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Short communication

Al^{3+} selective an efficient colorimetric receptor derived from 5-aminouracil

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ABSTRACT

An interference-free naked-eye recognition of Al^{3+} at its micromolar level has been done in 5% aqueous DMSO solution employing a Schiff base 5-[(2-hydroxy-5-nitro-benzylidene)-amino]-1*H*-pyrimidine-2,4-dione (receptor 1) which is an intramolecular charge transfer (ICT) probe. The pyrimidine and nitrophenyl groups serve as electron rich (donor) and deficient (acceptor) pockets in receptor 1 exhibiting a broad ICT band at 434 nm (olive green). The concomitant additions of Al^{3+} as its chloride salt to the 5×10^{-5} M aqueous DMSO solution of the receptor 1 lead hypsochromic shifting of its ICT band to 395 nm (colorless). The same ICT band undergoes a marginal bathochromic shifting (6 nm) along with a hyperchromic shift on separate additions of a basic anion like F^-, CH_3COO^- and $H_2PO_4^-$ to the receptor 1 and faced almost similar fate on concomitant additions of Al^{3+} as mentioned above.

1. Introduction

The selective recognition of cations at their low to ultra low concentrations through purposely designed naked-eye receptors are gaining momentum for last couple of decades [1,2]. A receptor involving simple synthetic protocol makes naked-eye recognition more demanding and eye catching [3,4]. Present communication is an outcome of our constant effort towards design, synthesis and evaluation of naked-eye receptors for recognition of a few biologically and environmentally relevant ions like Cu^{II}, Zn^{II}, Cd^{II} and Hg^{II} [5–7].

Al^{3+} is one of the notorious ion and its negative impact on human beings in the form of dementia, myopathy, anemia, Alzheimer's disease, bone and joint diseases have been documented in the literature [8,9]. Spectrophotometric methods using a variety of reagents including Schiff base [10–12], azo dyes [13,14] and some chromogenic reagents like aluminon, xylenol orange methylthymol blue, Erichrome cyanine R, 8-hydroxyquinoline, etc. have been well documented in the literature in the past several decades [15]. However, all these methods have substantial disadvantages, like aluminon requires heat for proper color development [16] while due to extremely low selectivity of 8-hydroxyquinoline it is generally inadvisable [17]. The most serious limitation of these reagents is cationic and anionic interferences [15]. Among the cations the most interfering ones are Mg^{2+}, Ca^{2+}, Cr^{3+}, and Fe^{3+} [15,18–20] while F^- is the main interfering anion [21].

Present study reports an interference-free naked-eye determination of Al^{3+} by the receptor 1 as the same was detected successfully in a competition experiment involving a series of cations including the most interfering ones *viz.*, Mg^{2+}, Ca^{2+}, Cr^{3+} and Fe^{3+}. At the same time a range of basic anions like F^-, CH_3COO^- and $H_2PO_4^-$ were also tested for their possible interferences with no result. No heating is required for the naked-eye detection of Al^{3+} with our receptor 1 as it is required in one of the most commonly used reagent for Al^{3+}, i.e., aluminon. Thus, present receptor has a clear superiority over all the receptors for Al^{3+} reported hitherto in terms of no obvious interferences by either type of ions among a wide range of ions. Hence, receptor 1 is an efficient and robust one.

Pyrimidine derivatives are components of the biologically important nucleic acid. Uracils are pyrimidine derivatives, and have been used as antitumor, antibacterial, and antiviral drugs [22]. However, it has not been used as a constituent of any molecular chemosensors hitherto. To the best of our knowledge, this is for the first time that any uracil derivative has been exploited as the naked-eye receptor for any ion. For the synthesis of receptor 1 the literature procedure was adopted [23] (see ESI).

2. Results and discussion

The energy-minimized structure of receptor 1 and corresponding HOMO–LUMO orbitals has been shown in Figs. 1 and 2. A perusal of HOMO and LUMO suggested that pyrimidine is electron rich while the nitrophenyl is electron deficient moiety making receptor 1 as a typical example of intramolecular charge transfer (ICT) probe [6,24,25].

