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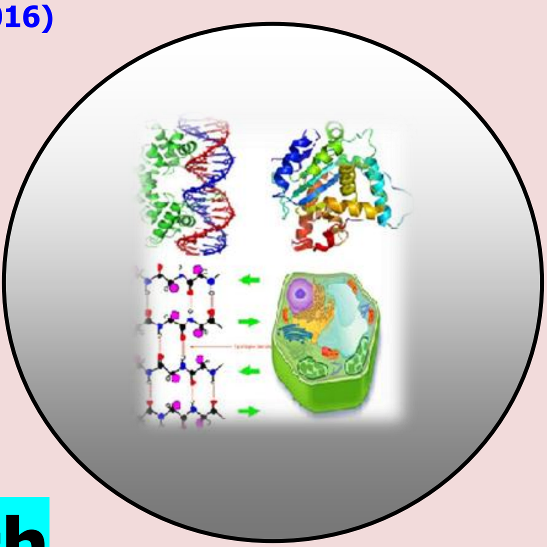

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Dr. Animesh Patra
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RESEARCH PAPER

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A Selective and Sensitive AL^{+3} Fluorescent Sensor Based on 5-Bromothiophene-2-Carboxilic Acid Hydrazide Schiff Base

Surajit Maiti[1,2], Mayukh mandal[1,2], Gobinda Prasad Sahoo[1*], Palash Setua[2*] and Animesh Patra[1*]
[1]Postgraduate Department of Chemistry, Midnapore College, Midnapore- 721101, India
[2]Department of Chemistry, Pingla Thana Mahavidyalaya, Maligram-721140, India

ABSTRACT

An efficient fluorescent Al^{3+} receptor, 5-bromothiophene-2-carboxilic acid (2-hydroxy-naphthalen-1-ylmethylene)-hydrazide (HL) has been synthesized by the condensation reaction between 2-hydroxy-1-naphthaldehyde and 5-bromo thiophene-2-carboxilic acid hydrazide. High selectivity and affinity of HL towards Al^{3+} in Methanol (MeOH) as well as in HEPES buffer at pH 7.4, makes it suitable to detect intracellular Al^{3+} with fluorescence microscopy. Metal ions, viz. Na^{+}, K^{+}, Cr^{3+}, Mn^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+}do not interfere.

Keywords: Schiff Base, UV, IR, Fluorescence Spectroscopy and Metal Ion Sensing.

INTRODUCTION

Aluminium is the third most abundant element in the Earth's crust. Aluminium is present in its ionic form Al^{3+} in natural waters and biological tissues Valeur et al. (2000). The solubility of Al minerals at lower pH increases the amount of available Al^{3+} which is deadly to growing plants and its ultimate effect is the environmental acidification Alvarez et al. (2005). Various compounds of aluminium is used in food, alloy, textile and cosmetics industry in a large amount Barcelo et al. (2002). Main sources of Al^{+3} to accumulate on human beings are food supplements, aluminium food containers, aluminium-based medicines and cooking utensils. High concentration of Aluminium in environment is very much toxic towards plants and animals easily can be entering into human body from plants through food chain Krewski et al. (2007). Al^{3+} has neurotoxic activities and been identified as a major cause of Alzheimer's disease Fasman et al. (1996), Percy et al. (2011) and Parkinson's disease Jain et al. (2010). There are several methods to estimate Aluminium, among them spectroflurimetry is mostly used and efficient method. Till now various fluorescent chemosensors have been synthesized for this purpose with moderate sensitivity Mukherjee et al. (2014). However, the majority of these probes have poor water solubility, interference caused by other ions, lack practical applicability in aqueous solutions, difficult synthesis procedure Dean et al. (2012).

A sensor molecule that acts as a dual channel sensor for the detection and sensing of the desired metal cations Singh et al. (2013) by changes in the electronic as well as fluorescence spectral properties induced by metal–ligand binding Maity et al. (2010), could be used both as colorimetric as well as fluorogenic sensor.

Colorimetric sensors allow easy in-field detection, while fluorescence-based sensors provide an edge in imaging studies.

Herein we report the synthesis and characterization of a Schiff base ligand (HL) obtained by condensing 2-hydroxy naphthaldehyde with 5-bromo thiophene-2-carboxylic acid hydrazide. It is used as an efficient fluorescent probe for the determination of Al (III) in MeOH as well as in HEPES buffer (0.1 M) solution (pH 7.4).

