for $H_2PO_4^-$ and competitive ions.



Scheme 1. Synthetic procedures of sensor **NG**.