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Bismuth Ions Selective Fluorescent Chemosensor Based on Rhodamine-B

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A new rhodamine-based compound (L1) has been synthesized and applied as an "off-on" chemosensor for Bi^{3+}. The complexation behaviour of chemosensor with different metal ions including Bi^{3+} ions in EtOH/H_2O (4:1, v/v) was studied on UV-visible absorption spectra and fluorescent spectra. Results showed that the chemosensor (L1) is highly selective for Bi^{3+} over other cations such as Hg^{2+}, Fe^{2+}, Mn^{2+} and Ca^{2+}. This selectivity can be attributed to the photoinduced electron transfer mechanism (PET) of the sensor in the presence of Bi^{3+}. The complex solution (L1-Bi^{3+}) exhibited reversibility with EDTA.

Keywords: Rhodamine-B, Fluorescent chemosensor, Bismuth ions.

INTRODUCTION

The design and synthesis of functional fluorescence probes for metal ions are of growing interest because of their potential application in biomedical and environmental chemosensors as well as molecular logic devices [1-3]. Although considerable efforts have been devoted to the elaboration of luminescence sensors for various metal ions in the last two decades, there are only a handful of reports on Bi^{3+} fluorescent chemosensors [4,5]. Bismuth ions have been widely applied to the biological preparation, low-temperature alloys, inorganic materials modification and the preparation of new materials such as magnetism and optics recently. Many techniques are available for determining bismuth concentration in samples such as gravimetric method, volumetric method and atomic absorption spectrophotometry, but these methods are both complicated and costly compared with fluorescence determination [6,7]. Therefore, the design of a reliable and sensitive analytical method to efficiently evaluate the Bi^{3+} level in environmental and biological systems is highly desirable [7].

So far, various fluorophores with different excitation and emission wavelengths have been employed to develop various chemical sensors with superior properties for the detection of metal ions [8]. Among the fluorophores developed, rhodamine and its derivatives are highly favourable because of their high absorption coefficients, high fluorescence quantum yields and long absorption and emission wavelengths. As we know, 2,2'-dipicolylamine (DPA) is also used as a receptor to bind certain metal ions [9,10]. Based on both rhodamine and 2,2'-dipicolylamine remarkable properties [11], a novel fluorescent chemosensor has been synthesized by connecting the rhodamine derivatives with 2,2'-dipicolylamine through an amido group bridge [12,13], which shows very high sensitivity and selectivity toward Bi^{3+} over other metal ions.

EXPERIMENTAL

All chemicals used in the experiments were of analytical grade and purchased from commercial suppliers. The UV-visible spectra were recorded on a Hitachi U-3900 spectrophotometer and fluorescence spectra were recorded with a Hitachi F-7000 spectrophotometer with excitation at 371 nm (slit width, 5 mm). ^{1}H NMR spectra were recorded at room temperature on a Bruker Avance-500 NMR spectrometer.

Synthesis and characterization of compound 1: To a solution of rhodamine-B (3.8 g, 7.95 mmol) in 100 mL of ethanol was added ethane-1,2-diamine (5 mL, 75 mmol). The mixture was refluxed for 12 h and was then taken to dryness under vacuum. The residue was dissolved in CH_2Cl_2 and then washed with H_2O and brine respectively. The organic layer was dried with $MgSO_4$. After the removal of the solvent, flash chromatography (silica gel; MeOH/CH_2Cl_2, 3:97, v/v) of the residue gave compound **1** as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (dd, J = 5.7, 3.0 Hz, 1H), 7.46-7.42 (m, 2H), 7.11-7.07 (m, 1H), 6.43 (d, J = 8.8 Hz, 2H), 6.37 (d, J = 2.5 Hz, 2H), 6.28 (d, J = 2.6 Hz, 1H), 6.26 (d, J = 2.6 Hz, 1H), 3.33 (q, J = 7.3 Hz, 8H), 3.19 (t, J = 6.5 Hz, 2H), 2.43 (t, J = 6.6 Hz, 2H), 1.56 (s, 2H), 1.16 (t, J = 7.1 Hz, 12H).