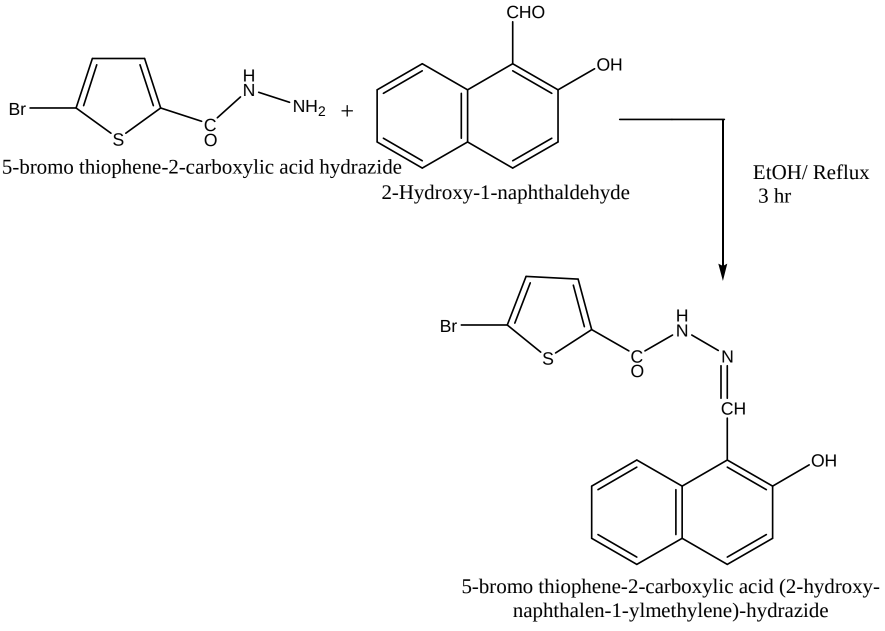
MATERIAL AND METHODS

All chemicals and reagents were obtained from commercial sources and used as received, unless otherwise stated. Solvents were distilled from an appropriate drying agent. The organic moieties were synthesized following the procedure. The elemental (C, H, N) analyses were performed on a PERKIN ELMER MODEL 2400 elemental analyzer. Electronic absorption spectra were recorded on a SHIMADZU UV-1800 spectrophotometer. IR spectra (KBr discs, 4000–400 cm^{-1}) were recorded using a PERKIN ELMER MODEL FTIR model RX1 spectrometer. Fluorescence spectra were recorded by HITACHI F-7000 MODEL fluorescence spectrophotometer.

Preparation of the ligand (HL)

Synthesize the ligand HL (Scheme 1) by placing 10 mL of 95% ethanol in a Round bottle that also has a small magnetic stirring bar. Heat the ethanol to boiling while stirring. Immediately, with continued heating and stirring, add 0.710 gm of 5-bromothiophene-2-carboxylic acid hydrazide and then 0.860 gm of 2-hydroxy naphthaldehyde. Stir the solution for 2 hour and then reflux up to 3 hour and kept over one night to get the precipitate of the yellow ligand. The precipitate was filter by filter paper using vacuum pump and washed several times using ethanol, followed by crystallization in ethanol and dry the solid compound. Yields > 70%.

$C_{16}H_{12}N_2O_2SBr$: Anal. Found: C, 51.06; H, 3.19; N, 7.44; Calc.: C, 51.02; H, 3.08; N, 7.42, m.p. 296 ± 1 ^{o}C; IR (KBr, cm^{-1}): $\nu_{O-H,}$ 3442, $\nu_{C=O}$, 1634, $\nu_{N=H}$,3220, 1472, $\nu_{CH=N}$, 1596; Yield: 90%, state: solid; m.p.: 239-241ºC.



Scheme 1. Synthetic procedure of the Ligand (HL).

Figure 1. IR spectrum of ligand HL.

RESULTS AND DIACUSSION

Structural characterization of HL

The IR spectra of Schiff base HL (Fig. 1) shows a broad band at 3397cm^{-1} for the –OH stretching vibration. The vibrational band at 3220 cm^{-1} corresponds to the N–H stretching vibration. In addition, the bands observed at 1634 cm^{-1}, 1596 $cm^{-1}$and 1291 cm^{-1} are assigned as C=O, C=N and C–OH respectively and show the existence of an enolic form in the solid state.

