Pyrimidine based highly sensitive fluorescent receptor for Al^{3+} showing dual signalling mechanism†

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A new fluorescent probe (*5*-[(*4-diethylamino-2-hydroxy-benzylidene*)-*amino*]-*1H-pyrimidine-2*, *4-dione*) (**Receptor 1**) has been synthesized by the Schiff base condensation of 5-aminouracil with 4-(diethylamino)salicylaldehyde. The receptor **1** exhibits high selectively for Al^{3+} in DMSO as well as in aqueous solution even in the presence of biologically relevant cations such as Na^+, K^+, Ca^{2+}, Mg^{2+}, Pb^{2+} and several transition metal ions. The lowest detection limit for the receptor **1** was found to be 1.62×10^{-10} M with its linear response towards Al^{3+} in the concentration range of 1.75×10^{-9} to 3.3×10^{-8} M in DMSO. Receptor **1** is the first ever example where a single molecular probe is able to show imine (C═N) isomerization inhibition along with twisted intramolecular charge transfer (TICT) in combinatorial fashion.

Introduction

Aluminium is widely used for industrial and domestic purposes. The toxicity of aluminium towards a variety of living beings including the human beings also is well discussed in the literature time to time.[1] The bone and joint diseases along with neuronal disorder leading to dementia, myopathy and Alzheimer's disease[2] are a few serious diseases caused by the toxicity of Al^{3+}. Out of various methods available for the detection of this ion[3] the spectrofluorometry is widely used one due to its high sensitivity. For this purpose several fluorescent probes such as hydrazones,[4] Schiff bases,[5] coumarin,[6] pyrollidine,[7] calixarene,[8] boron dipyrromethene,[9] hydroxyflavone,[10] 8-hydroxyquinoline,[11] oxazoline and imidazoline[12] derivatives have been synthesized and used time to time. All the fluorescent receptors reported for Al^{3+} till now have a few serious lacunae like interferences by Fe^{3+} and Cu^{2+} most commonly.[13] At the same time their synthetic protocols are a bit tedious one.

Through this communication we are reporting a Schiff base (**Receptor 1**) derived from the condensation of 5-aminouracil with 4-(diethylamino)salicylaldehyde as a fluorescent probe for the selective determination of Al^{3+} in DMSO as well as in aqueous solution with almost non-interference by Fe^{3+} although Cu^{2+} did interfere. The lowest detection limit for Al^{3+} with a recently reported fluorescent probe[14] is of the order of 10^{-9} M while the same for the receptor **1** was found to be 1.62×10^{-10} M and 4.03×10^{-9} M in DMSO and aqueous solution respectively.

To the best of our knowledge, this is for the first time that any uracil derivative has been exploited as the fluorescent receptor for any ion. Furthermore, the fluorescent probes for Al^{3+} detection in aqueous media is still rare. Hence a fluororeceptor like receptor **1** with high sensitivity towards Al^{3+} in aqueous solution with a lowest detection limit of the order of 10^{-10} M has its own worth.

Besides detecting the Al^{3+} selectively in aqueous solution through receptor **1**, present study also deals with the mechanistic aspect of the same. The inhibition of imine (C═N) isomerization[15] in association with twisted intramolecular charge transfer (TICT)[16] seem to be operating under present study. Hence, receptor **1** is the first ever example where a single molecular probe is able to show imine isomerization inhibition along with TICT in combinatorial fashion.

Furthermore, this is the only second report for Al^{3+} enhanced fluorescence of a chemoreceptor showing dual emission bands.[17] Most of the fluororeceptors exhibit only single emission band on their interaction with a particular analyte. Out of single and dual emissions it is always the second one which is preferred one due to its high accuracy and precision in terms of analyte sensing.[18] The solvent effect is always an important effect in most of the studies so is here also. The fluorescence measurement in aqueous medium showed single emission band. The mechanistic details have been explored in a systematic way by performing the Al^{3+} enhanced fluorescent studies with two controlled receptors besides receptor **1**. Present study is a part of our current research interest to evaluate the analyte sensing ability of receptors synthesized through simple reaction protocol.[19]

Experimental

Synthesis of (5-[(4-diethylamino-2-hydroxy-benzylidene)-amino]-1*H*-pyrimidine-2,4-dione) (Receptor 1)

An ethanolic solution of 4-(diethylamino)salicylaldehyde (4 mmol) was added dropwise, to a solution of 5-aminouracil (4 mmol) in 30 mL ethanol at room temperature (Scheme 1). The reaction mixture was further stirred for ~30 min at room temperature and then refluxed for 6 h on a boiling water bath leading to formation of a yellow colored product, which was filtered and dried under vacuum. Other probes **2** and **3** were synthesized through similar procedure.

