



# Selective Fluorescence Chemosensor for Al<sup>3+</sup> based on Antipyrine with Furfural Attached Allyl System

P. Banumathi<sup>1</sup>, G. Tamil Selvan<sup>2</sup>, P. Mosae Selvakumar<sup>3</sup>, P. Rajasingh<sup>1\*</sup>

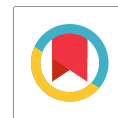
<sup>1</sup>Department of Chemistry, Chikkanna Government Arts College, Tirupur, TN, India

<sup>2</sup>Department of Chemistry, KITS, Coimbatore, TN, India

<sup>3</sup>Science and Math Program, Asian University for Women, Chittagong, Bangladesh

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\*sprajasingh@gmail.com



## ABSTRACT

By incorporating Furfural-Antipyrine as coordinate sites into the fragment of receptor Furfural Baylis Hillman-Antipyrine (FBH-AP), it can be used as an artificial chemosensor for selective recognition of transition metals. The strong fluorescence emission at 388 nm of the receptor FBH-AP is effectively and selectively quenched by Al<sup>3+</sup>. A 1:1 complex formed between the FBH-AP and Al<sup>3+</sup> is determined by the Jobs plot and their common interferent ions do not show any interference with Al<sup>3+</sup>. It is anticipated that the antipyrine could be a good candidate probe and has potential application for Al<sup>3+</sup> determination.

**Keywords:** Al<sup>3+</sup>; Antipyrine; Fluorescence Chemosensor.

## 1. INTRODUCTION

The design and synthesis of organic material used as a fluorescent chemosensor for selective recognition of transition metal ions have received special attention in the last decades due to the essential roles that cations play in biology, environmental chemistry and food safety (Rurack *et al.* 2002; Kim *et al.* 2011a; Vengaiyan *et al.* 2015; Yin *et al.* 2015). Current researches prefer fluorescence chemosensors for their exclusive qualities like sensitivity, selectivity, direct visual observation and immediate replica (Kim *et al.* 2011b). They are utilized in a variety of applications such as molecular devices (Pischel *et al.* 2007), nerve gas sensors (Burnworth *et al.* 2007), biological probes, environmental sensors (Kim *et al.* 2007) and pH sensors (Han *et al.* 2010). A suitable scaffold is required to anchor the binding sites close to interacting with cations (Kim *et al.* 2015).

The recognition of antipyrine derivatives is essential for pharmacological and clinical applications, including antifungal, antibacterial, antipyretic, analgesic, anti-inflammatory as well as antitumor activities. It was chosen as the fluorophore, the signalling unit particularly carbonyl oxygen and nitrogen of the amine act as binding sites provide excellent photophysical properties such as good photostability, strong absorption and emission signals (Dessingou *et al.* 2012; Gupta *et al.* 2014b; Selvan *et al.* 2018; Tamil Selvan *et al.* 2020). Baylis Hillman reaction is one of the most profit-making C-C bond formations and its functionalities are used as an intermediate for multiple organic transformations. In the series, C-N formation by using various nucleophiles with

Baylis Hillman adduct or acetate gains special attention (Shanmugam *et al.* 2002; Shanmugam *et al.* 2004; Shanmugam *et al.* 2005). Heterocycle scaffold is most attractive and has a strong binding affinity with cations that are widely employed in the construction of chemosensors (Guo *et al.* 2007; Maity *et al.* 2012; Chebrolu *et al.* 2014; Cheng *et al.* 2016).

Being the third most abundant metal, aluminium is widespread in the environment, particularly on the earth's crust. Due to its widespread use as food additives in aluminium-based pharmaceuticals and storage utensils, human beings are constantly being exposed to toxic levels of aluminium. Though Al<sup>3+</sup> has so many positives, the negatives should also be taken into consideration. World Health Organization recommends the aluminium concentration in our daily intake to be 3-10 mg, the excess of aluminium leads to damage to the central nervous system, Parkinson's disease and Alzheimer's disease (Andrási *et al.* 2005; Kaur *et al.* 2012; Gupta *et al.* 2014a). In agriculture, the release of aluminium ions from acidic soils is toxic to plant roots (Ahmad *et al.* 2002). Hence it is important that aluminium concentrations in the permissible level, in need for constant monitoring of human in vivo (Kim *et al.* 2012; Datta *et al.* 2013; Helal *et al.* 2013). Several Al (III) sensors have been reported in the literature (Saini *et al.* 2016; Selvan *et al.* 2018).