Absorption spectroscopic studies

The molecular interactions of HL with the aforementioned cations were initially studied using UV-visible spectral changes and the results are depicted in Fig. 2, the electronic spectra of HL in MeOH–H2O (1:4 v/v) solution displayed two absorbance bands at λ_{max} 327 and 365 nm. As evidenced from figure (Fig. 2), addition of cations such as alkali metal ions, alkaline earth metal ions, Mn^{+2} did not produce significant spectral change in the absorption spectra of HL.

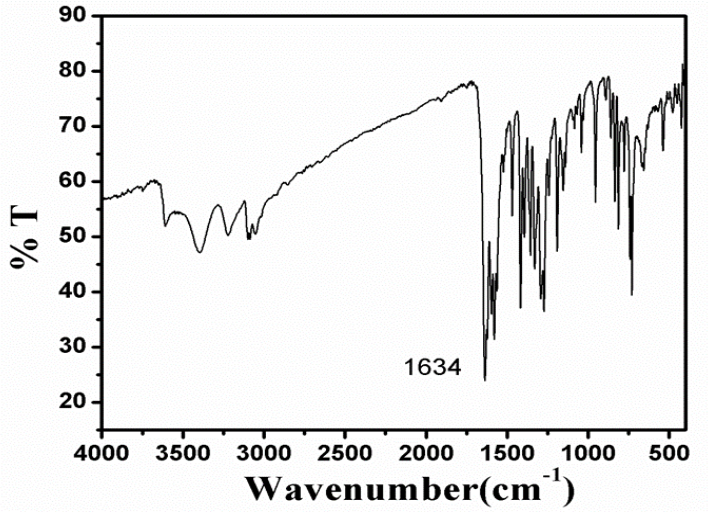
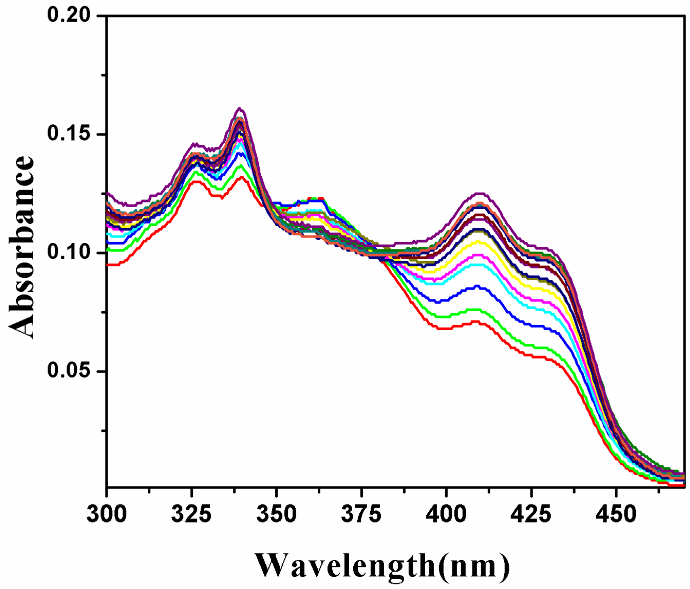


Figure 2. UV–vis absorption spectra of receptor HL observed upon addition of (Na^+, K^+, Cr^{3+}, Mn^{2+}, Al^{+3}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+}).

However, addition of Al^{+3} ions results in bathochromic shift (12–42 nm) Samanta et al. (2014) and exhibits two bands at 339 nm and 407 nm. This red shift may be due to the binding of aluminium with HL. The other transition metal ions viz. Na^+, K^+, Cr^{3+}, Mn^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} also perturb the UV-visible spectral pattern of the HL. Therefore, UV-visible studies show that the colorimetric detection of Al^{+3} in MeOH–H2O (1:4 v/v) solutions lacks selectivity. To further study the binding interaction of HL with Al^{+3} ions, a UV-visible titration was performed in MeOH–H2O (1:4 v/v) solution of HL (Fig. 3). With the addition of incremental amounts of Al^{+3} ions to the solution of HL, the absorption of the bands at 365 and 327 nm of HL diminished gradually with the concurrent growth of bands centred at 407, and 339 nm, corresponding to a colorimetric change from green blue to intense green.



