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A highly sensitive and selective optical probe for detection of Hg^{2+} based on a 2,5-bis[2-(benzylthio)aniline]-croconaine

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ABSTRACT

A highly sensitive and selective optical probe, 2,5-bis[2-(benzylthio)aniline]-croconaine (**BAC**) for sensing of Hg^{2+} was synthesized. The **BAC** can efficaciously recognize Hg^{2+} with the existence of competing cations (Ba^{2+}, Fe^{3+}, Na^{+}, Ca^{2+}, Co^{2+}, K^{+}, Mg^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+}, Al^{3+}, Pb^{2+}, Cr^{3+}, Cd^{2+}, Ag^{+}) in DMSO. The binding constant (Ka) of **BAC**-Hg^{2+} was calculated to be about $1.6 \times 10^5\,M^{-1}$. Simultaneously, the chelating mode of **BAC**-Hg^{2+} was confirmed by Job's plot, FT-IR and ^1H NMR. "Naked eye" detection has been performed, indicating the potential application of **BAC** on conveniently, selectively and fast detection of Hg^{2+}. Moreover, Hg^{2+} and EDTA could be employed as inputs and the fluorescence emission intensity which was 480 nm as output so that a molecular logic gate could be realized.

1. Introduction

Nowadays, the pollution of heavy metal cations has become an increasingly serious problem in the ecological environment. There is no doubt that they are a serious threat to human health [1–5]. For example, mercury ion has many hazards to human health, and if it exists in natural water bodies, it will pose a threat to a wide range of people [6–8]. It can accumulate in organisms and move through the food chain into the human body [9]. Accumulation of trance mercury in the body cannot be excreted through the body's own metabolism. Moreover, it will lead directly to heart, liver, thyroid diseases and cause nerve disorders [10], chronic mercury poisoning, and even malignant tumors [11]. Dissolved Hg^{2+} often has high chemical activity, and is the main form of mercury pollution in natural water [12]. The compounds of mercury have high water solubility, and it is also the pivot of various forms of mercury transformation. It has been stipulated that the concentration of mercury in drinking water must be less than 2 μg/L by WTO and EAP [13]. Therefore, exact recognition of Hg^{2+} is vital to early diagnose these disorders. Recently, there have been many methods for qualitative and quantitative detection of metal ion [14], such as electrochemical biosensor, fluorescence sensor and photochemistry sensor [15].

But most of them require sophisticated instruments and tedious procedures of sample preparation [16], which will limit the practical application and increase the cost in detection of Hg^{2+} [17]. Therefore, a highly selective and convenience analytical strategy of detecting Hg^{2+} is urgently needed in practical usage.

As scientists continue to study the near-infrared dyes, it has been applied in many fields such as biological, analytical studies,

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spectroscopic and metal ions detection [18,19]. Croconaine, as a kind of the near-infrared dye, it has a strong absorption in the near infrared region of 750–1400 nm. Moreover, it is readily bound to metal ions due to hetero-atom of croconaine structure. Recently, croconaine has been designed to be used in fluorescent probes for metal ions recognition due to its superior optical properties [20–24]. The design and synthesis of croconaine used to detect metal ions is very meaningful to the ecological environment.

Herein, we report a novel croconium dye, 2,5-bis[2-(benzylthio)aniline]-croconaine (**BAC**), which is a conjugate of 2-(benzylthio) aniline and 4,5-dihydroxycyclopent-4-ene-1,2,3-trione in the form of 2:1. The as-prepared croconaine acted as fluorescent probe, the selectivity and sensitivity in the identification of mercury ion were studied.

2. Experimental sections

2.1. Reagents and materials

Croconic acid was purchased from Shanghai chemical reagents company (Aladdin), and 2-aminothiophenol and benzyl chloride were purchased from Shanghai chemical reagents company (Fnty). Salts of the different cations were purchased from Shanghai chemical reagents company (China). And None of the above drugs has been further purified before use. Stock solution (1.0×10^{-2} M) of chlorinated salts (Cr^{3+}) and nitrate salts (Pb^{2+}, Na^{+}, Ni^{2+}, Fe^{3+}, Mg^{2+}, K^{+}, Hg^{2+}, Zn^{2+}, Ag^{+}, Ca^{2+}, Ba^{2+}, Cu^{2+}, Co^{2+}, Al^{3+} and Cd^{2+}) were prepared with deionized water.