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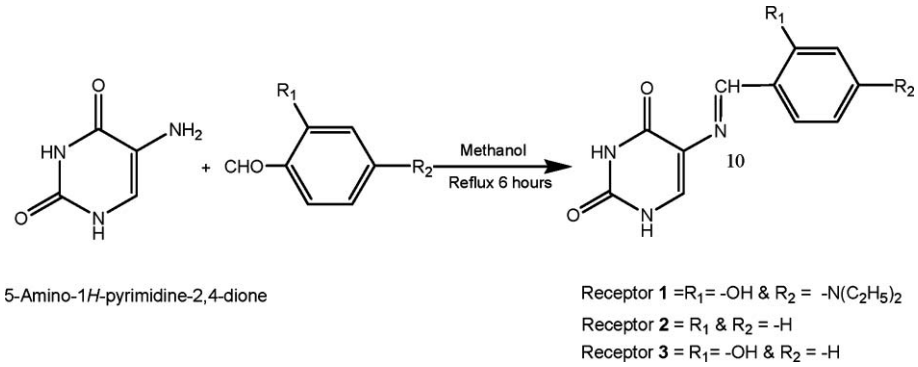
† Electronic supplementary information (ESI) available: General methods, ^1H & ^{13}C NMR, IR and Mass spectra of synthesized receptors; ESI-mass spectra of receptor **1**-Al^{3+} complex; UV-visible spectral titrations of receptor **1** with various analytes. See DOI: 10.1039/c0ob00171f



Scheme 1 Synthesis of fluorescent probes.

Important spectroscopic data for receptor 1

Yield 88%; mp >300 °C; MS [M+H] = 303.4 Calc. for $C_{15}H_{18}N_4O_3$ = 302.33; δ_H (400 MHz, DMSO-d_6, Me_4Si): 13.22 (1H, –OH), 11.31 (1H, $–N_3H$, Uracil), 11.02 (1H, $–N_1H$, Uracil), 8.99 (1H, –CH═N–, Imine), 7.59 (1H, Ar–H), 7.19 (1H, Ar–H), 6.27 (1H, $–C_6H$, Uracil), 6.03 (1H, Ar–H), 3.37 (4H, $–CH_2$), 1.23 (6H, $–CH_3$); δ_C (400 MHz, DMSO–d_6, Me_4Si): 162.47, 161.27, 160.67, 150.88, 150.06, 133.41, 132.84, 121.34, 108.51, 103.43, 96.91, 43.72, 12.44; ν_{max} (KBr)/cm^{-1}: 3147, 3064, 2971, 2905, 2816, 2743, 1703, 1574, 1518, 1422, 1352, 1297, 1243, 1213, 1126, 1071, 1006, 851, 815, 598, 550. λ_{max} (DMSO) nm: 387 nm.

Results and Discussion

UV-visible studies

The metal recognition properties of receptor **1** was initially evaluated by UV-visible spectral analysis. Fig. 1 shows the absorption spectra of receptor **1** in the absence and presence of different amounts of Al^{3+} (as its chloride salts). The UV-visible titrations were carried out in 10 μM DMSO solution of receptor **1**. Free receptor **1** displayed an absorption band with a maximum at 387 nm, which was red shifted (by 62 nm) to 449 nm (Fig. 1) upon addition of increasing concentrations of Al^{3+} ions. A clear isosbestic point at 410 nm indicated chemical interaction of Al^{3+} with receptor **1**. At this stage the color of solution was olive green, (see ESI;† Fig. 2) clearly observable to naked eye.