Recently our group reported (E)-cinnamic ester with antipyrine fluorescence chemosensor act as ONO tridentate for the detection of Zn<sup>2+</sup> ions (Banumathi *et al.* 2020). A heterocycles scaffold replaces the aromatic benzene scaffold of our previously reported BH-AP

compound to know the coordination ability of metal ions. The above-mentioned importance of antipyrine and heterocycles kept in our mind, we were interested in designing the probe having a heterocycle coordinate site for cation binding by connecting two of them. Herein we have designed and synthesised Baylis Hillman derivatives having furfural ring and antipyrine FBH-AP, which showed the potential to be a highly selective fluorescent chemosensor for  $\text{Al}^{3+}$  ions.

## 2. EXPERIMENTAL SECTION

### 2.1 Chemical and instruments

All reagents, chemicals and solvents were of analytical grade and double-distilled water was used throughout the analysis. Furfuraldehyde, ethyl acrylate, DABCO, acetyl chloride, pyridine and 4-aminoantipyrine were purchased from Sigma-Aldrich, India, solvents including ethyl acetate, ethanol, DMSO, DMF, acetonitrile and chloroform were obtained from Finar, India.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker 400 MHz FT-NMR spectrometer, respectively, in  $\text{CDCl}_3$  solution with TMS as internal standard. IR spectra were recorded on a Bruker FT-IR spectrometer. Fluorescence measurements were performed on a dual-beam UV-Visible spectrophotometer (JASCOV-630), the fluorescence analysis was performed on a fluorescence spectrometer (JASCO FP-8300) equipped with quartz cuvettes of 1 cm path length. The excitation and emission slit widths were 5.0 nm.

### 2.2 Synthesis of receptor FBH-AP

The designed FBH-AP from, FBH-Ac (100 mg, 0.4 mmol) and 4 amino antipyrine (1eq, 0.0789 g), were taken in 2 ml of ethanol and the reaction mixture was heated at  $60^\circ\text{C}$  for 12 hours. After the completion of the reaction, the product was separated by using water and ethyl acetate and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After evaporation of the solvent under vacuum, the product FBH-AP was obtained as dark brown colour oil in 80% yield. It was further purified using silica gel column chromatography taking ethyl acetate and hexane mixture (1:4) as eluent.

### 2.3 Studies on metal ions sensing

To check the cations binding property of the receptor, stock solutions for analysis and various metal ion solutions were prepared ( $1 \times 10^{-3}$  M) from the sulphate and nitrate salts of  $\text{K}^+$ ,  $\text{Al}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  immediately before the experiments. The UV- Vis and fluorescence spectrum were recorded by adding 100  $\mu\text{l}$  of FBH-AP with 100  $\mu\text{l}$  of metal solutions from their stock solutions and then mixed in DMF/ $\text{H}_2\text{O}$  (1:9 (v/v) at pH = 7.0 (Selvan *et al.* 2018). The cationic recognition property was calculated

from variations in the fluorescence spectrum of receptor FBH-AP in the existence of other metal ions.

### 2.4 Studies on the competitive binding

Fluorescence spectrum was recorded by adding 100  $\mu\text{l}$  of FBH-AP with 100  $\mu\text{l}$  of other metal solutions and 100  $\mu\text{l}$  of sensing metal  $\text{Al}^{3+}$  ions were mixed and made up to 10 ml of water (Tamil Selvan *et al.* 2018).

### 2.5 Jobs plot

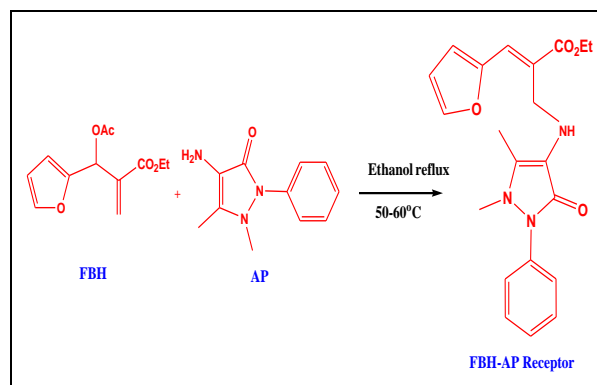
The binding stoichiometry of FBH-AP with  $\text{Al}^{3+}$  ions was studied by using a dilute concentration of a metal solution from 0.1 to 1.0 with a constant concentration of 100  $\mu\text{l}$  of FBH-AP were mixed and made up to 5 ml of water. The mole fraction of  $\text{Al}^{3+}$  was calculated using,

$$\text{Mole fraction} = [\text{Al}^{3+}] / [\text{FBH-AP} + \text{Al}^{3+}].$$

## 3. RESULT AND DISCUSSION

### 3.1 Synthesis and characterization of Receptor FBH-AP

The receptor FBH-AP was concisely synthesized from acetate of 2-Furfuraldehyde Baylis Hillman adduct with 4 amino antipyrine (1 eq.) through a single-step Nucleophilic addition as shown in Scheme 1.



