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A novel thiosemicarbazone Schiff base derivative with aggregation-induced emission enhancement characteristics and its application in Hg^{2+} detection

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ABSTRACT

A new acenaphtho[1,2-*b*]quinoxaline-based thiosemicarbazone Schiff base **M1** has been designed and synthesized, which was characterized by FT-IR, ^{1}H NMR, ^{13}C NMR and HR-MS (TOF-MS). The properties of **M1** were investigated by UV–vis absorption and fluorescence emission spectroscopy, founding that **M1** possessed aggregation-induced emission enhancement (AIEE) properties and exhibited "on-off" fluorescent responses to Hg^{2+}. The results of UV–vis and fluorescence titration experiments revealed that **M1** was selective and sensitive to Hg^{2+} in DMSO/H_2O (v/v = 9/1) buffered by 50 mM Tris-HCl at pH = 7.0. And the detection limit was calculated to be 9.07×10^{-7} M.

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1. Introduction

In recent years, there have been many research efforts to develop organic compounds with aggregation-induced emission (AIE) or aggregation-induced emission enhancement (AIEE) properties [1–7]. These compounds are weakly-emissive or non-emissive in solution, but exhibit intense emission upon aggregate formation, that is opposite to what we are known as aggregation-caused quenching (ACQ). Furthermore, their unique AIEE effect has also been successfully applied to develop fluorescent sensors [8–11], logic system modulation [12,13], electroluminescent materials [14–16] and so on.

Mercury is one of the primary metal elements, which play a very important role in current chemical industry [17,18]. Mercury has an extremely toxic impact on the environment and human health, excessive exposure to mercury and their derivations caused serious heart diseases and dysfunctions of brain, kidney, central nervous system [19–23]. Therefore, it is still highly desirable to develop new improved methods for the selective evaluation of Hg^{2+} ions.

Schiff bases contain C=N band which show good binding affinities toward metal ions and the synthetic procedures are relatively simple [24–26], many Schiff base chemosensors for detection of Cu^{2+} [27–29], Hg^{2+} [30–32], Ag^{+} [33–35], Cd^{2+} [36,37], Al^{3+} [38,39] have been reported. Moreover, containing a sulfur moiety with a substantially coordination ability toward transition metal ions [40–43] and anions [44–46], thiosemicarbazone Schiff bases have an enormous potential in metal ions detection.

On the basis of these studies and the research background of our group [47,48], we designed and synthesized a novel thiosemicarbazone Schiff base chemosensor **M1** by the condensation reaction of aldehydes and thiosemicarbazone (Scheme 1). After investigating the properties of **M1**, we found that **M1** exhibited a high selectivity for Hg^{2+} over other metal ions with drastically fluorescence quenching and color change.

2. Materials and methods

2.1. Apparatus

Melting points were determined on a X-4 digital melting-point apparatus and not corrected. ^1H NMR and ^{13}C NMR spectra were recorded at room temperature on a Varian Unity INOVA-400 NMR spectrometer in DMSO-d_6 or $CDCl_3$ with tetramethylsilane as an internal reference. IR spectra were recorded on an EQUINOX 55 FT-IR spectrometer with KBr pellets. UV–vis spectra were measured with an UV6000 pc spectrophotometer. Fluorescence spectra were measured with a F-320 fluorescence spectrophotometer. HR-MS (TOF-MS) were recorded on a Waters Q-TOF Premier.

2.2. Reagents

All chemical reagents were obtained from Adamas-beta Chemical Co. and used without further purification. The solution of various metal ions, with the exception of $Hg(OAc)_2$, were prepared from their nitrate or hydrochloride. Stock solution of **M1** (1 mM) was prepared by dissolving 6.1 mg **M1** in 10 mL DMSO. Tris-HCl buffer solutions of different pH were prepared by combining proper amounts of Tris and HCl under adjustment by a pH meter.