Synthesis and characterization of compound 2: 2-Chloroacetyl chloride (2 mL, 20.9 mmol) was dissolved in chloroform (10 mL) and added dropwise to a cooled and stirred

solution of compound **1** (2.6 g, 5.03 mmol) and pyridine (0.43 mL, 5.2 mmol) in chloroform (10 mL) within 1 h. After the reaction solution was stirred for 2 h at room temperature, the solvent was removed under reduced pressure and the white powder was washed with dichloromethane and diethyl ether. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 5.9, 2.7 Hz, 1H), 7.73 (s, 1H), 7.46 (dd, *J* = 5.0, 3.5 Hz, 2H), 7.08 (dd, *J* = 5.8, 2.6 Hz, 1H), 6.44 (d, *J* = 8.8 Hz, 2H), 6.38 (s, 2H), 6.28 (d, *J* = 8.0 Hz, 2H), 3.93 (s, 2H), 3.34 (q, *J* = 6.9 Hz, 10H), 3.09 (d, *J* = 4.8 Hz, 2H), 1.17 (t, *J* = 7.0 Hz, 12H).

Synthesis and characterization of L1: Compound **2** (0.56 g, 1.01 mmol), 2,2'-dipicolylamine (DPA) (0.19 mL, 1 mmol), N,N-diisopropylethylamine (0.18 mL, 1.01 mmol) and potassium iodide (4 mg) were dissolved in acetonitrile (30 mL), stirred and refluxed for 12 h under nitrogen atmosphere. The mixture was cooled to room temperature and the solvent was removed under reduced pressure to obtain yellow oil, which was purified by silica gel column chromatography using chloroform/methanol (30:1, v/v) as eluent to afford product (**Scheme-I**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 5.9, 2.7 Hz, 1H), 7.73 (s, 1H), 7.46 (dd, *J* = 5.0, 3.5 Hz, 2H), 7.08 (dd, *J* = 5.8, 2.6 Hz, 1H), 6.44 (d, *J* = 8.8 Hz, 2H), 6.38 (s, 2H), 6.28 (d, *J* = 8.0 Hz, 2H), 3.93 (s, 2H), 3.34 (q, *J* = 6.9 Hz, 10H), 3.09 (d, *J* = 4.8 Hz, 2H), 1.17 (t, *J* = 7.0 Hz, 12H).

RESULTS AND DISCUSSION

UV-visible studies of chemosensor with various metal ions: UV-visible absorption spectra of chemosensor (**L1**) in the presence of various metal ions Hg^{2+}, Al^{3+}, Bi^{3+}, Ag^{+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Fe^{2+}, K^{+}, Mg^{2+}, Mn^{2+}, Na^{+}, Ni^{2+}, Pb^{2+}, Sn^{2+}, Sr^{2+} and Zn^{2+} (conc. of 50 μM) were recorded in EtOH/H_2O (4:1, v/v) using a Hitachi U-3900 spectrophotometer. As seen in Fig. 1, the absorption spectrum of chemosensor **L1** exhibited a broad absorption band at 230 nm, two weak bands at 275 and 310 nm, respectively. The position of absorption band remained unchanged with the various metal ions, however a new absorption band at 385 nm was formed with Bi^{3+}.

