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Hydrolytically stable Schiff base as highly sensitive aluminium sensor

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ABSTRACT

A highly fluorescence sensitive sensor for selective detection of aluminium (III) and also to differentiate isomeric acids or two isomers of receptors are presented.

Aluminium is an indispensible element due to its abundance and use in every sphere of life from utensils to medicine [1–3]. Detection of aluminium in mixed metal environment is of general concern [4]. On the basis of their differences of response in fluorescence emission, Schiff bases and related heterocyclic compounds are generally used for detection of aluminium ions [5–9]. Schiff bases have tendency to undergo hydrolysis, so, hydrolytic stability of such receptor is important. Metal complexes having Schiff base ligands are often used in various organic transformations, thus fluorophore containing Schiff bases are of interest to monitor in situ catalytic reactions [10]. The use of Schiff bases in homogeneous or heterogeneous conditions may have long standing impact to design receptors for detection of aluminium ions. In the present study three imine containing ligands illustrated in Fig. 1, each of them having a chelating site which is one of the prerequisite structural features to have favourable interactions with metal ions is chosen to study their selectivity in sensing different ions. All these ligands **1**–**3** have two common features, namely a chelating site to metal ion and other is each of them possesses a naphthalene ring as fluorophore.

The imine group containing compound **1** is hydrolytically unstable; but it is stable in common organic solvents. Upon addition of a drop of water to a DMSO or methanol solution of **1**, it transforms to corresponding 1,4-phenylenediamine and the 2-hydroxynaphthaldehyde. The hydrolysis of **1** is studied in an NMR tube by recording ^{1}HNMR spectra of compound **1** by dissolving it in DMSO-d_6 and followed by recording the ^{1}HNMR of the same solution by adding a drop of deuterium oxide. In situ generated degraded products by addition of D_2O can be easily identified by interpreting the ^{1}HNMR (supporting information). Further the degraded products are purified and compared their spectroscopic properties with standard authentic samples. The compound **1** has absorption maximum at 487 nm; upon degradation the solution turns pink; new set of visible peak appears at 563 nm (Fig. 2). Generally, hydrolysis of imines is facilitated by acids, but it is found that compound **1** is relatively more stable in protonated state with respect to its neutral state, the later state undergoes facile hydrolysis. The compound **1**–**3** shows visible absorptions at 487, 389 and 445 nm respectively, hence the excitation in each case were done near the absorption maximum and fluorescence emissions were studied under different conditions. Hydrofluoric acid (5 μl) quenches fluorescence emission of **1** (5×10^{-6} M solution in methanol); other acids such as HCl, HNO_3 etc. also quench the fluorescence emission of **1** in the similar concentration. However, the compounds **2** and **3** follow a reverse trend with respect to the compound **1** in emission upon addition of these acids, and in the cases of **2** and **3** enhancement of emission intensity with a shift in emission maximum occurred. The compounds **1** and **3** are positional isomers, by comparing the trends in fluorescence emission of these two isomers **1** and **3** upon treatment with a mineral acid the two isomers can be differentiated. The compound **1** is highly solvatochromic and it shows a large shift in positions of absorption maxima in different solvents (refer supplementary materials). Due to hydrolytic instability, compound **1** is not useful for detection of metal ions. Attempt to study detection of metal ions by this compound in methanol, showed that the metal ions such as Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Al^{3+} cause reduction of fluorescence emission, such reductions in fluorescence intensity are so less that they are comparable with the dilution effect.

On the other hand, compounds **2** and **3** have the ability to recognize Al^{3+} very selectively. They show strong green fluorescence emission in the presence of traces of Al^{3+} ions. The fluorescence emission enhancement of **2** by Al^{3+} occurs at 445 nm ($\lambda_{ex} = 380$ nm) whereas it occurs at 489 nm ($\lambda_{ex} = 440$ nm) for compound **3**. The emission changes of a methanol solution of **2** on addition of Al^{3+} are shown

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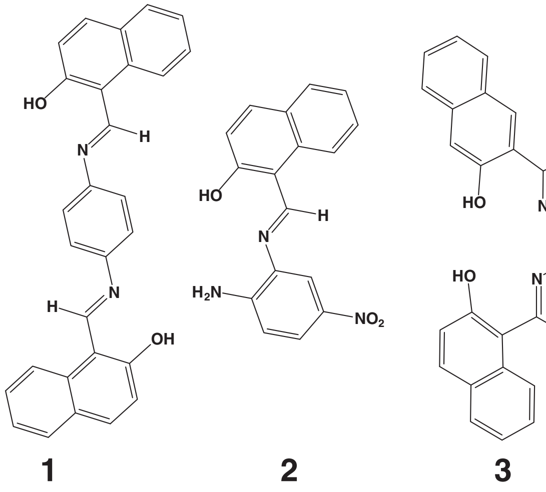

Fig. 1. Structure of the receptors.