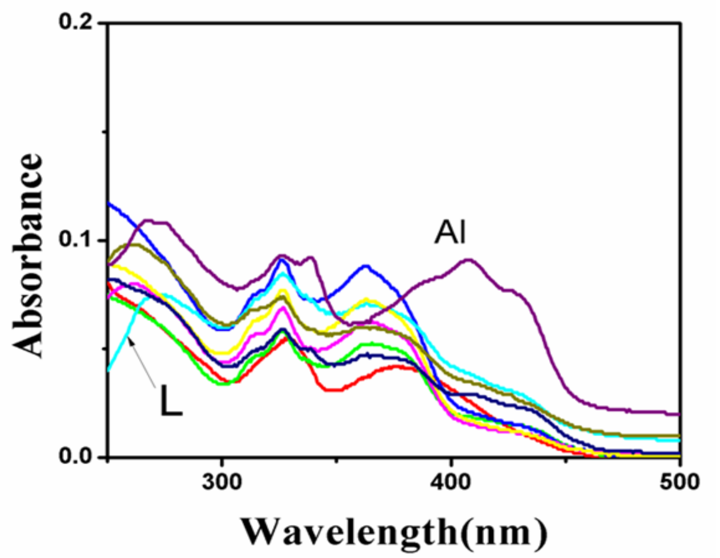


Figure 3. UV–vis titration spectra of HL upon incremental addition of Al $(NO_3)_3$.

Fluorescence spectroscopic studies of HL in presence of Al^{+3}

The fluorescence studies were performed to investigate the selectivity of receptor HL towards various metal ions viz. Na^+, K^+, Cr^{3+}, Mn^{2+}, Al^{+3}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} (Fig.4). As it can be seen from Fig. 5, HL (0.5 mM, MeOH–H2O solution, 1 : 4 v/v) is itself weakly fluorescent and exhibits emission peaks at 475 and 450 nm (λex: 407 nm). However, upon addition of two equivalents of Al^{+3} ions to the solution of HL, it becomes highly fluorescent showing emission bands at 476 and 452 nm. Although, the addition of 1 equivalent of the other cations under investigation in a MeOH–H2O (1: 4 v/v) solution of HL did not show any considerable enhancement in the fluorescence intensity under similar experimental conditions. From Fig. 5, it can be observed that there was no interference for the detection of Al^{3+} in the presence Na^+, K^+, Cr^{3+}, Mn^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+}. The selectivity of HL towards Al^{+3} may be explained on the basis of smaller ionic radii (0.5 Å) and higher charge density (r = 4.81) of the Al^{+3} ion. The smaller radii of the Al^{+3} ion permits suitable coordination geometry Gupta et al. (2014)with the chelating receptor HL and the larger charge density which allows strong coordination ability between HL and Al3+. Fluorescence titration experiments (Fig. 6) were performed by increasing the amount of Al^{+3} (0–1 mM) in a 0.5 mM MeOH–H2O (1:4 v/v) solution of HL. This shows that the emission intensity of the HL at 475 and 450 nm steadily increases with the gradual addition of Al^{+3} ions and achieved saturation (at 476 and 452 nm) on addition of 2 equivalents of Al^{+3} ions.