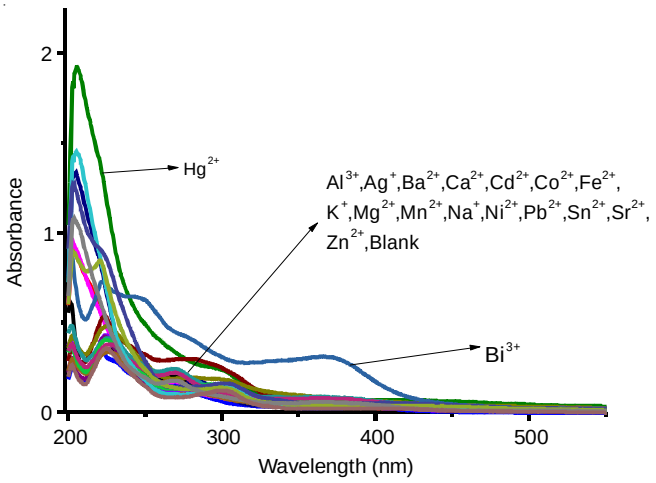
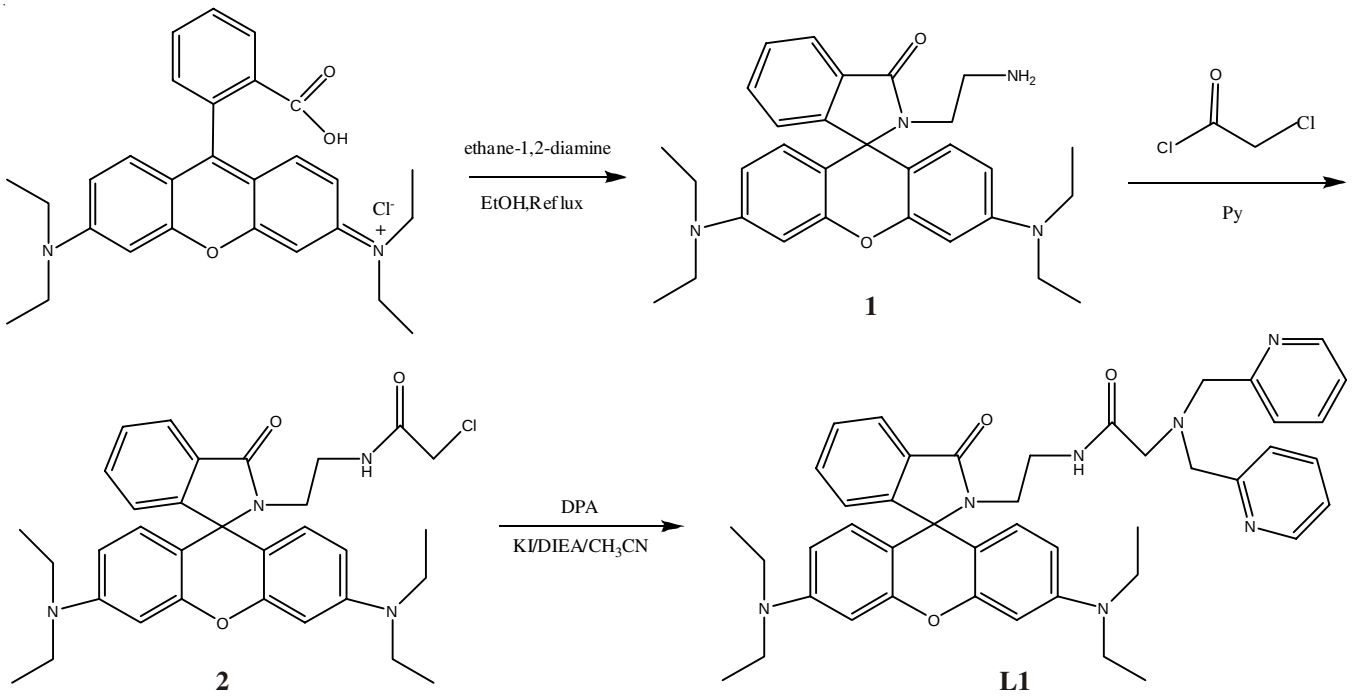


Fig. 1. UV-visible absorption spectra of chemosensor **L1** (5 μM) in absence and presence of different metal ions (50 μM) at room temperature

