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Full Length Article

Simple-structured, hydrazinecarbothioamide derivatived dual-channel optical probe for Hg^{2+} and Ag^{+}

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ABSTRACT

A type of simple-structured, hydrazinecarbothioamide-containing Schiff-base derivative, 2-(4-(diphenylamino)benzylidene)hydrazinecarbothioamide **(M1)**, was synthesized through condensation reaction between 4-(diphenylamino)benzaldehyde and thiosemicarbazide. In the mixture of DMSO/H_2O (DMSO/H_2O=9:1(v:v), pH=4.5), distinct “turn-off” fluorescence alterations of **M1** were observed upon the addition of Hg^{2+}, and the addition of Ag^{+} induced fluorescence bathochromic shift. The detection limits of Hg^{2+} and Ag^{+} reach~0.19 μM and ~0.59 μM, respectively, as evaluated by the detailed fluorescence response of **M1** toward incremental target ions. The different extent of photo-induced electron transfer (PET) between **M1** and these two ions might be the plausible reason for such different optical response behaviors.

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1. Introduction

Over the past few decades, research on sensors for metal ions has attracted continual interest because of the wide application of them in environmental science, medicine, chemistry and biotechnology, etc. [1–8]. The development of sensors for probing Hg^{2+} and Ag^{+} has drawn special interest, which stems from the great disservice and widespread utilization of them in nowadays society. Hg^{2+} is a type of highly toxic heavy metal ion and currently exists in many fields [9–13]; it can be accumulated over time in the bodies of human and animals, introducing serious damage to brain, kidneys and endocrine system [14–17]. Ag^{+} is a type of important precious metal ion and has been widely used in industry [18]. Despite of the sterilization function of Ag^{+}, recent reports have discovered that Ag^{+} can cause severe damage to both environment and human beings [19,20]. Therefore, exploring efficient method to detect Hg^{2+} and Ag^{+} is of crucial importance.

Many methods, such as atomic absorption spectrometry [21], inductively coupled plasma mass spectrometry [22], electrochemical workstation [23], etc., have been utilized to realize the detection of Hg^{2+} and Ag^{+}. Comparing to these methods, optical probes exhibit attractive advantages, such as their high selectivity and sensitivity, short response time, practical-simple sample preparation and relatively low-cost of relevant equipments [24–26]. Despite of the available advances regarding the single-channel optical detection for solely Hg^{2+} [27–32] or Ag^{+} [33–36], the investigation about the simultaneous detection of Hg^{2+} and Ag^{+} by a single probe, and with different optical output signals, are still scarcely reported [5,37–39].

Hydrazinecarbothioamide is a type of well-known ion-coordinative functional groups, which is owing to the presence of C=S, –N–H–, and –NH_2 fractions in its chemical structure. Hydrazinecarbothioamide has been introduced into various optical motifs to realize the optical detection of metal ions [33,34,40–45]. Benefits from the mild reaction condition, high reactivity, spread generality and needs no special catalyst, the commonly-adopted protocol for the introduction of hydrazinecarbothioamide into optical platforms is through the condensation between thiosemicarbazide and aldehyde-containing chromophores, and affords hydrazinecarbothioamide-containg Schiff-base derivatives [44–46]. This provides the opportunity to adjust the coordinative properties of resulted compounds due to the formation of another active agent, the imine (C=N) fraction [47–50].

Along with this line, in this contribution, we successfully synthesized a simple-structured, hydrazinecarbothioamide-containing fluorescent Schiff-base derivative **(M1)**. We systematically investigated the optical response of **M1** toward common metal ions and anions. We found that with the addition of Hg^{2+}, **M1** displayed significant fluorescence quenching. While for Ag^{+}, bathochromic shift and partial quenching of emission was observed. This suggests that **M1** can act as dual-channel optical probes for Hg^{2+} and Ag^{+}.

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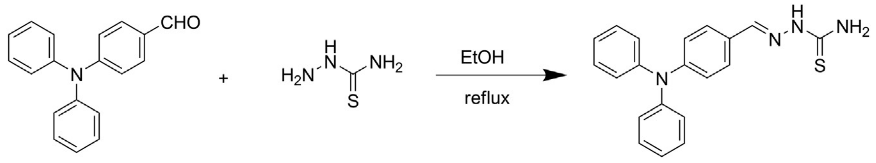

Scheme 1. The synthesis of **M1**.

