



Novel oligothiophene-based dual-mode chemosensor: “Naked-Eye” colorimetric recognition of Hg²⁺ and sequential off-on fluorescence detection of Fe³⁺ and Hg²⁺ in aqueous media and its application in practical samples



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ABSTRACT

A novel oligothiophene-based dual-mode chemosensor **A3TA** was designed and synthesized for Fe³⁺ and Hg²⁺ in aqueous media. The sensor **A3TA** showed high selectivity and sensitivity toward Fe³⁺ and Hg²⁺ over other competitive metal ions. Hg²⁺ was detected by changing color from khaki to reddish brown, could be easily distinguished by bare eyes. Moreover, the sensor also acted as a “turn-on” type fluorescent sensor toward Fe³⁺ and Hg²⁺. The detection limits for Fe³⁺ and Hg²⁺ were found to be as low as 3.52×10^{-8} and 5.0×10^{-8} M, respectively. The stoichiometric ratio of the sensor toward Fe³⁺/Hg²⁺ ions was obtained to be 1:2. Furthermore, the proposed sensor **A3TA** was also found to have high association constants (10^5 M^{-2}), wide pH range (4–12) and short response time (3–5 min). In addition, the sensing mechanism was proposed based on chelation-enhanced fluorescence (CHEF) and investigated in detail by fluorescence spectroscopy, ¹H NMR titrations, FT-IR and HRMS spectra analysis. Importantly, the proposed sensor **A3TA** has been successfully used to quantify trace amounts of Fe³⁺ and Hg²⁺ in real samples.

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1. Introduction

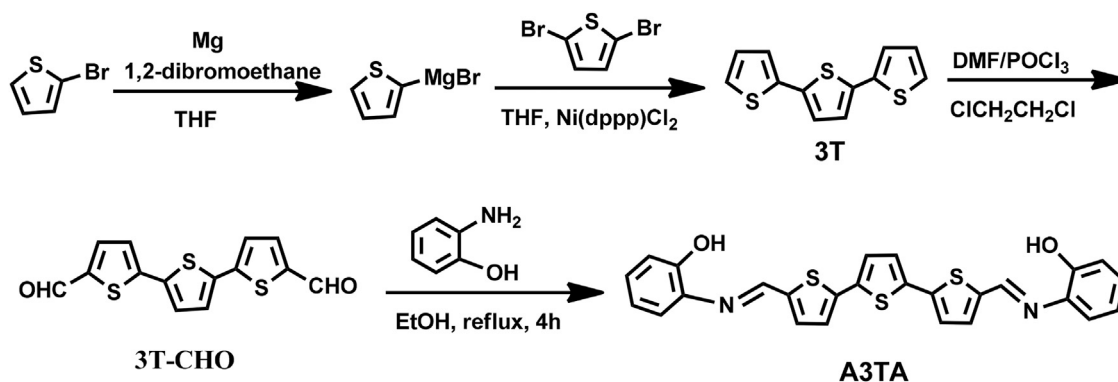
Pollution by heavy metal ions has become a serious and urgent problem worldwide in terms of their potential damage to the environment and the human body even at very low concentrations. Among heavy metals, iron is one of the indispensable metal ions and plays an important function in a wide range of organic and biological processes such as oxygen-carrying, cellular metabolism, enzymatic reaction and various biosyntheses [1,2]. However, the deficiency or overload of iron in humans eventually cause various diseases such as anemia, liver damages and hemochromatosis [3–5]. Mercury is one of the most prevalent toxic metals in both the environment and biological system [6,7], which can lead to serious and irreversible DNA damage, mitosis impairment as well as nervous system defects [8–10]. Even at a very low concentration level, the Hg²⁺ ion can readily penetrate through biological membranes. Hence, it is urgently important to explore an effective advanced

method for the sensitive and selective detection of trace amounts of Fe³⁺ and Hg²⁺ ions in biological systems and natural environment.

Among various detection methods for metal ions, fluorescent sensing techniques are preferred due to their simplicity, instantaneity, high sensitivity, remarkable selectivity and real time monitoring [11–16]. The development of fluorescent chemosensors for biologically and environmentally important metal ions has recently received a great deal of attention due to their significant roles in industry, medicine, human health and the environment [17–22]. To date, a large number of fluorescent chemosensors for selective and sensitive detection of Hg²⁺ [23–30], and Fe³⁺ [31–36] have been reported, but most of which can only detect one target. However, in many reports most of them showed fluorescence “turn off” response due to the paramagnetic nature of Fe³⁺ [37,38] and the heavy atom effect of Hg²⁺ [39–41]. As is well known, bifunctional and multifunctional fluorescent sensors utilize a single host to recognize two and more analytes by distinct fluorescence responses through the same or different channels. To the best of our knowledge, very few dual-mode sensors have been reported for simultaneous detection of Hg²⁺ and Fe³⁺ [42–47]. Hence, developing multifunctional sensors with fluorescent “turn on” response

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Scheme 1. The synthetic route to sensor **A3TA**.

for simultaneous sensing of Fe³⁺ and Hg²⁺ that are inexpensive, rapid and applicable to the environmental and biological systems is very decisive and still a challenge.