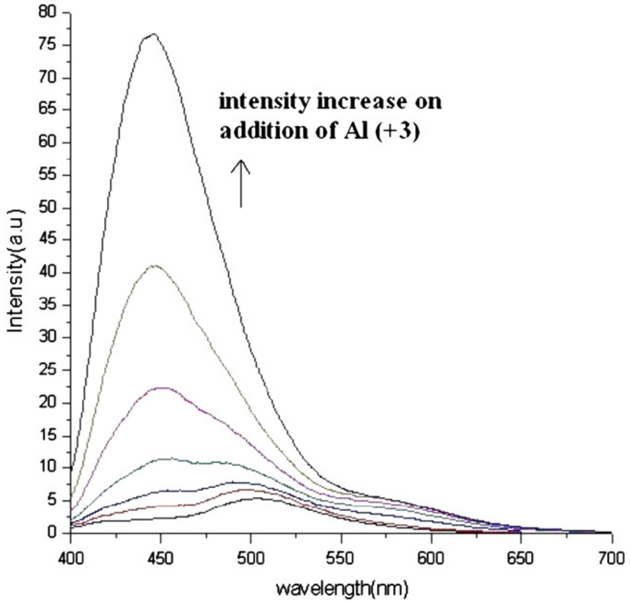

Fig. 3. Fluorescence ($\lambda_{ex} = 380$ nm) enhancement of **2** (2 ml, 10^{-4} M in methanol) on addition of aluminium chloride hexahydrate (3.8×10^{-3} M, 20 μL in methanol in each aliquot).

in Fig. 3. The fluorescence enhancement of **3** in methanol by Al^{3+} ions of identical concentration is about approximately 2.2 times higher relative to fluorescence enhancement of **2** under similar conditions. Addition of Al^{3+} solution in methanol (20 μl of 10^{-4} M) to a solution of **2** (2 ml, 10^{-5} M in methanol) shows about 60 times fluorescence intensity enhancement; whereas the same solution on dilution by equal volume of methanol shows about 200 times higher fluorescence intensity enhancement with respect to the fluorescence intensity of fluorescence emission of a solution of compound **2** in a similar concentration. The compounds **2** and **3** have characteristic fluorescence emission features; from the changes in these features the sensing properties and selectivity towards an ion can be made.

Similar to the compound **2**, dilution affects the enhancement of the fluorescence intensity while detecting aluminium. This indicates that discrete units of compound **2** are associated with aluminium ions probably through chelation and these units are responsible for increase in fluorescence intensity. The ions like Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}, quench the fluorescence emission of **2**. Thus the receptor **2** provides fluorescence-on with Al^{3+} and fluorescence-off with Zn^{2+}. The fluorescence-on by Al^{3+} can be made to off by Zn^{2+} whereas the reverse is not observed. The visible spectroscopic titration of **2** with Zn^{2+} clearly shows isosbestic point showing complexation of Zn^{2+} to ligand **2** (Fig. S7). The compound **2** does not recognize Hg^{2+}, and Cd^{2+}. The compound **3** shows fluorescence quenching with Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Fe^{3+}. It was reported that ions of Fe^{3+}, Cu^{2+}, interfere in the fluorescence emission caused by Al^{3+} of a Schiff base derived from salicylaldehyde [6]. Our compounds **2** and **3** are superior in this regard, for example, the compound **3** shows fluorescence enhancement when a mixture of Al^{3+} and Fe^{3+} (1:4 molar ratio) is added to methanol solution of **3**, in this case the emission intensity is changed insignificantly with respect to fluorescence emission obtained by adding a pure solution of Al^{3+} to a solution of **3** in methanol. A similar observation was found in the case of Al^{3+} and Cu^{2+} in 1:4 ratio, which causes 40% fluorescence quenching, and similarly in the case of a addition of Al^{3+} and Zn^{2+} in 1:4 ratio causes about 80% fluorescence quenching with respect to emission intensity shown by only Al^{3+} ion containing methanol solution of **3** (refer to supplementary bar diagrams). The fluorescence emission spectra of **3** is insignificantly affected by In^{3+}; and In^{3+}, Co^{2+}, Ni^{2+} do not interfere in the emission changes of **3** caused by Al^{3+} ions. In this study we have used aluminium chloride as the source of Al^{3+} for