Fluorescence studies of chemosensor: The fluorescence behaviour of chemosensor (**L1**) was investigated in Hitachi F-7000 fluorescence spectrometer upon the addition of various metal ion solution. Chemosensor (**L1**) did not show any significant quenching alone when the excitation wavelength was at 317 nm. After the addition of Hg^{2+}, Al^{3+}, Bi^{3+}, Ag^{+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Fe^{2+}, K^{+}, Cu^{2+}, Mg^{2+}, Mn^{2+}, Na^{+}, Ni^{2+}, Pb^{2+}, Sn^{2+}, Sr^{2+} and Zn^{2+} (Fig. 2), chemosensor (**L1**) did not exhibit any significant fluorescent quenching (except Al^{3+}, Sn^{2+}, Cu^{2+} and Bi^{3+} ions). Only in case of Bi^{3+} ions it exhibited a clear fluorescent quenching (about 15-fold) (Fig. 2). Interferences of cations had been investigated by treating chemosensor **L1** with 10 equiv. of Bi^{3+} in the presence of 10 equiv. of other metal ions.



Scheme-I

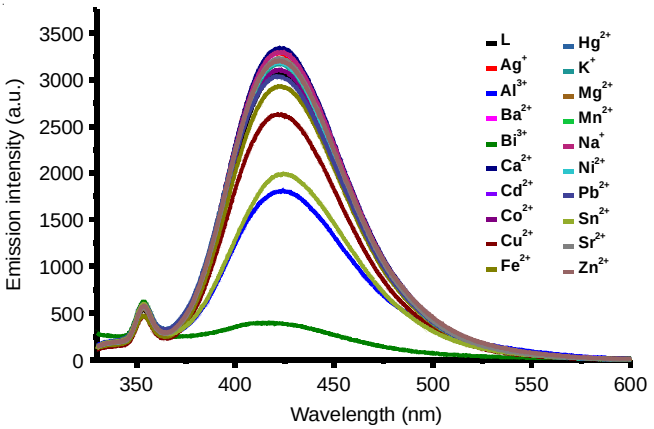


Fig. 2. Fluorescence emission spectra of **L1** (5 μM) in EtOH/H_2O (4:1, v/v) in the presence of different metal ions (50 μM) such as Hg^{2+}, Al^{3+}, Bi^{3+}, Ag^{+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Fe^{2+}, K^{+}, Cu^{2+}, Mg^{2+}, Mn^{2+}, Na^{+}, Ni^{2+}, Pb^{2+}, Sn^{2+}, Sr^{2+} and Zn^{2+}. Excitation wavelength was at 371 nm and emission maximum was 418 nm

As shown in Fig. 3, the response of chemosensor (**L1**) for Bi^{3+} in the presence of competing metal ions were not affected.

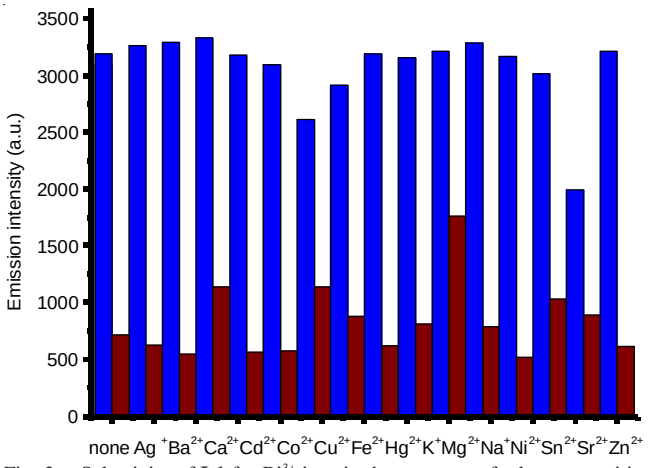


Fig. 3. Selectivity of **L1** for Bi^{3+} ions in the presence of other competitive metal ions in (5 μM), excitation wavelength and emission maximum are 371 and 418 nm, respectively. Blue bars represent fluorescent intensity after the addition 50 μM of the appropriate metal ion (Hg^{2+}, Al^{3+}, Bi^{3+}, Ag^{+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Fe^{2+}, K^{+}, Cu^{2+}, Mg^{2+}, Mn^{2+}, Na^{+}, Ni^{2+}, Pb^{2+}, Sn^{2+}, Sr^{2+} and Zn^{2+}) in a 50 μM solution of **L1**. Red bars represent the subsequent addition of same equiv. of Bi^{3+} ions in each of the samples