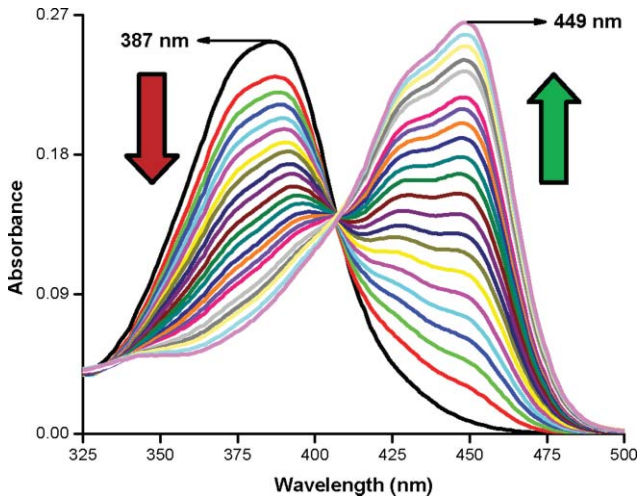


Fig. 1 UV-visible spectral changes of 10 μM DMSO solution of receptor **1** upon concomitant additions of Al^{3+} (0–5 equivalents).

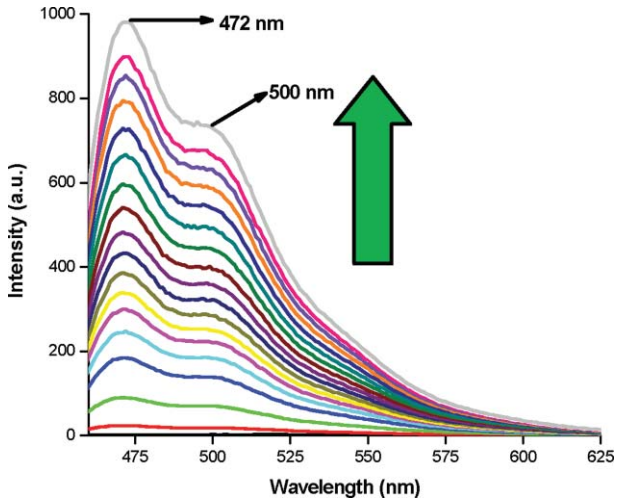


Fig. 2 Fluorescence titration curve of 0.5 μM DMSO solution of receptor **1** upon concomitant additions of Al^{3+} ion (0–3 equivalents).

A series of biologically important transition metal ions such as Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} (as its chloride salts) also perturbed the UV-visible spectral pattern of the receptor **1** (see ESI;† Fig. 1). Addition of Cu^{2+} to the receptor **1** solution produce absorption bands at 431 and 441 nm while Zn^{2+} and Co^{2+} produced at 430 nm and 436 nm respectively on their concomitant additions to the receptor solution separately. The spectral change for Ni^{2+} was almost similar to that of Al^{3+} and a new absorption band was observed at 449 nm with lesser intensity than Al^{3+}. In all these cases the color of the solution turned light yellow from colorless (see ESI;† Fig. 2). The alkali, alkaline and Cd^{2+}, Hg^{2+} or Pb^{2+} were not able to produce either spectral or visible color change (see ESI;† Fig. 2) upon their respective additions to the DMSO solution of receptor **1**. Thus the colorimetric detection of Al^{3+} in DMSO solution of receptor **1** lacked selectivity.

The binding stoichiometry between Al^{3+} and receptor **1** was confirmed through Job's plot (see ESI;† Fig. 3) which clearly showed a 1 : 1 stoichiometry between guest (Al^{3+}) and host (receptor **1**). The 1 : 1 stoichiometry for host–guest interaction was further supplemented by ESI-MS of receptor **1**-Al^{3+} complex as its chloride salt with receptor **1** (see ESI;† Fig. 4) showing a peak