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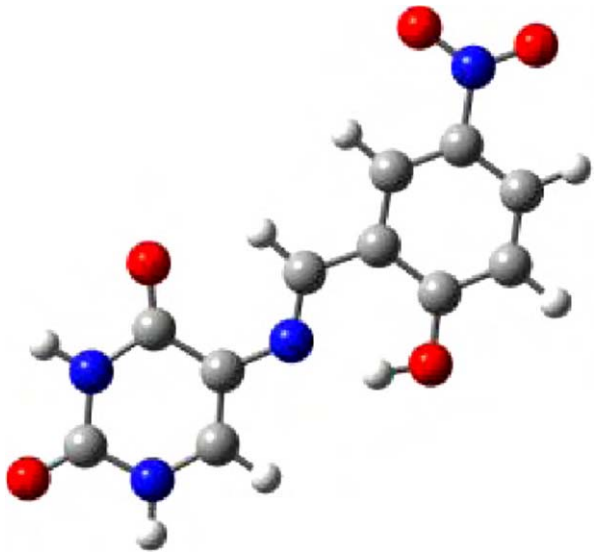

Fig. 1. Energy-minimized structure of receptor 1 calculated by B3LYP method with the 6-31G** basis set.

2.1. UV–visible studies

The naked-eye recognition of Al^{3+} with the receptor 1 was studied in following two ways:

(1) By direct concomitant additions of varying equivalents of Al^{3+} as its chloride salt to the 5×10^{-5} M aqueous DMSO solution and (2) by addition of 1 equivalent of various uninegative ions (F^-, CH_3COO^-, $H_2PO_4^-$, etc.) as their tetrabutylammonium salts separately to the 5×10^{-5} M aqueous DMSO solution of receptor 1 followed by concomitant additions of Al^{3+}.

The 5% aqueous DMSO solution (5×10^{-5} M) of receptor 1 was of olive green color (Fig. 3a) and showed an absorption band in visible region at 434 nm (Fig. 4a) due to intramolecular charge transfer (ICT) from pyrimidine to nitrophenyl. The other two absorption bands for the same were in UV region at 312 and 352 nm. Direct concomitant additions of Al^{3+} to the receptor 1 resulted into emergence of a new band at 327 nm and a broad band at 395 nm (Fig. 4a) accompanied by vanishing of absorption bands at 312, 352 and 434 nm. At this stage, the solution of receptor 1 became colorless (Fig. 3a). The formation of an isosbestic point at 375 nm (Fig. 4b) indicated the chemical interaction between receptor 1 and Al^{3+}. The binding stoichiometry between Al^{3+} and receptor 1 was confirmed through Job's plot (Fig. 4c) which clearly showed a 1:1 stoichiometry between guest (Al^{3+}) and host (receptor 1).

The blue shift in the ICT band of receptor 1 is a consequence of the involvement of donor atoms situated on its pyrimidine moiety (donor) in complexation with Al^{3+} hence restricting the flow of electron density from pyrimidine to nitrophenyl (acceptor). Since Al^{3+} is a strong Lewis acid, hence deprotonation of phenolic moiety of the receptor 1 is most likely. Hence, at this juncture following chemical structure image of the species between Al^{3+} and receptor 1 (Fig. 5a) is expected. The same structure was found to be of lowest energy through density functional theory calculations by B3LYP method using 6-31G** as basis set (Fig. 5b).

On the other hand, in yet another method we added 1 equivalent of uninegative ions such as F^-, CH_3COO^- and $H_2PO_4^-$ as their tetrabutylammonium salts separately to the 5% aqueous DMSO solution (5×10^{-5} M) of receptor 1 leading to minor bathochromic shifting of 6 nm along with a hyperchromic shift in ICT band of the receptor 1 (Fig. 6a). At this stage, the color of solution became dark yellow from olive green (Fig. 3a) with an isosbestic point at 368 nm (Fig. 6a).