2.2. Synthesis of 2-(benzylthio)aniline

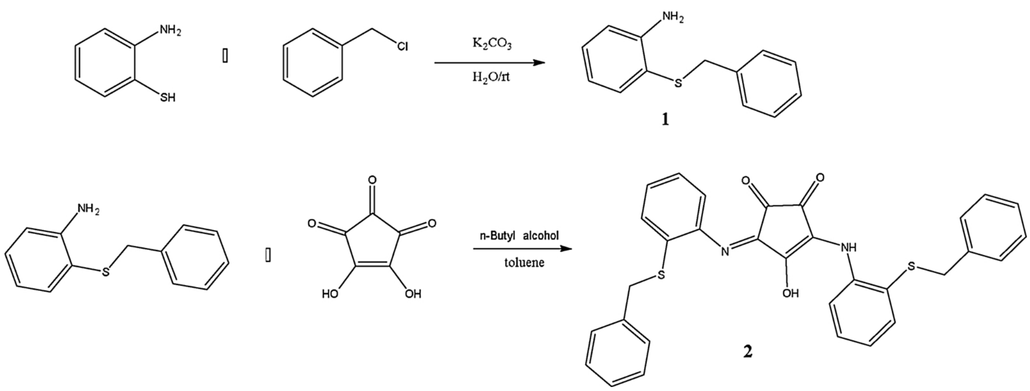
In brief, preparation of 2-aminothiophenol (0.375 g, 3 mmol), benzyl chloride (0.379 g, 3 mmol), potassii (0.442 g, 3.2 mmol) were added to pure water (50 ml) mixture and agitated overnight. After reaction, the crude product were extracted with methylene chloride 3 times and purified by column chromatography to obtain compound 1 (Scheme 1) as a hoar solid (0.459 g, yield: 60.8%). ^{1}H NMR (300 MHz, $CDCl_3$-d_6) δ (ppm) : 7.24–7.02 (m, 7H, aromatic), 6.65–6.54 (m, 2H, aromatic), 4.10 (d, J = 30.2 Hz, 2H, $-NH_2$), 4.10 (S, 2H, $-CH_2-$).

2.3. Synthesis of 2,5-bis[2-(benzylthio)aniline]-croconaine

As shown in Scheme 1, the medium product 2-(benzylthio)aniline was prepared as Lin had done before work [25]. Briefly, preparation of 2-(benzylthio)aniline (0.213 g, 1.0 mmol), croconic acid (0.071 g, 0.5 mmol) were dissolved toluene (20 mL) and butanol (20 mL) mixture, and refluxed for 6 h azeotropically removal of water. After reaction, the crude product was filtered off and purified by column chromatography to afford compound 2 as a yellow solid. (0.156 g, yield: 54.9%). FT-IR (KBr): 1184.88 cm^{-1} ($-C{=}O$), 1486.87 cm^{-1}, (the benzene ring frame vibration), 1254.48 cm^{-1} (C–O), 1324.45 cm^{-1} (C–N), 1505.65 cm^{-1} ($-C{=}N$), 745.36 cm^{-1}, 749.22 cm^{-1} (2-substituted benzene), 614.51 cm^{-1} (C–S). ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm): 7.26–7.22 (m, 18H, aromatic), 4.10 (d, J = 2.6 Hz, 4H, $-CH_2-$). The synthesized BAC was dissolved in DMSO (5.0×10^{-5} M).

2.4. Characterization

The infrared spectra were performed on a Protégé460 spectrometer, using KBr discs. ^{1}H NMR was obtained by a Bruker advance III (300 MHz) using deuterate dimethyl sulfoxide-d_6 (DMSO-d_6) as the solvent and tetramethylsilane as an internal standard. Ultraviolet and visible spectrophotometer (UV–vis) was collected on an UV-759 spectrophotometer in DMSO, using a quartz cell with a path length of 1 cm. Fluorescence emission spectra were recorded on a Cary eclipse spectrometer with a scan rate 2400 nm/min at temperature. Fluorescence measurements were carried out with excitation and emission slits widths of 20 nm and the excitation was at 460 nm.



Scheme 1. Synthesis of 2,5-bis[2-(benzylthio)aniline]-croconaine.