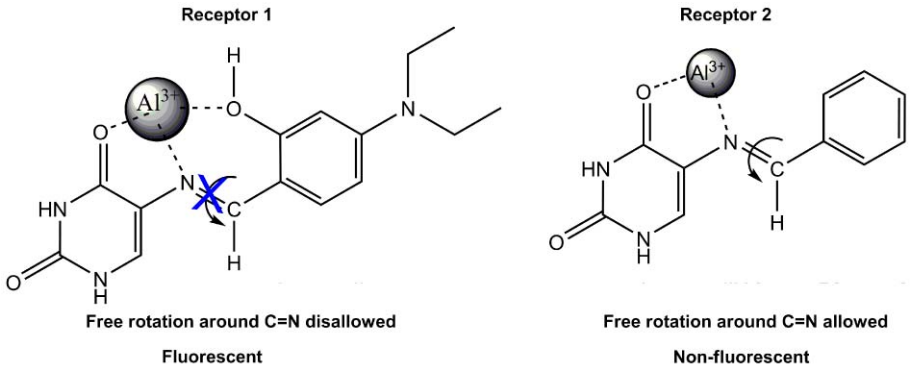


Fig. 3 (a) Proposed binding mode for interaction of Al^{3+} with receptor 1 (b) Non-fluorescent nature of receptor 2 even after binding with Al^{3+}.

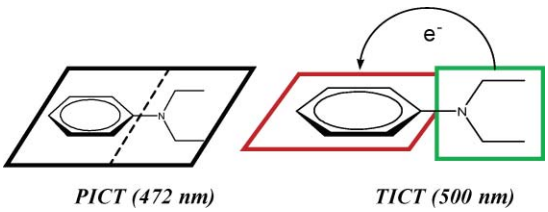


Fig. 4 Schematic representation of the formation of PICT (planer intramolecular charge transfer) and TICT (twisted intramolecular charge transfer) states of receptor 1.

at *m/z* 435.4 (Calc. for $C_{15}H_{18}N_4O_3AlCl_3 = 435.67$) corresponding to the 1 : 1 complex. The same mass spectrum showed a relatively more intense peak at 453.6 (Calc. for $C_{15}H_{18}N_4O_3AlCl_3{\cdot}H_2O$ = 453.68) which may be due to monohydrated form of the receptor 1-Al^{3+} complex. The binding constant for the complex between receptor **1** and Al^{3+} was determined by the non-linear fitting of the corresponding UV-visible titration data (see ESI;† Fig. 5) in 1 : 1 binding equation[20] as $(3.02 \pm 0.18)\times10^5$ M^{-1} with satisfactory correlation coefficient value ($R = 0.9983$).

Fluorescence studies

Since receptor **1** lacked the specificity towards Al^{3+} in colorimetric measurement hence the fluorescence emission was further investigated to test the specificity of receptor **1** towards Al^{3+} through excitation at 449 nm (Fig. 2). The receptor **1** itself was not fluorescent but it became fluorescent when 1 equivalent of Al^{3+} as its chloride salt was added to 0.5 μM DMSO solution of receptor **1** (Fig. 2).

In order to have an idea about the binding characteristics of the receptor **1** towards Al^{3+} the fluorescent titrations (Fig. 2) were carried out in 0.5 μM DMSO as well as in aqueous medium by the concomitant addition of Al^{3+}. The absence of any noticeable emission in receptor **1** itself on excitation at 449 nm may be attributed to the *cis-trans* isomerization of the receptor **1** across imine (C═N) bond.[15]

The addition of Al^{3+} (1 equiv.) elicits a drastic increase in the emission intensity of receptor **1** in the form of dual emission bands at 472 nm and 500 nm in DMSO (Fig. 2). The binding of Al^{3+} with the receptor **1** seems to be responsible for the fluorescent emission of the same. The Al^{3+} binding with receptor **1** may lead to the inhibition of its *cis-trans* interconversion (Fig. 3a) and making it fluorescent active according to recently reported *Wang et.al.*, mechanism.[15a] At the same time an obviously blue–green emission (see Graphical abstract) of receptor **1** solution upon addition of Al^{3+} can also be easily observed by the naked eye.