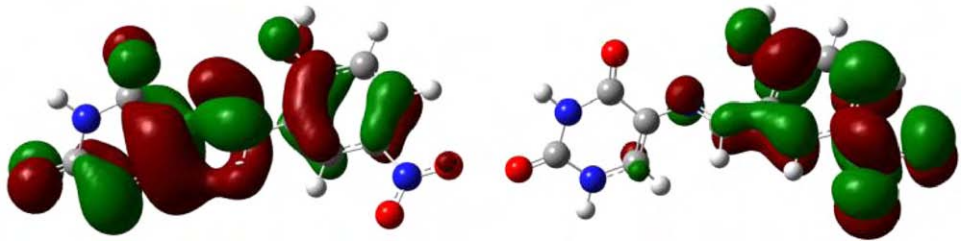

Fig. 2. HOMO and LUMO orbital of receptor 1 calculated by B3LYP method with the 6-31G** basis set.

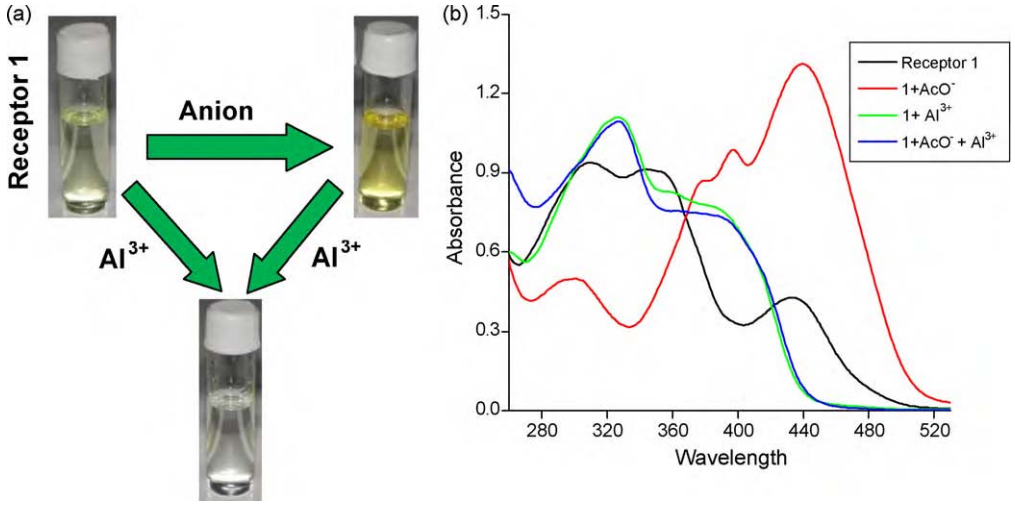

Fig. 3. (a) Color changes of receptor upon additions of Al^{3+} and AcO^- ion. (b) Individual spectral changes of receptor 1 upon addition of Al^{3+} and AcO^-.

