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A New Electrochemical and Optical Senor for Al(III) Ions Based on 5-hydroxy-1-methyl-3H-benzo[f]chromen-3-one.

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A simple benzo[f]chromenone (M1) probe was synthesized and evaluated for its electrochemical and optical sensing response to Al(III) ions. Probe M1 exhibits a selective on-off colorimetric and off-on fluorescent sensing in the appearance of Al(III) ion. This probe also exhibits electrochemical sensing via DPV studies. The high sensitivity of M1 for Al(III) is exhibited with low detection limit 0.458 ppm. The resultant sensing is an outcome of CHEF and π–π interaction in rings.

Keywords: Probe M1, Al(III), Optical sensing, Electrochemical sensing.

1. INTRODUCTION

Trivalent metal ions have an important role owing to environment and biological significance. Aluminium is the third most abundant metal in the Earth’s crust, is also one of the extensively used metal species our daily life, such as aluminium-based pharmaceuticals industries and owing to light weight and durability, it is highly important in different areas of transportation and building [1-3]. Due to high conductivity and relatively low price make it important metal in electrical transmission. Which results in a moderate increase in the Al(III) concentration in environment. These are responsible for acidic rain and a wide range of diseases, such as Alzheimer’s disease, anaemia, headache, memory loss and osteoporosis [4-8].

Consequently, the careful control of Al^{3+} in environment and biological system are necessary. Many analytical techniques have been used for low level detection of Al^{3+} ions in various samples, such as inductively coupled plasma mass spectroscopy (ICP-MS), HPLC, atomic absorption spectrometry, voltammetry, and ion selective membrane electrodes [9-14]. In past decade, the fluorescent sensors attract significant awareness owning to the distinct advantages of easy operation, low cost, rapid response, high sensitivity and selectivity, and real-time monitoring [15-20]. A great number fluorescent sensors for Al^{3+} based on 1,8-naphthalimide, imine Schiff base, rhodamine, coumarin, and anthracene have been developed [21-30], but the overall activity of these optical sensors exhibited in limits due to some shortcomings, such as complicated synthesis method, high cost material, low selectivity and sensitivity,. However, the successful design of a small molecular sensor for Al^{3+} which can give a naked eye signal is still a challenging task. We are working with this task to design small molecular sensor with low cost price [31-35].

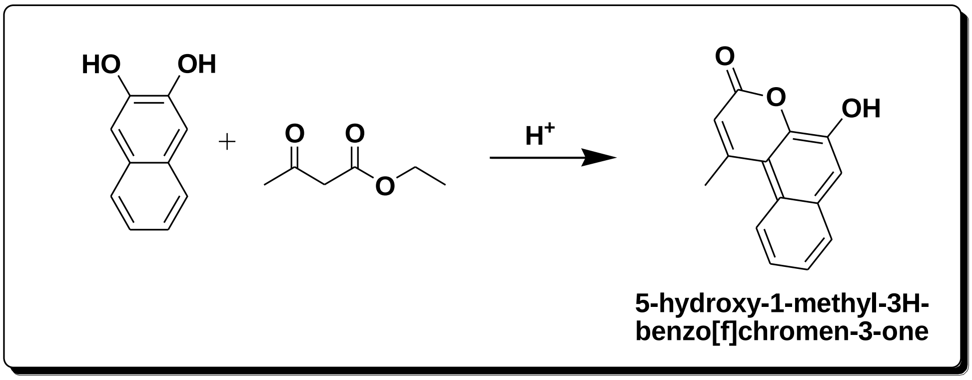
Here, we designed and synthesized a fluorescence chemosensor based on 5-hydroxy-1-methyl-3H-benzo[f]chromen-3-one [M1]. Chemosensors are characterized by NMR and their sensing phenomena were examined by photofluorescent spectroscopy. Therefore, highly sensitive and selective Al^{3+} fluorescent sensor can be utilising as a desirable sensor in aqueous methanolic solutions.

2. EXPERIMENT

2.1. Materials and Methods.

2,3-dihydroxynaphthalene and ethyl acetoacetate have been purchased from Sigma Aldrich and used as received. All other chemicals and solvents are of analytical grade and used without further purification. Stock solution of various metal ions such as Ag^{+}, Cu^{2+}, K^{+}, Ca^{2+}, Co^{2+}, Mg^{2+}, Al^{3+}, Hg^{2+}, Cd^{2+}, Zn^{2+}, Pb^{2+}, Cr^{3+} and Mn^{2+} ions were prepared in aqueous methanolic solution (10%). Absorption and fluorescence spectra have been recorded on a Shimadzu UV-2450 absorbance spectrophotometer and Horiba FluoroMax-4 spectrofluoro-photometer (Japan), respectively. The molecular weight of M1 was occurred on Bruker-micrOTOF II (USA). All pH effect on the sensing phenomena was measured with Eutech pH-510. All sensing experiments were explored between probe M1 (40 mM) and various metal ions (40 mM) in methanol solution.

2.2. Synthesis of chemosensor M1



Scheme 1. Synthesis process of **M1**.