**Scheme 1: Synthesis of receptor FBH-AP**

The final structure of the FBH-AP was confirmed by the usual IR, NMR ( $^1\text{H}$  and  $^{13}\text{C}$ ) and MASS spectrum. IR: (KBr,  $\text{cm}^{-1}$ ) 3368, 2860, 1704, 1614, 1472, 1107, 1035.  $^1\text{H}$  NMR ( $\text{CDCl}_3$  / TMS):  $\delta$  1.21 ( $\text{CH}_3$ , t, 3H), 1.83 (C-Me, s, 3H), 2.64 (N-Me, s, 3H), 3.94 ( $\text{CH}_2$ , s, 2H), 4.21 ( $\text{CH}_2$ , q, 2H), 7.29 (NH, s, 1H), 7.32 (Ar-phenyl, m, 9H), 7.86 (=CH, s, 1H).  $^{13}\text{C}$  NMR: ( $\text{CDCl}_3$  / TMS):  $\delta$  10.25 ( $-\text{C}-\text{CH}_3$ ), 14.10 ( $-\text{CH}_2\text{CH}_3$ ), 37.09 (N- $\text{CH}_3$ ), 44.23 (N- $\text{CH}_2$ ), 61.04 (O- $\text{CH}_2$ ), 115.08-140.67 (Aromatic), 162.09 (ketone,  $\text{C}=\text{O}$ ), 167.50 (ester,  $\text{C}=\text{O}$ ). The proton of secondary amine appears at the aromatic region, merged with phenyl protons.

### 3.2 Fluorescence spectra of FBH-AP

The excitation wavelength of the receptor with different metal ions is standardized at 288 nm by using UV-Vis spectrometer. The binding ability of receptor FBH-AP in the presence of  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  was tested in DMF/ $\text{H}_2\text{O}$  (1:9 v/v) medium by using fluorescence spectrum. Receptor FBH-AP exhibits an emission peak at 388 nm and the addition of above metal ions induced almost no considerable changes in the emission intensity of  $\text{Al}^{3+}$  as shown in Fig. 1. Only the addition of  $\text{Al}^{3+}$  with FBH-AP showed the fluorescence quenching compared to the strong fluorescence of FBH-AP and with other metals. Thus the fluorescence emission demonstrated that FBH-AP functions as a highly sensitive and selective fluorescent chemosensor for  $\text{Al}^{3+}$ .

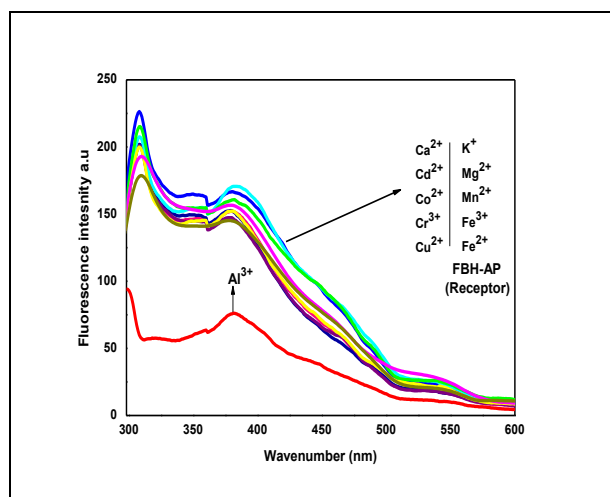


Fig. 1: Fluorescence emission spectrum of FBH-AP with various metal ions

### 3.3 Selectivity of FBH-AP

Selectivity is an important characteristic of an ion-selective chemosensor (Geddes, 2005), experiments on the  $\text{Al}^{3+}$  selectivity from mixtures of different metal ions were carried out. Fig. 2 shows the fluorescence emission spectra in the presence of  $\text{Al}^{3+}$ ; the fluorescence intensity of FBH-AP decreases to the minimum. However, most of the other metal ions do not cause any fluorescence quenching because of their open shell d-orbitals. These results showed a strong selectivity of compound FBH-AP for  $\text{Al}^{3+}$  over all other metal ions.

### 3.4 Jobs plot

The binding stoichiometry was determined using Jobs plot analysis by continuously varying the mole fraction of FBH-AP with  $\text{Al}^{3+}$ . The testing was executed in an aqueous solution by varying the total concentration of  $\text{Al}^{3+}$  from  $1 \times 10^{-6}$  to  $1 \times 10^{-4}$  M to the constant FBH-AP concentration. Fig. 3 depicts that the binding

stoichiometry of  $\text{Al}^{3+}$  with FBH-AP showed a higher value of 0.5, which directed 1:1 (FBH-AP:  $\text{Al}^{3+}$ ).