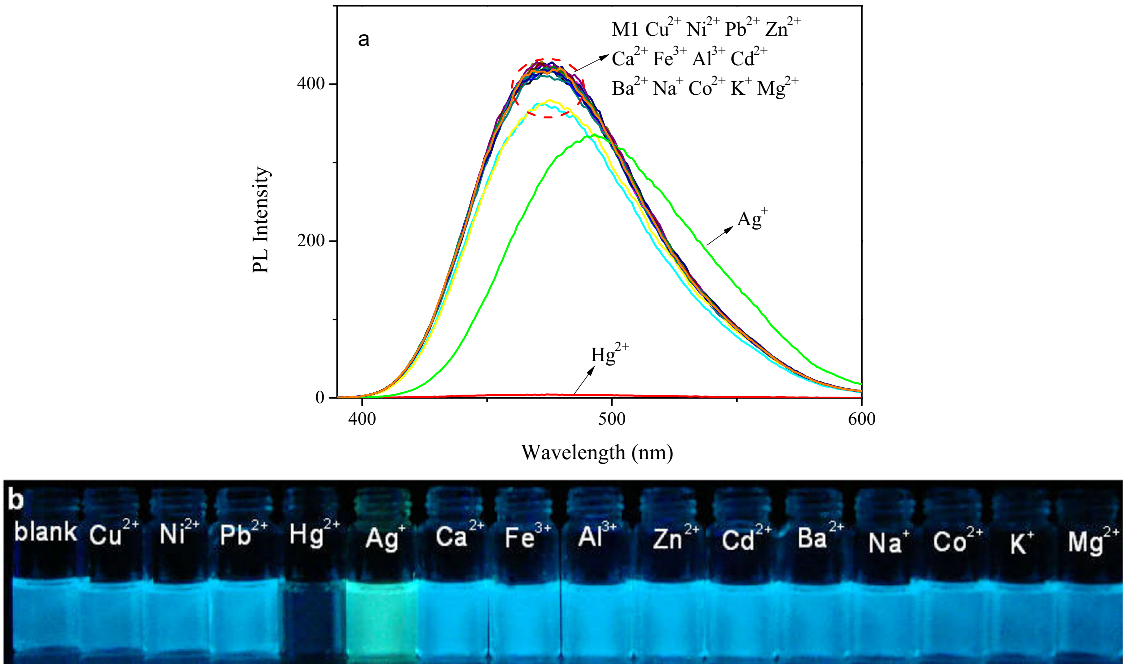

Fig. 1. Fluorescence emission spectra (a) of **M1** ($\sim 1.0 \times 10^{-5}$ M) in DMSO/H_2O ($V_{DMSO}/V_{H2O}=9/1$) (pH=4.5) upon the addition of 10 eq. of various metal ions (excited by 375 nm) and corresponding visual photographs (b) under portable UV lamp (365 nm).

2. Experimental

2.1. Materials

All chemical reagents, unless otherwise specified, were purchased from Adamas-beta Chemical Co. and used without further purification. In the titration experiments, all of the metal ions (Ag^+, Al^{3+}, Ba^{2+}, Ca^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, K^+, Mg^{2+}, Na^+, and Ni^{2+}) were dissolved in distilled water from their sulfate or nitrate salts, Hg^{2+} was prepared from its acetate salt. All of the anions (F^-, Cl^-, Br^-, I^-, SCN^-, OH^-, CO_3^{2-}, $H_2PO_4^-$, HPO_4^{2-}, SO_4^{2-}, HSO_4^-, AcO^-, and NO_3^-) were dissolved in distilled water tfrom their Na^+ or K^+ salts, CN^- was prepared from its tetrabutylammonium salt. The solution of **M1** was prepared in DMSO.

2.2. Apparatus

Melting point was measured on X-4 digital melting-point apparatus. IR spectra were recorded on an EQUINOX 55 FT-IR spectrometer with KBr pellets. UV–visible absorption spectra were recorded on a SHIMADZU UV-2450 spectrophotometer. PL spectra were recorded by a SHIMADZU RF-5310PC spectrofluorimeter. ^1H NMR and ^{13}C NMR spectra were collected on a VARIAN INOVA-400 spectrometer operating respectively at 400 MHz (for ^1H) and 100 MHz (for ^{13}C) using TMS as the internal standard in DMSO-*d6* solvents. The calculations were performed within the spin-unrestricted density functional theory (DFT) framework as implemented in DMol^3 code [51,52]. The generalized gradient approximation with the Becke (exchange) and the Lee–Yang–Parr (correlation) functional (BLYP) [53], together with double-numeric quality basis set (DNP), was used throughout all calculations. The convergence tolerance for energy change, max force, and max displacement were 2×10^{-5} Ha, 0.004 Ha Å^{-1}, and 0.005 Å, respectively.

2.3. Synthesis of 2-(4-(diphenylamino)benzylidene)hydrazinecarbothioamide (*M1*)

4-(diphenylamino)benzaldehyde (0.273 g, 1 mmol), thiosemicarbazide (0.091 g, 1 mmol), and 10 mL of ethanol were added to round-bottom flask, and then 5 drops of CH_3COOH was added to the system. The reaction mixture was stirred at room temperature for 5 h. The precipitate was filtered after the final reaction mixture was cooled by ice. The precipitate was washed repeatedly with ethanol and dried under vacuum to obtain pale green compound (88% yield). M.p: 206–208 °C. FT-IR (KBr, cm^{-1}): 3428, 3382, 3249, and 1266. ^1H NMR (400 MHz, DMSO-*d6*, ppm): δ 11.34 (s, 1 H, N–**NH**–C=S), 8.12 (s, 1 H, –$\mathbf{NH_2}'$), 7.97 (s, 1 H, Ar–**CH**=N), 7.85 (s, 1 H, –$\mathbf{NH_2}''$), 7.66 (d, *J*=8.8 Hz, 2 H, Ar), 7.34 (t, *J*=8.0 Hz, 4 H, Ar), 7.13–7.05 (m, 6 H, Ar), 6.89 (d, *J*=8.8 Hz, 2 H, Ar). ^{13}C NMR (100 MHz,

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