5-hydroxy-1-methyl-3H-benzo[f]chromen-3-one (M1) was synthesized by simple coumarin synthesis process. Mixed 10 mmol ethyl acetoacetate and 0.5 mmol MTSA in 100 ml two neck round bottom flask and heated under stirring. After 10-15 minutes stirring, 10 mmol 2,3-dihydroxynaphthalene was added in this mixture and followed by reflux for 6 hours (Scheme 1). A brownish solid product was filtered and dried over anhydrous P_2O_5. The Resultant product was characterized by NMR and mass spectrum studies. Yield: 77%; Proton NMR (400 MHz, $CDCl_3$, TMS): δ ppm = 11.33 (s, 1H, –OH), 8.22–8.18 (t, 2H, Ar–H), 7.90 (d, 2H, Ar–H), 7.13 (d, 1H, Ar–H), 5.92 (s, 1H, =CH), 1.56 (s, 3H, –CH3). ESI MS m/z (M+H): 227.0734, Calculated for $C_{14}H_{11}O_3$ = 227.0708.

3. RESULTS

3.1. The design of Probe M1

5-hydroxy-1-methyl-3H-benzo[f]chromen-3-one (M1) is contained C=O and –OH binding group as a potentially selective site for the detecting metal ions. These sites have high binding affinity towards Aluminium ions comparatively to other metal ions. Firstly, 5-hydroxy-1-methyl-3H-benzo[f]chromen-3-one (M1) was constructed by single-step reaction between ethyl acetoacetate and 2,3-dihydroxynaphthalene and structure of molecule M1 was characterized *via* NMR and HRMS (Fig. 1,2).

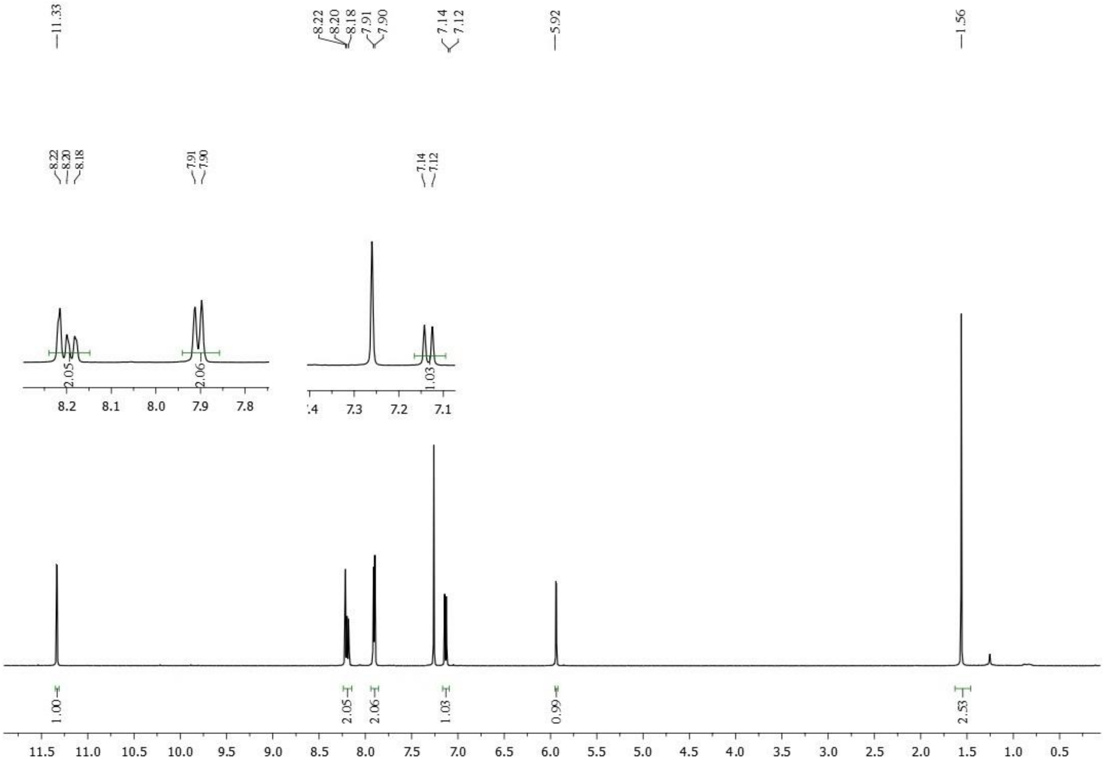


Figure 1. ^{1}H NMR spectra of receptor **M1**.

