A single thiourea-appended 1,8-naphthalimide chemosensor for three heavy metal ions: Fe^{3+}, Pb^{2+}, and Hg^{2+}

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ABSTRACT

A 1,8-naphthalimide-thiourea conjugate was developed for highly selective and sensitive colorimetric detection of Fe^{3+} and Pb^{2+} in $MeCN/H_2O$ (99/1, v/v) and fluorescent recognition of Hg^{2+} in $MeCN/H_2O$ (85/15, v/v). The linear concentration ranges for Fe^{3+}, Pb^{2+}, and Hg^{2+} were 0–150, 0–80, and 0–90 μM with the detection limits of 6.86 μM, 5.09 μM, and 82.1 nM, respectively. The sensor responded to Fe^{3+}, Pb^{2+}, and Hg^{2+} rapidly and a large number of coexisting ions such as Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, Cu^{2+}, Zn^{2+}, Cr^{3+}, Ni^{2+}, Mn^{2+}, Co^{2+}, Cd^{2+}, and F^- showed almost no obvious interference with the detection. Sensing mechanism of the sensor to Fe^{3+}, Pb^{2+}, and Hg^{2+} was investigated through job's plot experiment, reversible experiment, LC–MS and ^1H NMR analysis. Moreover, the off-on sensor was successfully employed to monitor Hg^{2+} in pond and tap water as well as in living cells.

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1. Introduction

Heavy metal ions are toxic to the environment. They are not biodegradable and have the potential for accumulation in different body organs [1]. Among these ions, mercury is a huge threat because it is widely spread in air, soil, and water which subsequently bio-accumulates through the food chain. Once mercury exists in human body, it can lead to lots of health problem in the brain, kidney, digestive and central nervous system [2]. Pb^{2+} is another poisonous metal ion. The presence of lead causes much health problem such as anemia, kidney damage, disorder of the blood, memory loss, muscle paralysis and mental retardation [3]. Not the same as mercury and lead, iron is an essential trace element for lives. However, high level of Fe^{3+} in body is related to increased incidence of certain cancers and dysfunction of organs [4]. For the above reasons, there is a high demand for tracking these metal ions. Owing to high sensitivity, selectivity, low cost, and feasibility of in situ and real time monitoring, chemosensor has an attractive application prospect in detecting metal ions [5–7]. To date, a large number of chemosensors for Fe^{3+}, Pb^{2+}, and Hg^{2+} have been reported [3,4,8–15], but most of which can only detect one target.

Recently, a new chemosensor design concept of "single sensor for multiple analytes" gets more and more attention. The concept can be realized mainly by distinguishing different ions with different excitation wavelengths [16,17], detecting different ions in different solvents [18–21] or recognizing different ions by UV–vis and fluorescence spectra [22–24]. The development of novel sensors for multiple metal ions is of great significance because they are more efficient compared with sensors for single target.

1,8-Naphthalimide derivatives are widely used as reporters in colorimetric and fluorescent chemosensors because introduction of various substituents to the 4 and 5 positions of the naphthalic ring can modulate both UV–vis absorption and fluorescence properties [25–28]. Thiourea is a commonly used receptor for anion [25]. 1,8-Naphthalimide-thiourea conjugates were usually reported as highly selective and sensitive spectral chemosensors for anions like F^- and AcO^- [26,29]. However, in some rhodamine-based chemosensors thiourea was also used to recognize Hg^{2+} [30–32]. Inspired by these work, in this article, we explored the possibility of thiourea attached to 1,8-naphthalimide for discern cations and found that a single thiourea-appended 1,8-naphthalimide was able