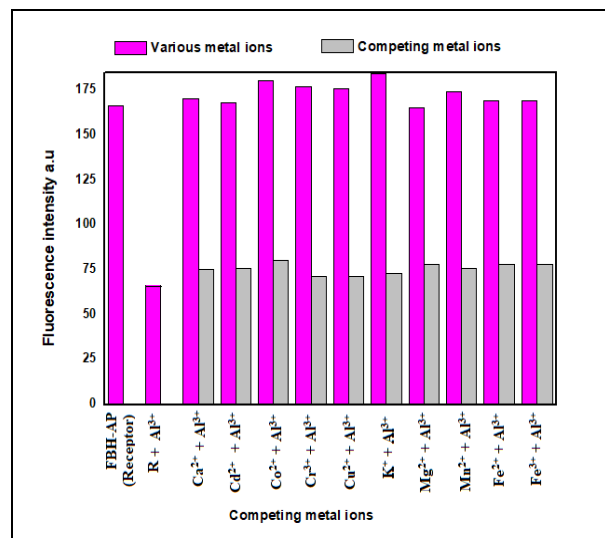


Fig. 2: Competitive study of other metal ions with  $\text{Al}^{3+}$

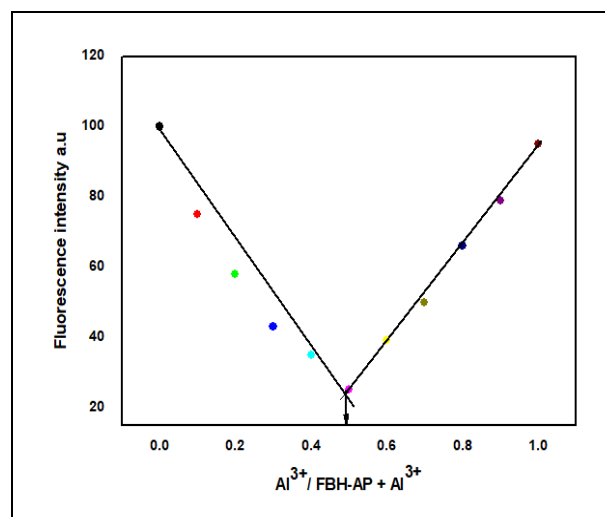
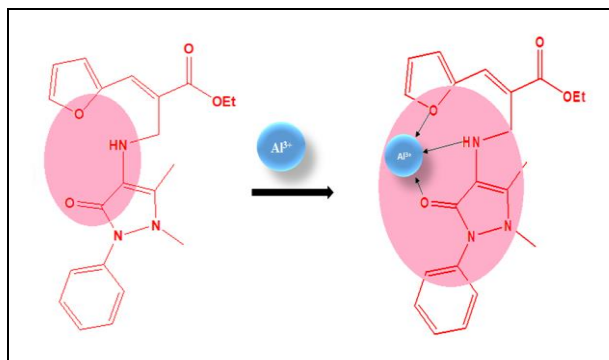


Fig. 3: Jobs plot analysis of FBH-AP with  $\text{Al}^{3+}$

### 3.5 Proposed binding interaction of FBH-AP

Based on the above results, a possible mechanism is shown in Scheme 2. As per the design of the chemosensor, it has three heteroatoms containing a lone pair of electrons in the furfural ring 'O' and the antipyrine 'N' and 'O' that are connected covalently through an unsaturated carbon-carbon ( $\text{C}=\text{C}$ ) double bond with extending conjugation. This conjugation is responsible for the photo-induced electron transfer process (PET) (You *et al.* 2012). The heteroatom moiety possesses a strong electron-donating ability and enhances the electron density of the receptor, which makes FBH-AP display a strong fluorescence emission. Hence, upon complexation of  $\text{Al}^{3+}$  with FBH-AP, the lone pair of electrons was involved in bonding with the electron-

deficient  $Al^{3+}$ , decreasing the fluorescence intensity. This is because the bonding FBH-AP with  $Al^{3+}$  weakens the electron-donating ability of the heteroatoms. As a result, the fluorescence intensity of FBH-AP with  $Al^{3+}$  is almost quenched.



**Scheme 2: Proposed binding mode of FBH-AP with  $Al^{3+}$**

#### 4. CONCLUSION

In summary, we have reported a new furfural ring cycle of Baylis Hillman adduct with Antipyrine receptor FBH-AP as a fluorescent chemosensor for  $Al^{3+}$  ions. The receptor FBH-AP behaves as a highly selective and sensitive chemosensor for the recognition of  $Al^{3+}$  over the other metal ions without any interference. The 1:1 complex formation stoichiometry has been established by the Jobs plot method. The binding mode of the FBH-AP with  $Al^{3+}$  has been followed by the PET mechanism. The quenching in fluorescence of the receptor FBH-AP when it binds with  $Al^{3+}$  can be used for the detection of the  $Al^{3+}$  ions. Hence, the receptor FBH-AP could be used as a potential probe to detect  $Al^{3+}$  in biological and environmental monitoring works.

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#### CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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