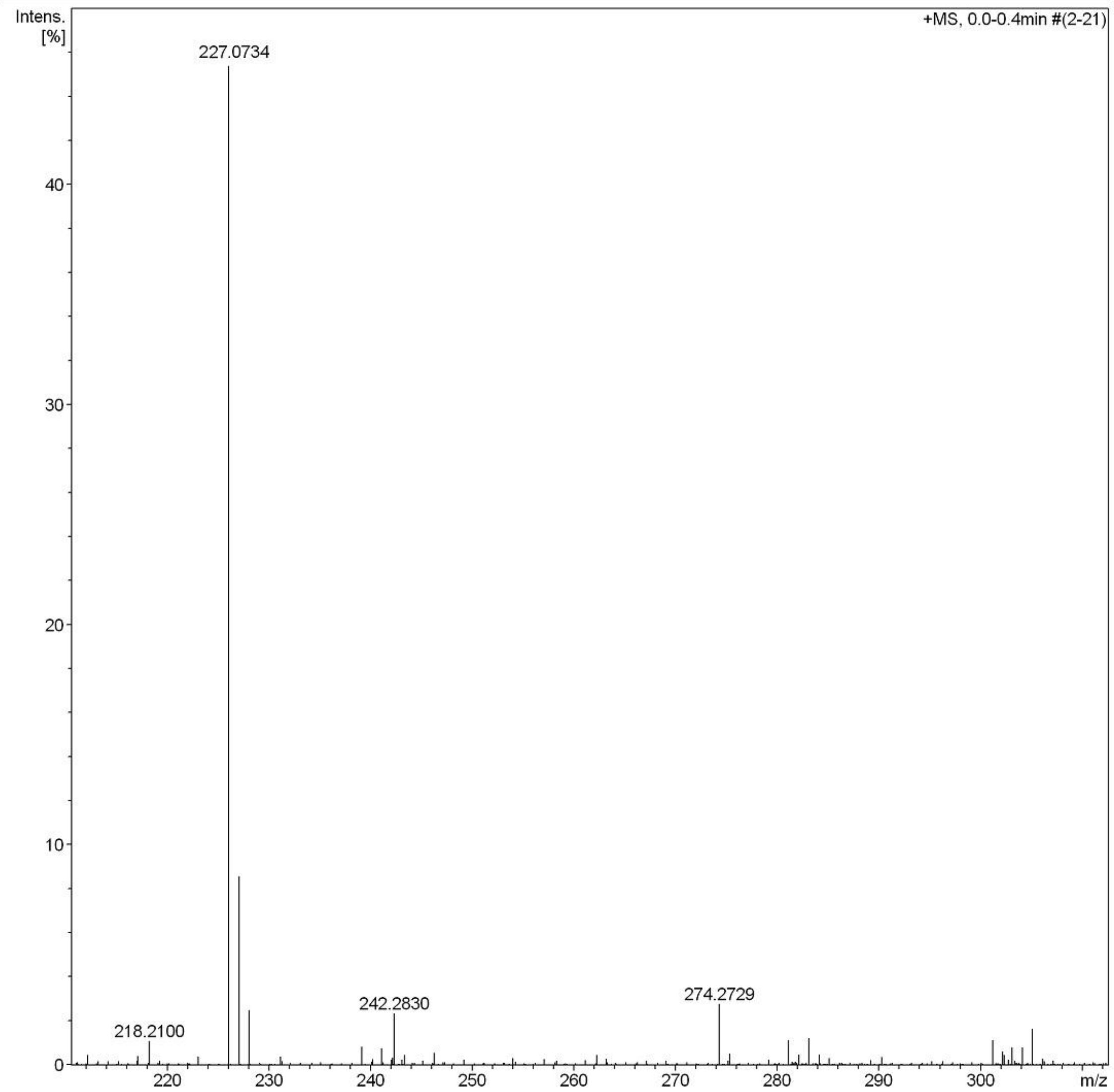


Figure 2. HRMS spectra of receptor **M1**.

3.2. Absorbance studies

The absorbance spectroscopic properties of chemosensor M1 was evaluated in 40 μM aqueous methanol solution (10:90, v/v). Probe M1 demonstrated two strong absorption band due to π–π* transitions localized at 291 and 352 nm. After the addition of equal concentration of various metal ions viz., Ag^+, Na^+, Co^{2+}, Mg^{2+}, K^+, Ca^{2+}, Mn^{2+}, Cr^{3+}, Zn^{2+}, Ni^{2+}, Pb^{2+}, Hg^{2+} and Cd^{2+} solution, maximum absorbance band remained unchanged (Fig. 3). However, the addition of Al(III) ions absorbance spectral band shifted to lower wavelength with low intensity and yellow color of resultant solution turn into colorless solution due to blue shift. These color change can make feasible for naked eye detection in methanolic solution (Fig. 4).