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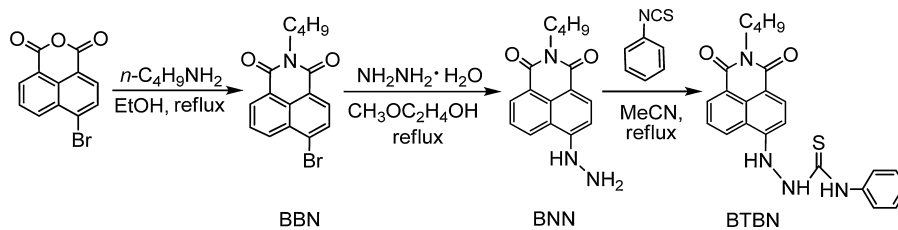
Scheme 1. Synthetic route of BTBN.

to highly selective and sensitive colorimetrically detect Fe^{3+} and Pb^{2+}, and fluorimetrically detect Hg^{2+} in appropriate conditions. This result can provide a fresh idea for the design of multifunctional chemicalsensors.

2. Experimental

2.1. Materials

4-Bromine-1,8-naphthalic anhydride (98%) was purchased from Anshan HIFI Chemical Co., Ltd., phenyl isothiocyanate (98%) was bought from Yake Chemical Reagent Co., Ltd., n-butylamine, tetra-butylammonium chloride, $NH_2NH_2 \cdot H_2O$ (85%), the solvents and the metal cation sources, NaCl, KCl, $MgCl_2$, $CaCl_2$, $CrCl_3 \cdot 6H_2O$, $MnSO_4 \cdot H_2O$, $FeCl_3 \cdot 6H_2O$, $FeCl_2 \cdot 7H_2O$, $CoCl_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $CdCl_2 \cdot 2.5H_2O$, $HgCl_2$, $Pb(CH_3COO)_2$, were provided by Sinopharm Chemical Reagent Co., Ltd. All the reagents were used without further treatment. The solvents used in synthesis were analytical grade, others were spectroscopic grade.

2.2. Apparatus

LC-mass was performed on an Agilent 1200/6220 spectrometer (Agilent Co., USA) unless otherwise specified. ^{1}H NMR was carried out on a 300 MHz Varian Unity Inova spectrometer (VarianCo., USA). High performance liquid chromatography was measured on an Agilent 1260 Infinity HPLC (Agilent Co., USA), using SB-C18 column (250 mm * 4.6 mm * 5.0 um) and $MeCN/H_2O$ (50/50, v/v) as an eluent (the total flux was 1 mL/min), and the detection wavelength was 392 nm. UV–vis spectra were taken on a U-3900 spectrophotometer (Perkin–Elmer Co., USA). Fluorescence spectra were recorded on a Fluoromax-4 spectrofluorometer (HORIBA Jobin Yvon Co., France). The pH values were measured with a Mettler-Toledo FE20 pH meter (Mettler-Toledo Co., USA). Colorimetric and fluorescent pictures were taken by an IXUS105 camera (Canon Co., Japan). Cell images were taken on Nikon IX71 fluorescence inverted system microscope. (Nikon Co., Japan). All the detections were carried out at 25 °C unless otherwise specified.

2.3. Synthetic procedures and characterization data for BTBN

BTBN was synthesized by three-step reactions between 4-bromo-1,8-naphthalic anhydride, n-butylamine, hydrazine monohydrate and phenyl isothiocyanate, as shown in Scheme 1.

2.3.1. Synthesis of intermediate BBN

According to the Ref. [33], 4-bromo-1,8-naphthalic anhydride (2 g, 7.2 mmol) and n-butylamine (1.5 mL, 15.6 mmol) were heated to reflux in 30 mL ethanol for 24 h. The solution was poured into 50 mL ice water to precipitate out a solid, which was collected by filtration, washed with water, and recrystallized from ethanol to produce a pale yellow solid 1.8660 g (78.3%). Its Melting point was 102–104 °C, in line with that reported the literature.

2.3.2. Synthesis of intermediate BNN

According to the Ref. [34], BBN (0.5 g, 1.6 mmol) and hydrazine monohydrate (0.5 mL, 5.3 mmol) were heated to reflux in 15 mL 2-methoxyethanol for 4 h. The reaction mixture was cooled to room temperature and an orange solid 0.3847 g (89.9%) was collected by suction filtration and then washed with ethanol. Its melting point was 220–222 °C, as reported in the reference.