Sensitivity of **L1** for bismuth ions was examined with the titration of different concentration of Bi^{3+} ions (0.0, 0.025, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.5, 1.8, 2.0, 2.5 and 3.0 equiv.) at 418 nm (Fig. 4). The fluorescence intensity gradually decreased with increasing the concentration of Bi^{3+}. As shown in Fig. 4, the fluorescence intensity of **L1** didn't reduce any more when the {[Bi^{3+}]/[**L1**]} was at a molar ratio of **1**. Hence, it is concluded that the binding ratio between the chemosensor and Bi^{3+} was 1:1.

Binding mode of chemosensor: The proposed binding mechanism is shown in Fig. 5. As can be seen, Bi^{3+} is bound to the amide oxygen and the nitrogen atom of 2,2'-dipicolylamine.

The reversibility nature of chemosensor **L1** was showed by the titration of EDTA with fluorescent chemmosensor (**L1**+Bi^{3+}), results are shown (Fig. 6) that chemosensor **L1** in (**L1**+Bi^{3+}) was replaced by EDTA and formed (EDTA+Bi^{3+}).

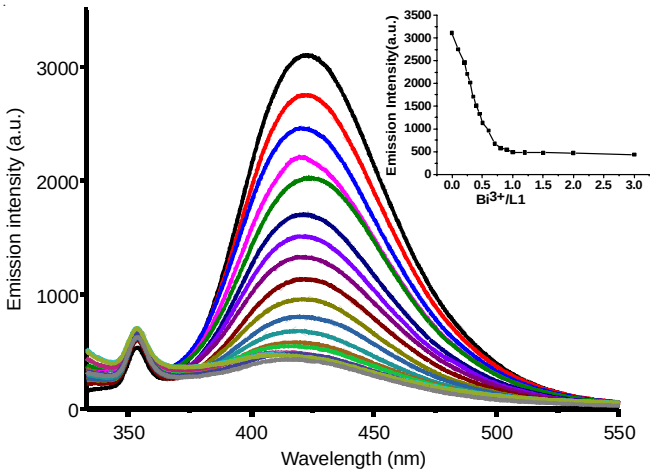


Fig. 4. Fluorescence emission spectra of **L1** upon addition of Bi^{3+} (0.0, 0.025, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.2, 1.5, 2.0, 2.5, 3.0 equiv.) with an excitation of 317 nm