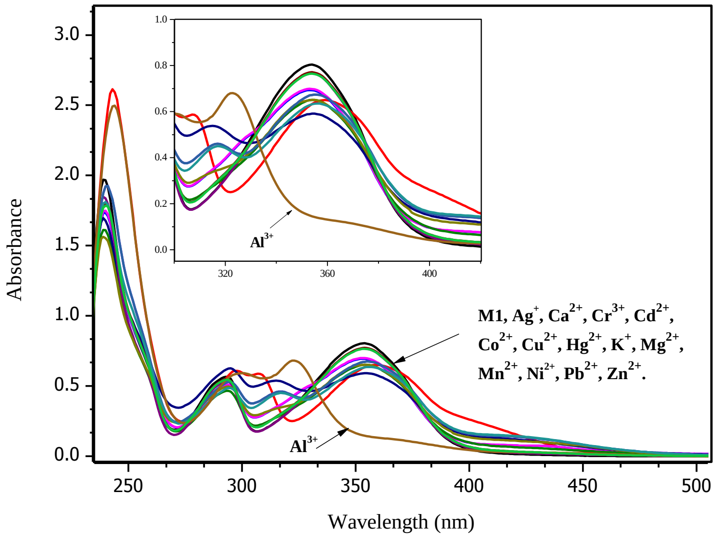


Figure 3. Absorbance spectra of the probe **M1** (40 µM) in the presence of a variety of metal ions, such as Al^{3+}, Cd^{2+}, Ag^{+}, Ca^{2+}, Mn^{2+}, Hg^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, K^{+}, Pb^{2+}, Ni^{2+}, Mg^{2+} and Zn^{2+} in MeOH.

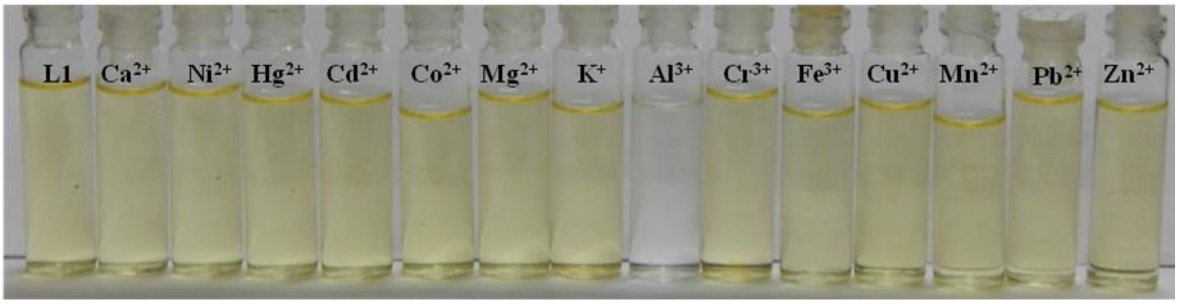


Figure 4. Naked eye colorimetric sensing studies of M1 with Al(III).

3.3. Fluorescence sensing studies

The fluorescence intensity of probe M1 in aqueous methanolic solution (10:90, v/v) exhibited with very low intensity at 436 nm. This band intensity remained unchanged after the addition of equal concentration of various metal ions viz., Ag^{+}, Co^{2+}, Mg^{2+}, K^{+}, Ca^{2+}, Cr^{3+}, Cu^{2+}, Mn^{2+}, Zn^{2+}, Ni^{2+}, Pb^{2+}, Hg^{2+} and Cd^{2+} ion. Therefore, In the presence of equal concentration of Al^{3+}, a strong fluorescence emission band occurred at maxima 436 nm (Fig. 5). Probe M1 with a –OH and C=O group has non-fluorescence moiety due to electronic transition between hydroxyl group and naphthalene ring via CHEF mechanism, after the formation of complexation with Al(III) these electronic transition goes to stop and exhibited a blue-green fluorescence (Fig. 6). This efficient blue-green turn-on fluorescence response to Al(III) make it feasible for naked-eye detection.

Moreover quantitatively evaluate, titration studies was performed between probe M1 with Al(III) ions. The sensing of probe M1 for Al(III) ion was examined at variable concentrations (0.0

equivalents to 2.0 equivalents) of Al(III) ions. The fluorescence emission intensity gradually enhanced with a linear range ($R^2 = 0.989$) at maximum wavelength (436 nm) as evaluated in Fig. 7.

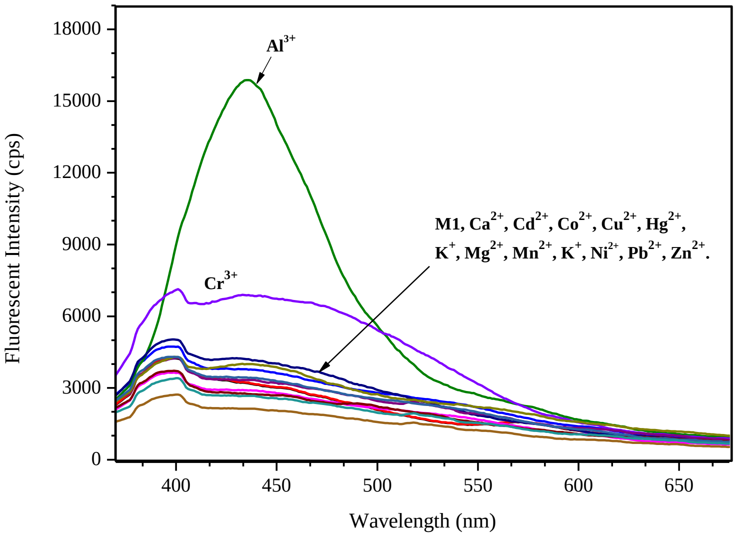


Figure 5. Fluorescence spectra of the probe M1 (40 μM) in the presence of a variety of metal ions, such as Al^{3+}, Cd^{2+}, Ag^{+}, Ca^{2+}, Mn^{2+}, Hg^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, K^{+}, Pb^{2+}, Ni^{2+}, Mg^{2+}, and Zn^{2+} in MeOH.