Our above mechanistic proposal was further supported by the non-fluorescent and fluorescent behaviours of the control compounds **2** and **3** respectively in the presence of Al^{3+}. The only structural difference between them is of phenolic –OH. Due to absence of phenolic –OH in compound **2** it is not able to have three way coordination with Al^{3+} (Fig. 3b) on the similar line of receptor **1** (Fig. 3a) hence the free rotation around C═N is not expected to

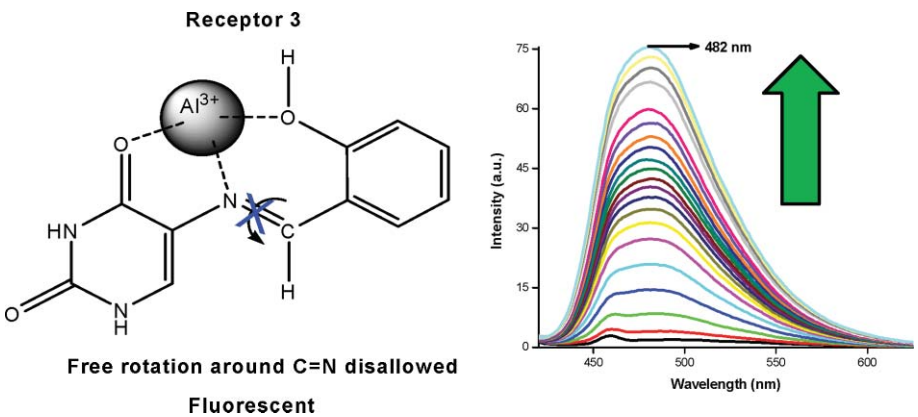


Fig. 5 (a) Proposed binding mode for interaction of Al^{3+} with receptor 3 (b) Fluorescence titration curve of 0.5 μM DMSO solution of receptor 3 upon concomitant additions of Al^{3+} ion (0–3 equivalents).

be quenched in this case which was observed in its non-fluorescent nature. On the other hand the receptor **3** possesses phenolic –OH hence it is able to have the three way coordination with Al^{3+} (Fig. 5a) on the similar pattern of receptor **1**. Hence the free rotation around C=N is expected to be quenched here also and this was reflected in the form of its fluorescent behaviour. A number of research papers in the recent past describing the specific detection of metal ions of various types through Schiff base receptors have resorted on the above C=N isomerization mechanism.[15] In all these papers the three way coordination of the concerned metal ion with corresponding receptors has been a common feature for the locking of the receptors into their *trans* form and hence making them able to fluoresce.

Furthermore, the presence of dual fluorescence (at 472 and 500 nm) in DMSO solution of receptor **1** with Al^{3+} may be a consequence of presence of the normal planar intramolecular charge transfer (PICT) state due to quenching of imine isomerization and twisted intramolecular charge transfer (TICT) state due to presence of *N*,*N*-diethylamino group (**DEA**) respectively. In the excited state, the donor part (**DEA** group) of the initially planar molecule rotates around the amino-phenyl bond which may be accompanied by the development of a charge separation between donor and acceptor moieties (Fig. 4). Here it is worth to mention that in the present study even in the presence of quenching of imine (C=N) isomerization signalling mechanism the TICT process is observable in the system while in the previous reports[15a,b] the TICT process was inhibited.

To further support our above explanation of dual fluorescence of receptor **1** in DMSO, we synthesized another controlled compound as receptor **3** (Fig. 5a) where *N*,*N*-diethylamino group (**DEA**) was absent. Our strategy really worked when we observed only one emission band at 482 nm (Fig. 5b) upon binding of receptor **3** with Al^{3+}.

The absorption spectra of receptor **3**-Al^{3+} complex absorbed at 400 nm (see ESI;† Fig. 6). When 0.5 μM DMSO solution of receptor **3** having one equivalent of Al^{3+} was excited at 400 nm a single emission band at 482 nm was observed (Fig. 5b). Thus the receptor **3** did not show the dual fluorescence phenomena as it was observed with receptor **1** and this proved our above explanation regarding the dual emission of receptor **1** in its DMSO solution with Al^{3+}.