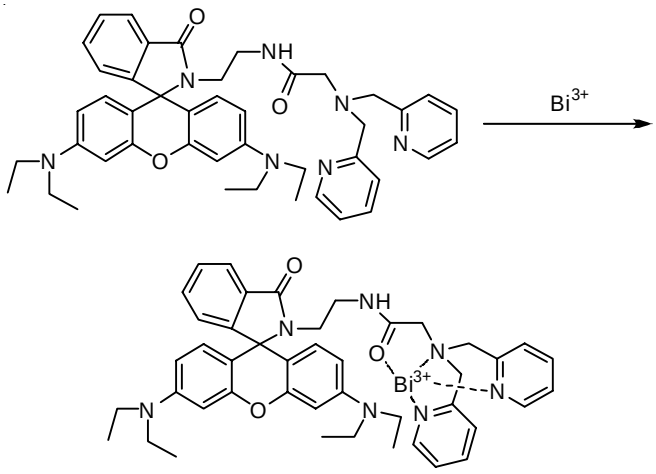


Fig. 5. Proposed binding mechanism of the chemosensor **1** with Bi^{3+}

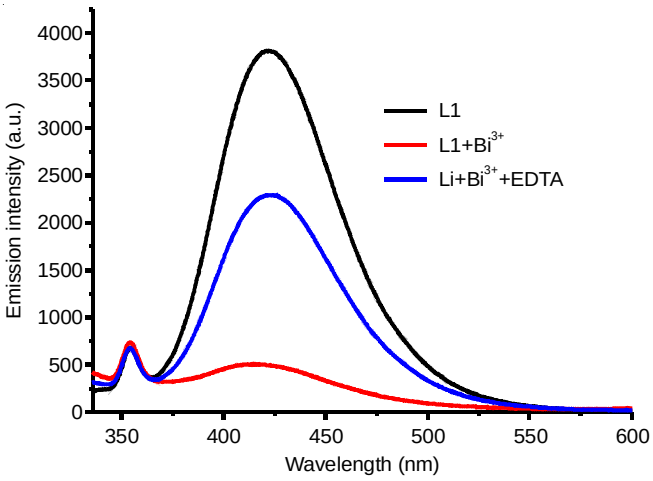


Fig. 6. Fluorescent emission spectra of **L1** (10 μM) in the presence of Bi^{3+} ions (1.0 equiv.) or EDTA (0.6 equiv.) in EtOH/H_2O (4:1, v/v)

Therefore, fluorescent chemosensor **L1** could be recyclable simply through treatment with a proper reagent such as EDTA.

The effect of different solvents DMSO, THF, DMF, acetonitrile, dichloromethane and methanol on the detection of Bi^{3+} ions by **L1** had been explored and the results were showed in Fig. 7, it can be seen that the fluorescence is changed variously

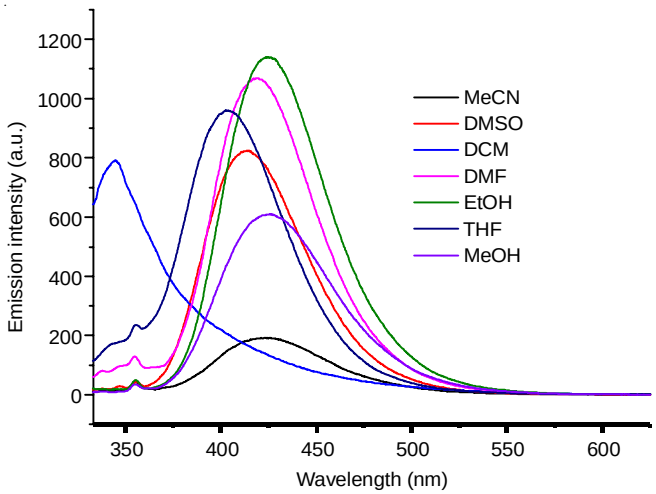


Fig. 7. Solvent effect on fluorescent intensity of **L1** probe in different solvent DMSO, DMF, DCM, methanol, THF and aetonitrile, ethanol

due to different solvents. The best result was observed with ethanol.

Conclusion

In conclusion, a bismuth-sensitive fluorescent chemosensor was synthesized, which showed high sensitivity and selectivity toward Bi^{3+} over other competitive metal ions. The presence of metal ions such as Hg^{2+}, Al^{3+}, Ag^{+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Fe^{2+}, K^{+}, Cu^{2+}, Mg^{2+}, Mn^{2+}, Na^{+}, Ni^{2+}, Pb^{2+}, Sn^{2+}, Sr^{2+} and Zn^{2+} had little influence on the selectivity and sensitivity of Bi^{3+}. The fluorescent nature of **L1**-Bi^{3+} complex goes to "turn-off" in presence of Bi^{3+} and EDTA. This type of sensor design is promising to evaluate the Bi^{3+} level in environmental and biological systems.

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