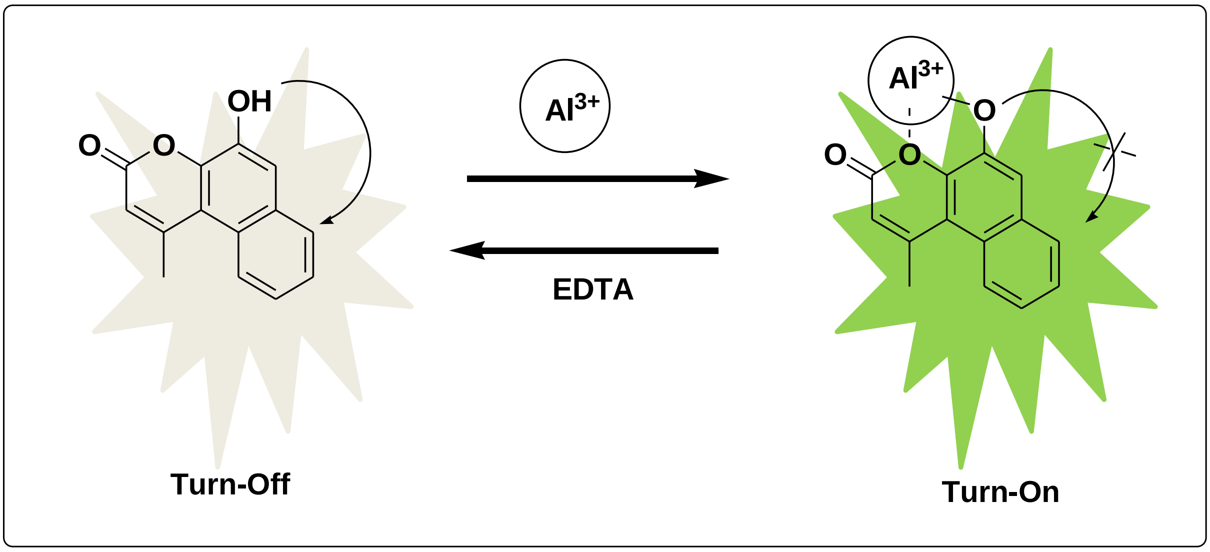


Figure 6. Proposed mechanism for fluorescent sensing nature of probe M1.

Furthermore, the binding constant of M1+Al(III) complex was observed with the help of Benesi−Hildebrand plot [36]. The binding constant (Ka) was calculated 3.89 x 10^4 M^{-1} through the linear plot of concentration titration (Fig. 8).

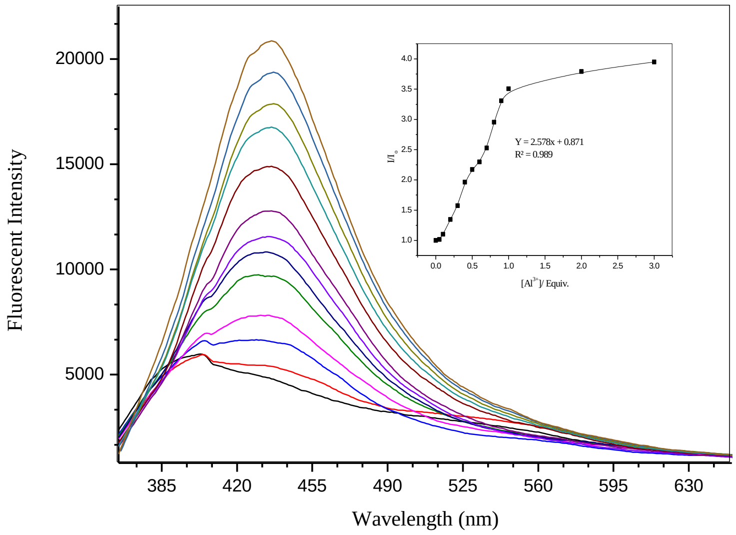


Figure 7. Fluorescence emission spectra of sensor **M1** (40 μM) in the increasing concentration of Al^{3+} (0, 3, 6, 9, 12, 15, 20, 25, 30, 35, 40, 80 μM) at λ_{max} of 436 nm.