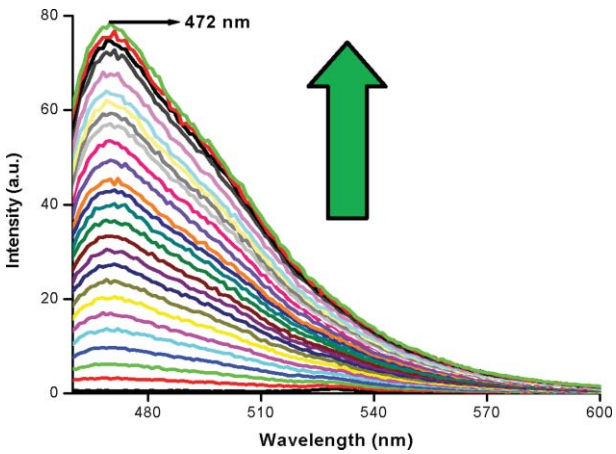


Fig. 6 Fluorescence titration curve of 0.5 μ M aqueous solution of receptor **1** in upon concomitant additions of Al^{3+} ion (0–18 equivalents).

Table 1 Linear response of receptors and value of detection limit with R^2

Receptor	Linear Range/M	Detection Limit/M	R^2
1 (*in DMSO*)	1.75×10^{-9} to 3.30×10^{-8}	1.62×10^{-10}	0.99948
1 (*in Water*)	8.00×10^{-7} to 2.80×10^{-6}	4.03×10^{-9}	0.99966
3 (*in DMSO*)	1.00×10^{-8} to 1.00×10^{-7}	2.70×10^{-9}	0.99963

The detection limit was calculated (see ESI;† Fig. 7) using fluorescence titration data according to the IUPAC definition.[21] The corresponding values of detection limits for the respective receptors have been given in Table 1. A perusal of the same clearly established an edge of receptor **1** over **3** in terms of detection limit. Moreover receptor **1** is certainly more effective in DMSO as compared to the aqueous medium. At the same time receptor **1** has also an edge over the previously reported fluorescent probes[4–12,14,22] for the Al^{3+} in terms of its detection limit.

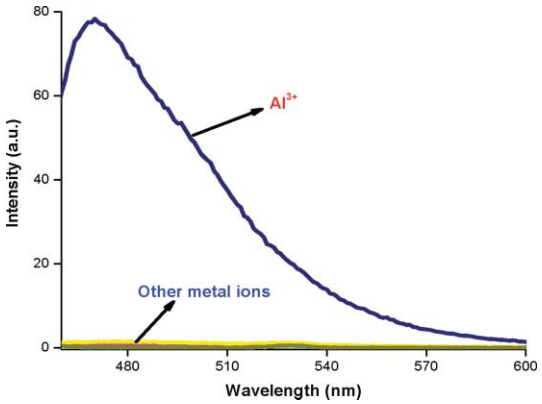


Fig. 7 Fluorescence spectra (excitation at 449 nm) of receptor 1 (0.2 μM) in aqueous solution in the presence of 1 equivalent of Al^{3+}, Na^{+}, K^{+}, Mg^{2+} Ca^{2+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+}.

Moreover, when the fluorescence titration of receptor **1** was performed in aqueous medium (0.5 μM) with concomitant additions of Al^{3+} only one emission band at 472 nm (PICT) while the another band at 500 nm (TICT) was not observed (Fig. 6). The non-occurrence of TICT band in aqueous solution[23] may be attributed to extremely high polarity of water and its involvement in hydrogen bonding with N-atom of **DEA** group of the receptor **1**. The twisting of **DEA** group along amino-phenyl bond is thus inhibited due to involvement of N atom in hydrogen bonding interaction with water through its lone pair. Thus the fluorescent detection of Al^{3+} by the receptor **1** is possible in aqueous medium also however the detection limit calculated for Al^{3+} in water with receptor **1** was of the order of 10^{-9} M (Table 1).

Competition experiment of receptor 1 towards Al^{3+}

In order to establish the selectivity of the receptor **1** towards Al^{3+} we performed the competition experiment by adding one equivalent each of Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+} and Al^{3+} in 0.2 μM aqueous solution of the receptor **1** separately. Fluorescence spectra were obtained in each case by exciting receptor **1** at 449 nm. As shown in Fig. 7, receptor **1** exhibited a selective fluorescence enhancement only with Al^{3+} with emission band at 472 nm.