Thiophene and its derivatives have been utilized as good sensor to detect the metal ions because of their excellent photophysical properties [46,48–50]. Recently, some researches induced oligothiophene derivatives in OLEDs, solar cells, sensitizers and field-effect transistors [51–57]. It is well known that Schiff bases contain C=N bond, which offer electron pair to the bind and improve the ability to chelating metals [58]. And C=N isomerization in Schiff bases generally causes weak fluorescence emission due to the attached chromophore, but high-intensity emission can be obtained after this isomerization is blocked by binding to metal ions [59]. In this regard, we designed and synthesized a new Schiff base sensor **A3TA** based on the oligothiophene building block (Scheme 1), which was expected to detect various analytes through the change of unique photophysical properties.

In a continuation of our research interest in the fluorescent chemosensors, we herein report a new dual-mode colorimetric and fluorescent chemosensor **A3TA**, which could not only realize the visual recognition of Hg²⁺ by an obvious color change from khaki to reddish brown but also directly detect Hg²⁺ and Fe³⁺ ions simultaneously by an obvious fluorescence enhancement in aqueous media. Based on Job plots, fluorescence titrations, FT-IR analyses and ¹H NMR titrations, their binding modes and sensing mechanisms were proposed and explained. In addition, the detection results of Hg²⁺ and Fe³⁺ ions in real samples including tap water, river water and distilled water showed that the method is reasonable and feasible, suggesting that **A3TA** could be a potential fluorescent chemosensor for tracking trace amounts of Hg²⁺ and Fe³⁺ ions in aqueous environment.

2. Experimental

2.1. General information

All solvents and chemicals (analytical grade) were obtained from commercial suppliers and used without further purification. All ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were acquired on a Bruker AV-400 spectrometer, with DMSO-*d*₆ used as the solvent and tetramethylsilane (TMS) as an internal standard. Infrared measurements with the KBr pellet technique were performed within the 4000–400 cm⁻¹ region on a Bruker ALPHA FT-IR spectrometer. High resolution mass spectra (HRMS) were carried out using an Agilent 6510 Accurate-Mass Q-TOF LC/MS system. The pH was determined with a PHS-25C Precision pH/mV Meter (Aolilong, Hangzhou, China). Fluorescence spectra were recorded on a Hitachi F-4600 fluorescence spectrophotometer with a scan rate at 1200 nm/min. Excitation was carried out at 360 nm with all excita-

tion and emission slit widths at 5 nm. All experiments were carried out at room temperature.

2.2. Synthesis of

2,2'-(2,2':5',2''-terthiophene)-5,5''-diylbis(methanylylidene))bis(azanylylidene)diphenol (**A3TA**)

Compounds **3T** and **3T-CHO** were synthesized according to the reported method [60,61].

[2,2':5',2''-terthiophene]-5,5''-Dicarbaldehyde (**3T-CHO**) (0.60 g, 2.0 mmol) and 2-aminophenol (0.44 g, 4.0 mmol) were dissolved in dry EtOH (30 mL), then the mixture was heated to reflux for 4 h. The resulting mixture was cooled down to room temperature, and the precipitate was collected by simple filtration to afford the desired product of **A3TA** (0.92 g, 1.90 mmol, 93% yield) as a brick-red solid. Mp=232.1–232.8 °C; ¹H NMR: (400 MHz, DMSO-*d*₆) δ=9.09 (s, 2H), 8.75 (s, 2H), 7.56 (d, *J*=4.0 Hz, 2H), 7.44 (s, 2H), 7.42 (d, *J*=4.0 Hz, 2H), 7.08 (d, *J*=8.0 Hz, 2H), 6.97 (t, *J*=8.0 Hz, 2H), 6.82 (d, *J*=8.0 Hz, 2H), 6.74 (t, *J*=8.0 Hz, 2H). ¹³C NMR: (100 MHz, DMSO-*d*₆) δ=152.64, 150.80, 142.17, 139.64, 137.46, 136.13, 134.02, 127.21, 126.65, 125.13, 120.54, 119.49, 116.16; FT-IR:(KBr, cm⁻¹) ν=3376 (O–H), 3045 (C–H), 1617 (C=N), 1584 (C=C), 736 (C–S); HRMS (ESI): *m/z* [M+H]⁺ calcd for: C₂₆H₁₈N₂O₂S₃: 487.0530, found: 487.0596.

2.3. General procedures for spectroscopic analysis

The stock solutions of metal salts (K⁺, Na⁺, Ag⁺, Ca²⁺, Hg²⁺, Cd²⁺, Pb²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Fe²⁺, Cr³⁺, Al³⁺ and Fe³⁺) were first prepared with 3.0 mM in deionised water. **A3TA** was dissolved in MeCN to give the stock solution (3.0 mM) and then diluted with a mixed solution of MeCN/H₂O to prepare the analytical solution (30 μM) (MeCN/H₂O, 6/4, v/v). The wide pH range solutions were prepared by adjustment of HAC-NaAc (50 mM, pH 4.76) solution with 1 mM HCl or 1 mM NaOH.

2.4. Detection of Fe³⁺ and Hg²⁺ in water samples by **A3TA**

The water samples including tap water, distilled water and river water were all collected from Qilu University of Technology and used to prepare the required samples. The river water was filtered through a 0.22 μm membrane to remove the insoluble materials. All the water samples (3 mL) were spiked with different Fe³⁺ and Hg²⁺ concentrations (0–30 μM), respectively. Then **A3TA** (30 μM) was added and experiments were run after equilibration for 1 min. All water samples were analyzed by using ultraviolet spectrophotometer.

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