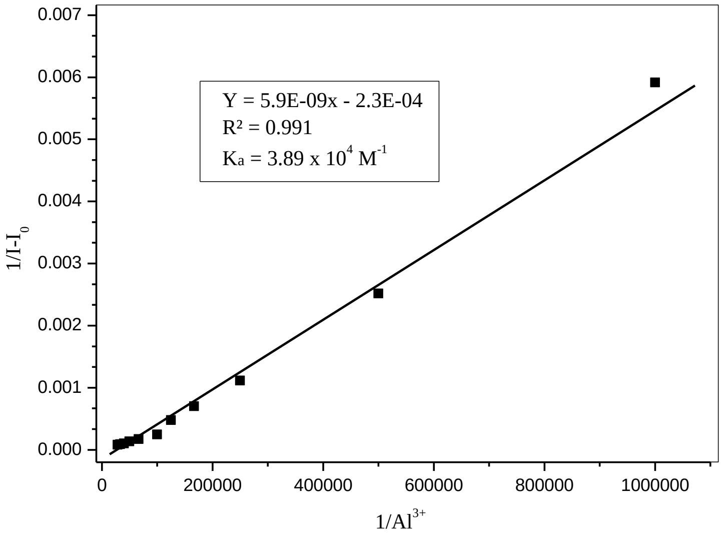


Figure 8. Binding constant measurement for probe M1 via Benesi−Hildebrand plot.

3.4. The Selectivity and detection limit (LOD) for Al(III)

Moreover, the selectivity of M1 for Al(III) was examined with equal concentration of various metal Na^+, Ag^+, Co^{2+}, Mg^{2+}, K^+, Ca^{2+}, Cr^{3+}, Co^{2+}, Mn^{2+}, Zn^{2+}, Ni^{2+}, Pb^{2+}, Hg^{2+} and Cd^{2+} ion aqueous methanolic solution (10 : 90, v/v). Interestingly, the ‘turn-on’ fluorescence intensity of M1 at 436 nm remained unchanged except Cu^{2+} and Cr^{3+} ions. In the case of Cu^{2+} and Cr^{3+} the fluorescent intensity of M1+Al(III) quenched but it was also detectable. Moreover, The limit of detection (LOD) of M1 for Al(III) was calculated 4.25×10^{-7} M (Fig. 9) according to the standard blank measurement (3σ/slope) and a linear concentration titration slop [37].

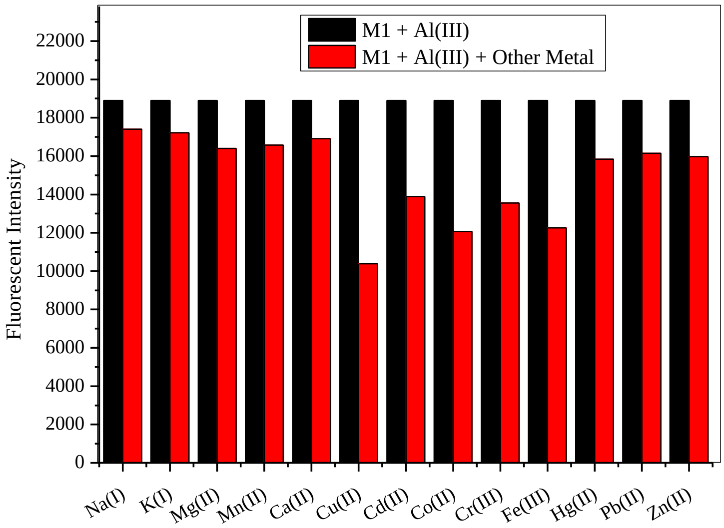


Figure 9. Interferences effect of other metal ions on the optical sensing determination of Al^{3+} ion..

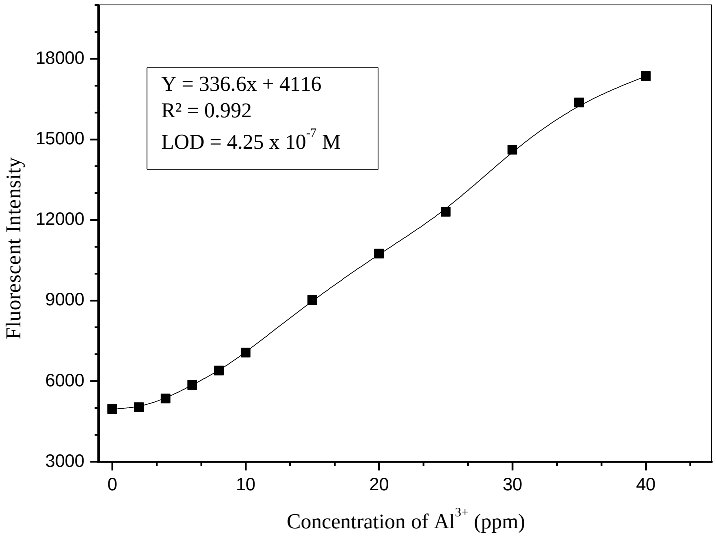


Figure 10. The linear relation spectra of M1 (40 μM) with Al^{3+} (0-40 μM).

The reversible sensing properties is an important parameter of chemosensor. Probe M1 also exhibited reversible sensing phenomena in the presence of EDTA. Upon the addition of 0.6 equivalents of EDTA, fluorescence intensity declined at the lower level of probe M1 (Fig. 10).