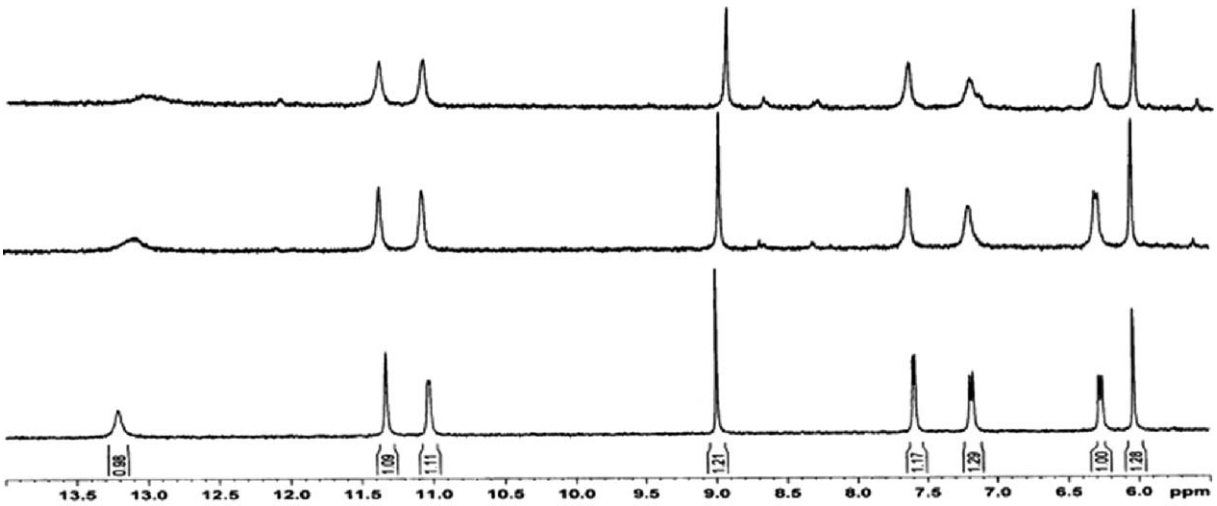


Fig. 8 Partial ^{1}H NMR titration experiment of receptor 1 with Al^{3+} ion; from bottom to top: receptor 1; 1+ 1 equiv. Al^{3+}; 1+2 equiv. of Al^{3+}.

In contrast, other metal ions did not induce any significant fluorescence enhancement of receptor **1**. This interesting feature reveals that **1** can serve as a selective fluorescent chemosensor for Al^{3+}.

In another set of competition experiment the mixture of one equivalent of receptor **1** and Al^{3+} in aqueous solution was added to the solutions of above metal ions separately having 1 equivalent of each ions. This time our observation was a bit different. The presence of either Mn^{2+} or Cu^{2+} inhibited the fluorescence emission of the receptor **1** even in the presence of Al^{3+}.

^{1}H NMR studies

In order to further support the above UV-visible and fluorescent studies for the sensing of Al^{3+} by the receptor **1** the ^{1}H NMR titrations were performed by the concomitant addition of Al^{3+} as its chloride salt to the 1×10^{-3} M DMSO-d_6 solution of the receptor **1**. As it can be seen in Fig. 8 that the concomitant additions of Al^{3+} to the receptor **1** induced significant changes in its ^{1}H NMR spectral pattern. Although the extent of the chemical shifts in various proton absorptions of the receptor 1 on the concomitant addition of Al^{3+} are small ones (see ESI;† Table 1) but they are well within the range observed earlier by us[19] and other workers[11,24] for the similar type of studies.

The –OH proton became broad and imine C–H peak move towards upfield region. Furthermore $-N_1H$ as well as $-N_3H$ were shifted marginally downfield supporting the involvement of carbonyl group (C═O) of uracil, imine nitrogen (–CH═N–) as well as phenolic oxygen (–OH) towards binding of Al^{3+} (Fig. 3a).

Conclusions

We have demonstrated successfully a pyrimidine based fluorescent probe for the detection of Al^{3+} with a high sensitivity in DMSO as well as in aqueous media. Present fluorescent probe has an edge over all the previously reported probes for the same purpose in terms of further lower detection limit for Al^{3+} as well as in terms of mechanistic aspect discussed above. Hence present study opens up the new possibility of highly sensitive chemosensors for cations based on pyrimidine bases.

Acknowledgements

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