2.3.3. Synthesis of BTBN

BNN (0.1 g, 0.35 mmol) was dissolved in 15 mL acetonitrile (MeCN). Phenyl isothiocyanate (0.06 mL, 1.41 mmol) was added and the resulting reaction mixture was stirred at reflux. After completion, the mixture was cooled to room temperature; the precipitate was collected by suction filtration and washed with MeCN. The crude product was purified by recrystallization with chloroform and dried in vacuum to afford BTBN 0.0867 g (58.7%) as a yellow solid. ^{1}H NMR (DMSO-d6, 400 MHz, δ ppm): 10.12 (d, J = 8.0 Hz, 2 H, NH), 9.89 (s, 1H, NH), 8.70 (d, J = 8.7 Hz, 1H, ArH), 8.50 (d, J = 7.2 Hz, 1H, ArH), 8.43 (d, J = 8.5 Hz, 1H, ArH), 7.85–7.69 (m, 1H, ArH), 7.42 (d, J = 7.5 Hz, 2H, ArH), 7.32 (t, J = 7.7 Hz, 2H, ArH), 7.16 (t, J = 7.4 Hz, 1H, ArH), 6.99 (d, J = 8.4 Hz, 1H, ArH), 4.15–3.97 (m, 2H, CH_2), 1.73–1.52 (m, 2H, CH_2), 1.34 (d, J = 14.8, 7.4 Hz, 2H, CH_2), 0.92 (t, J = 7.3 Hz, 3H, CH_3) (Fig. S1). LC–MS m/z calcd. For $C_{23}H_{22}N_4O_2S$ (M + H$^+$): 419.0, found: 419.0 (Fig. S2). HPLC: 97.8% (Fig. S3).

2.4. Testing and calculating methods

BTBN was dissolved in MeCN to form a 10^{-3} M stock solution. Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, Fe^{2+}, Cu^{2+}, Zn^{2+}, Cr^{3+}, Pb^{2+}, Ni^{2+}, Mn^{2+}, Co^{2+}, Cd^{2+}, Hg^{2+} and F^- sources were dissolved in deionized water (H_2O) to obtain 10^{-2} M stock solutions. For colorimetric detection of Fe^{3+} and Pb^{2+}, stock solution of BTBN (100 μL) and one of the ion stock solutions (100 μL) were added in a 10 mL volumetric flask and diluted with CH_3CN. For fluorescent measurement of Hg^{2+}, the mixed stock solutions were diluted to 10 mL with CH_3CN and H_2O to form CH_3CN/H_2O (99/1, 85/15 and 50/50) solutions. For the titration experiments, BTBN stock solution (100 μL) was mixed with a certain amount of the tested ion (Fe^{3+}, Pb^{2+}, or Hg^{2+}) stock solution and diluted to 10 mL with CH_3CN and H_2O to form CH_3CN/H_2O (99/1 or 85/15) solutions. pH was adjusted by 0.1 M HCl and 0.1 M NaOH aqueous solutions.

The detection limit was calculated by $3s/k$, in which s is the standard deviation of six times blank measurement, k is the slope of the fit line in titration experiment.

The binding constant K_s was calculated by Benesi-Hildebrand Eq. (1) [18,28,35]. Where I_0, I, and I_{max} are the absorbance of BTBN at 362 nm for Fe^{3+}, at 546 nm for Pb^{2+}, or fluorescent intensity of BTBN at 517 nm for Hg^{2+} in the absence of the metal ion, at a certain concentration of the metal ion and at a complete-interaction concentration of the metal ion. $[M^{m+}]$ is the concentration of Fe^{3+}, Pb^{2+} or Hg^{2+}. n is the binding stoichiometry for BTBN and the metal ion.

$$\frac{1}{I - I_0} = \frac{1}{Ks(I_{max} - I_0)[M^{m+}]^n} + \frac{1}{I_{max} - I_0} \tag{1}$$