3.5. Job's plot analyse

Stoichiometry of M1+Al(III) complex was evaluated via Job's titration method. In this titration method, the total concentration of probe M1 and metal ion (Al^{3+}) remained constant (40.0 μM) and the molar ratio of aluminium ions consistently changed from 0.1 to 0.9 equivalent. In result, the fluorescence emission intensity occurred maximum at 0.5 molar fraction (Fig. 11), signifying 1:1 complex between probe M1 and Al(III) ions.

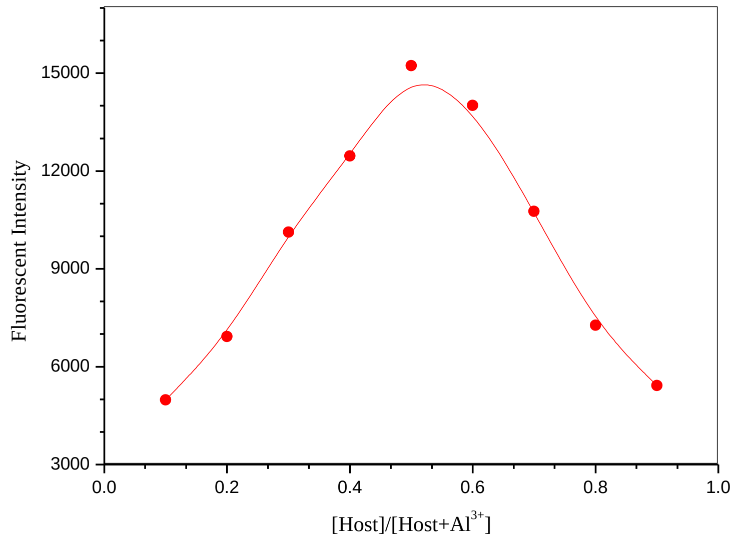


Figure 11. Job's plot spectra for chemosensor M1 and Al(III) ions.

3.6. Electrochemical Studies of probe M1.

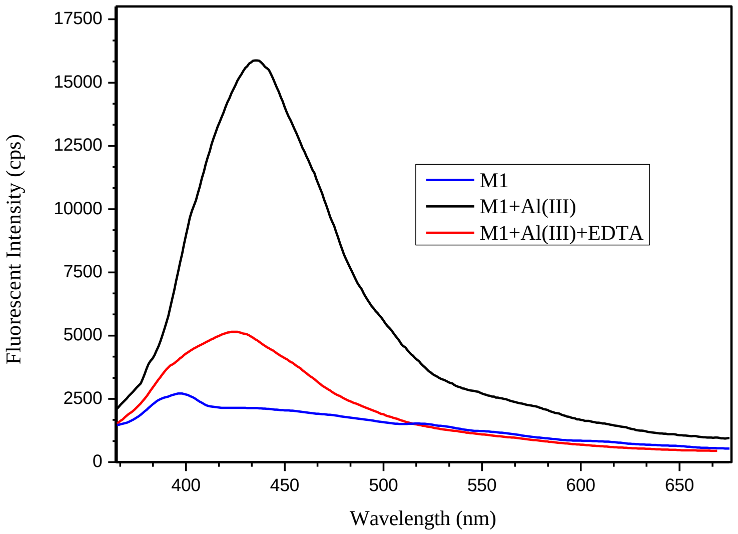


Figure 12. Reversible sensing of M1 (40 µM) towards Al(III) at 436 nm after the addition of EDTA (0.6 equiv.)

Probe M1 also exhibited an electrochemical sensing nature for Al(III) ions. All electrochemical studies were observed on CHI760E electrochemical workstation (USA). The oxidation potential ($E_{ox.}$)

for probe M1 in methanolic solution (100 ppm) was recorded at 0.421 V. After the addition of Al(III) ions, oxidation potential for M1+Al(III) was recorded at 0.649 V. As visualized in Fig. 12, the oxidation potential ($E_{ox.}$) for metal complex shifted to high positive value compare the probe M1. This notable changes in oxidation potential ($E_{ox.}$) was exhibited bonding affinity in between the probes M1 and Al(III) ions.

3.7. pH study

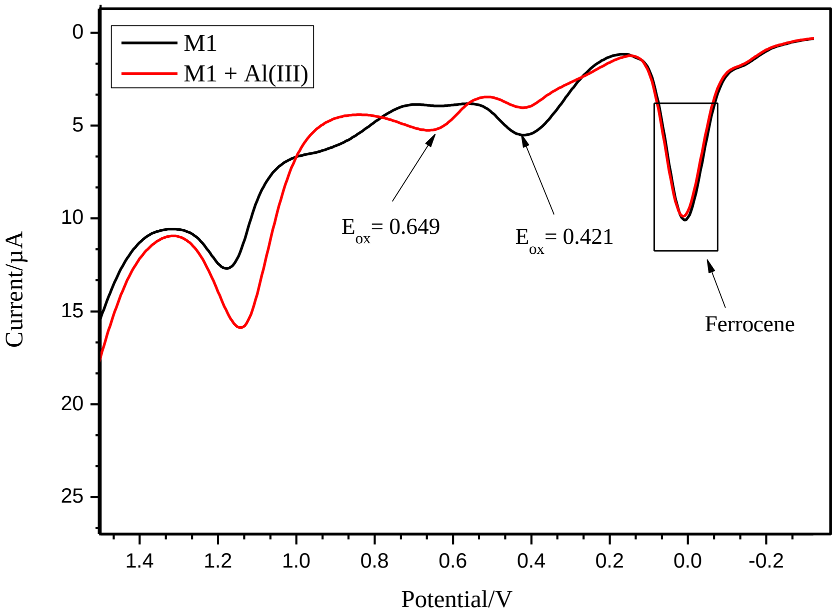


Figure 13. Electrochemical sensing response studies of **M1** with Al(III).