2.3. Synthesis of **M1**

The synthesis of (2E,2′E)-2,2′-(4,4′-(acenaphtho[1,2-*b*]quinoxaline-8,11-diyl)bis(4,1- phenylene))bis(methan-1-yl-1-ylidene)bis(hydrazinecarbothioamide) (**M1**) is outlined in Scheme 1. The intermediate compound **3** was synthesized and purified via procedures similar to the reported literature [49,50].

8,11-Dibromoacenaphtho[1,2-*b*]quinoxaline (0.412 g, 1 mmol), 10 mL of 1.0 M K_2CO_3 aqueous solution and a catalytic amount $Pd(PPh_3)_4$ (5 mol%) in 40 mL THF were heated to reflux for 0.5 h and then injected 20 mL THF containing 4-formylphenylboronic acid (0.750 g, 5 mmol). The reaction mixture was allowed to reflux for 12 h under nitrogen atmosphere. The yellow precipitate was filtered after the reaction mixture was cooled to room temperature, and washed three times with ethanol, water and ethanol to give orange precipitate (**4**) in 80% yield. FT-IR (cm^{-1}): 3030, 2809, 2715, 1695. ^1H NMR (400 MHz, $CDCl_3$) δ 10.19 (s, 1H), 8.32 (d, J = 6.9 Hz, 1H), 8.12 (dd, J = 8.3, 4.9 Hz, 3H), 8.07 (d, J = 8.3 Hz, 2H), 7.93 (s, 1H), 7.87–7.78 (m, 1H).

Synthesis of (2E,2′E)-2,2′-(4,4′-(acenaphtho[1,2-*b*]quinoxaline-8,11-diyl)bis(4,1-phenylene))bis(methan-1-yl-1-ylidene)bis(hydrazinecarbothioamide) (**M1**):

To a solution of 4,4′-(9a,13a-dihydrodibenzo[a,c]phenazine-10,13-diyl)dibenzaldehyde (**4**) (0.5 mmol, 230 mg) and thiosemicarbazide (0.25 mmol, 50 mg) in absolute ethanol (10 mL) was added glacial acetic acid (0.5 mL). The mixture was refluxed for 7 h to give a light yellow precipitate, the resulting precipitate was filtered and dried under vacuum to obtain the pure desired compound in 90% yield. FT-IR(cm^{-1}): 3379, 3254, 3152, 1586, 1528, 1281. ^1H NMR (400 MHz, DMSO-d_6) δ 11.52 (s, 1H), 8.27 (dd, J = 11.5, 7.7 Hz, 3H), 8.21 (s, 1H), 8.07 (s, 1H), 8.04–7.96 (m, 3H), 7.90 (dd, J = 7.7, 6.0 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 178.16, 152.78, 142.20, 139.98, 139.65, 138.68, 136.13, 133.65, 131.42, 131.27, 130.26, 130.02, 129.95, 129.32, 127.12, 122.36. HR-MS (TOF-MS): m/z = 609.1622, calcd for $(C_{34}H_{25}N_8S_2)^+$ = 609.1643 ($[M+H]^+$).

3. Results and discussions

3.1. Synthesis and characterization

The chemosensor **M1** was synthesized by coupling of 4,4′-(9a,13a-dihydrodibenzo[a,c]phenazine-10,13-diyl)dibenzaldehyde (**4**) and thiosemicarbazide (Scheme 1). The structures were characterized by FT-IR, ^1H NMR, ^{13}C NMR and TOF-MS (Fig. S5–S7). As exhibited in the IR spectrum (Fig. S5), a group of strong stretching bands at 3418 cm^{-1}, 3261 cm^{-1} and 3154 cm^{-1} show the presence of –NH, –NH_2 groups. The IR band at 1528 cm^{-1} confirms the presence of C=N group. Fig. S6 shows ^1H NMR spectra of **M1**. The signals at 11.55, 8.32 and 8.10 correspond to –NH, –NH_2 groups, while the signal at δ 8.20 indicates the formation of imine (CH=N) group. In ^{13}C NMR (Fig. S7), signals for CH=N and C=S appear at δ 152.80 and 178.18, respectively. The formation of **M1** was also confirmed by the signal peak at m/z