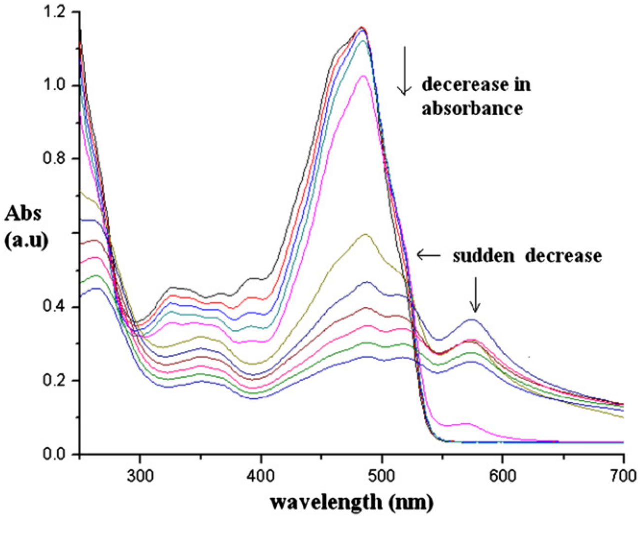

Fig. 2. The changes in visible absorption of **1** (2 ml, 10^{-5} M solution in methanol) upon addition of water (100 μL in each aliquot).

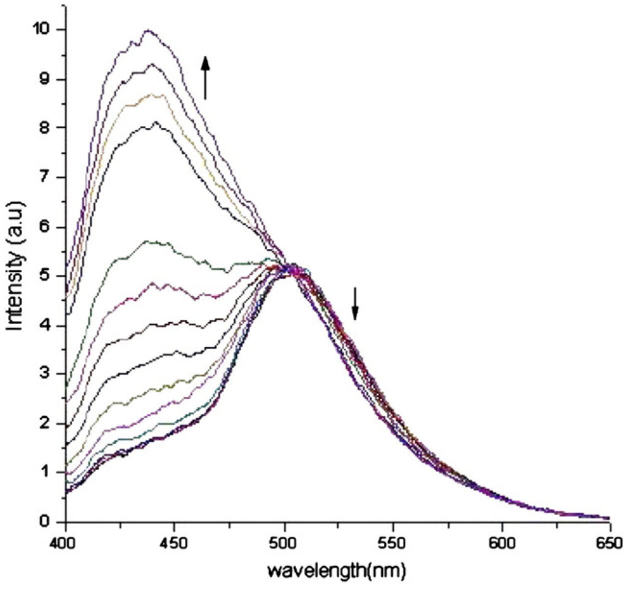

Fig. 4. Changes in fluorescence emission ($\lambda_{ex} = 380$ nm) of compound **2** (2 ml, 10^{-5} M in methanol) upon addition of maleic acid (10^{-2} M in methanol, 10 μL per aliquot).

it's detection, Al^{3+} can also be easily produced from aluminium scrap by treatment with hydrochloric acid, however, the acidic solutions are not very sensitive for aluminium detection by **3**, hence we have to carry out such detection in neutral condition. The compound **2** has an extra ability to distinguish maleic acid and fumeric acid. Independent addition of these two isomeric acids to the solution of **2** in methanol show different fluorescence responses. When maleic acid solution is added to a solution of **2** in methanol, a new emission peak at 438 nm is generated ($\lambda_{ex} = 380$ nm) (Fig. 4); whereas the addition of fumeric acid shows only fluorescence intensity enhancement of the **2** without appearance of a new emission peak. The compound **3** shows fluorescence enhancement upon addition of either of these isomer. The visual distinction of these two isomers namely maleic acid and fumeric acid by treating with a quinoline based receptor [11] was shown, but from a sensitivity point of view there is advantage to use a higher sensitive fluorescence tool for detection of such isomers.

To conclude, two highly sensitive sensors capable of detecting aluminium is demonstrated; out of which the compound **3** can detect aluminium in the presence of other essential metals under neutral condition.

Appendix A. Supplementary material

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2012.05.032.

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