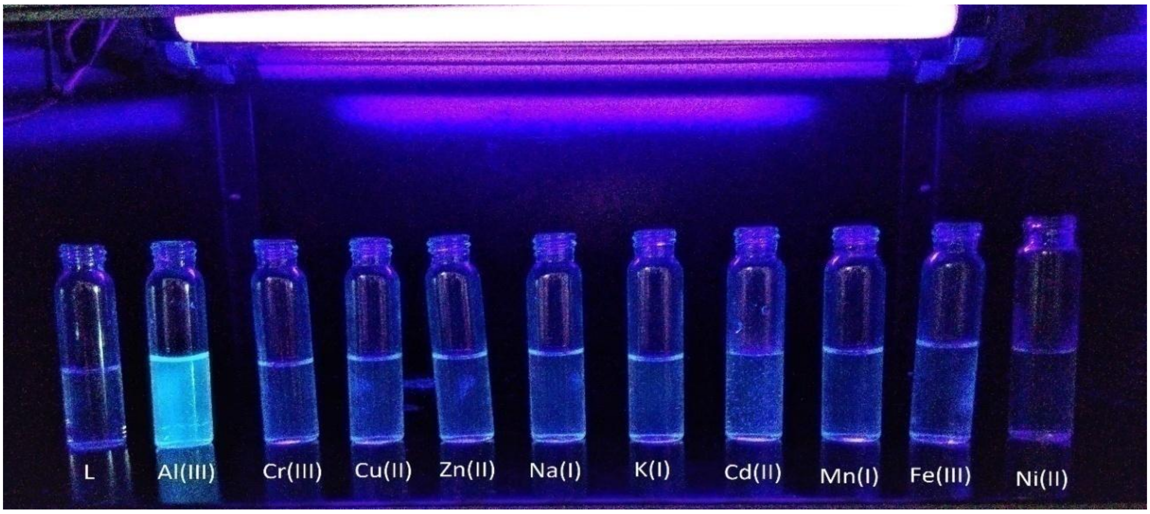


Figure 4. Visual change in the fluorescence of HL in presence of various metal ions.

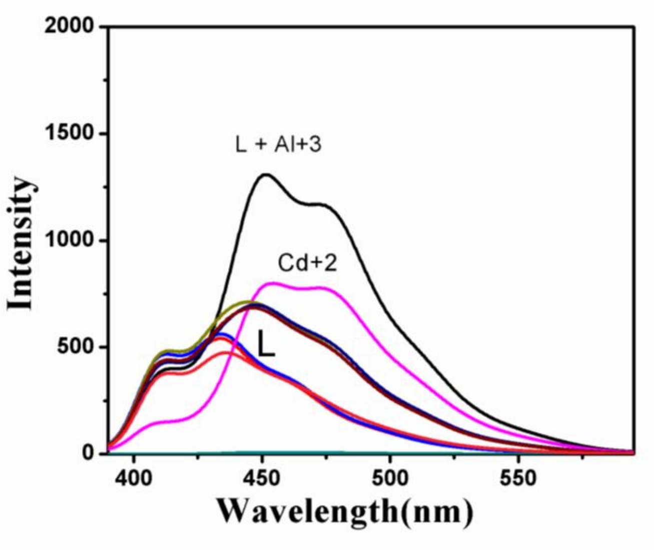


Figure 5. Changes in the fluorescence emission of receptor HL observed upon addition of metal ions.

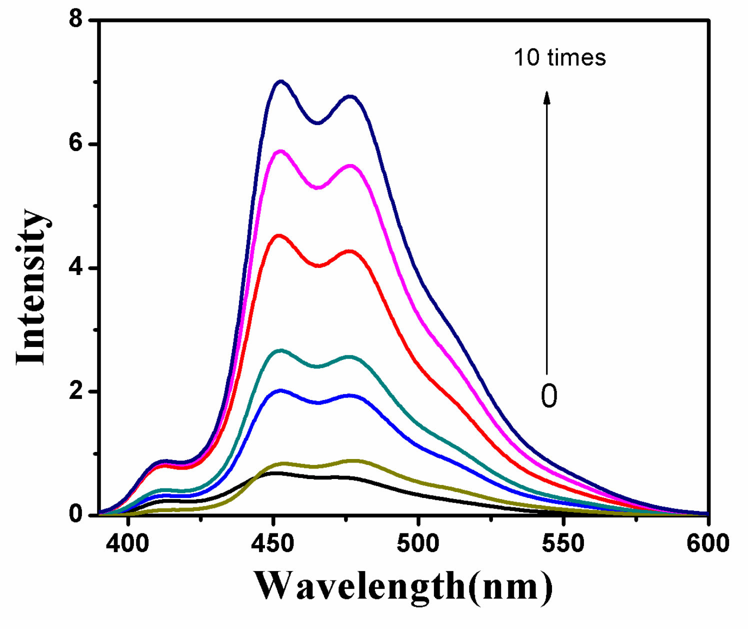


Figure 7. Fluorescence titration spectra of HL upon incremental addition of Al^{+3}.

CONCLUSION

In summary, a synthesis of 5-bromothiophene 2-carboxylic acid hydrazide based Al^{+3} selective fluorescent chemosensors 5-bromothiophene-2-carboxylic acid (2-hydroxy-naphthalen-1-ylmethylene)-hydrazide has been described. The synthesized chemosensor (HL) has been characterized by using physicochemical, spectroscopic tools. Fluorescent enhancement of HL was shown after the incremental addition of Al^{+3}. The present sensor shows merits over existing sensors, represents the second high detection limit and least interference by different metal ions.

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Corresponding author: Animesh Patra, Postgraduate Department of Chemistry, Midnapore College, Midnapore- 721101, India
Email: animeshpatramc@gmail.com