The fluorescence emission changes of M1 and M1+Al(III) (40 μM) in different 2.0–12.0 pH range. Therefore, a significant quenching in the fluorescence emission intensity of probe M1 and M1+Al(III) occurred at maximum wavelength 436 nm due to interference with H^+ and OH^- ions in high acidic (2–5) and basic pH range (8–10). Thus, Probe M1 exhibited maximum fluorescent sensing towards Al(III) the pH range 6–8, which was make useful for Al^{3+} detection in industrial analysis and environmental sample (Fig.13).

3.8. Comparative sensing studies of M1 with previous sensor

A relative sensing studies in between probe M1 and previously reported fluorescent and electrochemical sensor based on the binding constant, response time, pH range, limit of detection, and selectivity was reported in Table -1. The comparative data were exhibited excellent sensing ability of chemosensor M1.

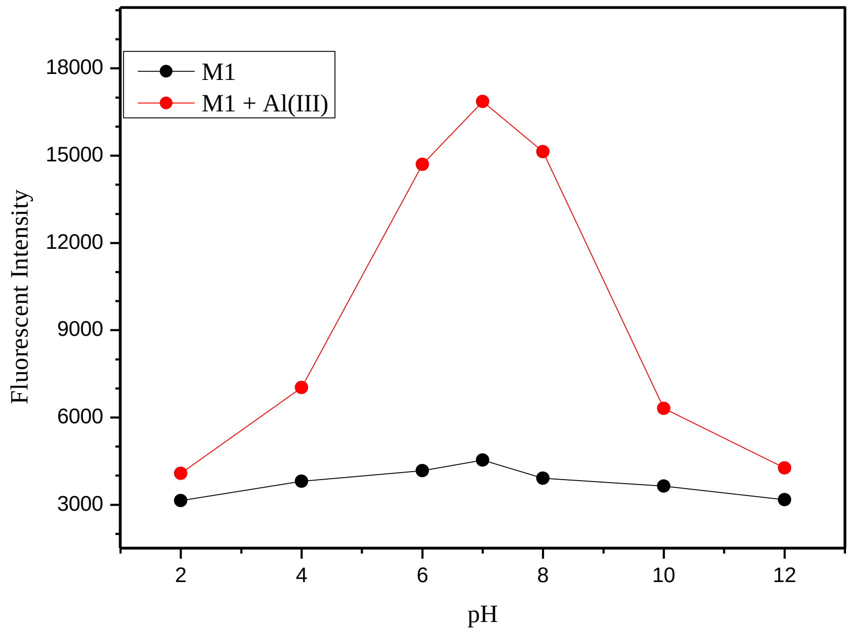


Figure 14. Fluorescence emission intensity changes of M1 and M1–Al^{3+} complex with pH variations.

Table 1. Comparative studies of probe M1 with other reported sensor.

Ref.	**Binding Constant (M^{-1})**	**Detection Limit (M)**	**Response nature**	**Interfering ions**
22	3.14×10^{5}	3.26×10^{-6}	Turn-On	Cu(II)
26	1.02×10^{3}	5.86×10^{-6}	Turn-On	Zn(II)
27	1.38×10^{5}	6.90×10^{-7}	Turn-On	Fe(III), Ni(II)
28	1.24×10^{5}	5.0×10^{-7}	Turn-On	Fe(III), Cu(II)
29	4.0×10^{5}	5.0×10^{-5}	Turn-On	Cu(II)
33a	-	1.0×10^{-6}	Turn-On	Cu(II), Ni(II)
33b	-	7.0×10^{-7}	Turn-On	Cu(II), Ni(II)
Probe M1	1.07×10^{4}	4.58×10^{-7}	Turn-on	Cu(II)

4. CONCLUSION

A new designed and synthesized probe 5-hydroxy-1-methyl-3H-benzo[f]chromen-3-one (M1) was exhibited a high selective and sensitive electrochemical and fluorescence sensing nature. The probe M1 showed a dramatic turn on fluorescence sensing nature for Al(III) ions with a low detection limit 4.25 x 10^{-7} M. Furthermore, High selectivity of probe M1 with Al(III) in excess of other metal ions was further verified with high value of binding constants. The chemosensor M1 was exhibited 1:1 stoichiometry coordination complex nature for Al(III) ions. All results were favoured high sensing nature of chemosensor M1 toward the routine analysis of Al(III) ions.

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