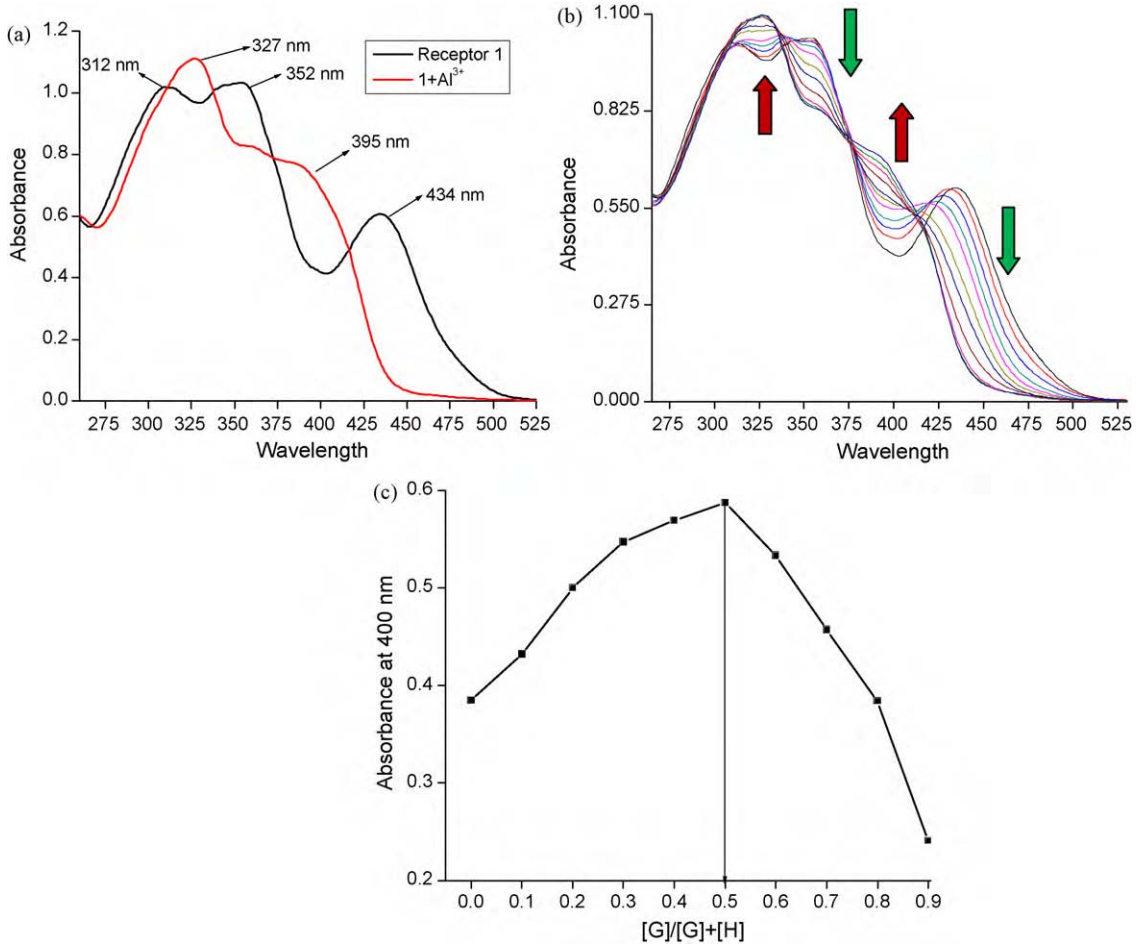

Fig. 4. (a) Changes in UV–visible spectra of receptor 1 upon addition of 1 equivalent of Al^{3+}. (b) UV–visible spectral pattern of receptor 1 upon concomitant additions of Al^{3+}. (c) Job's plot of Al^{3+} with receptor 1 showing 1:1 stoichiometry.

On concomitant additions of Al^{3+} as its chloride salt to the above solution of receptor 1 having 1 equivalent of respective anion, an almost similar UV–visible absorption pattern (Figs. 3b and 6b) and color changes were obtained (Fig. 3a) as they were obtained on the direct concomitant additions of Al^{3+} to the solution of the receptor 1.

To further evaluate the practical applicability of receptor 1 as an Al^{3+} selective colorimetric probe, a competition experiment was performed. The 5×10^{-5} M aqueous DMSO solution of receptor 1 having 1 equivalent each of Mg^{2+}, Ca^{2+}, Cr^{3+}, Fe^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+} as their chloride salts was treated with 1 equivalent of Al^{3+} as its chloride salt. The resulting naked eye and spectral changes have been given in Fig. 7a and b. A look of the same proved categorically that there is no obvious interference either by any chosen cation. Moreover, the vanishing of dark yellow color of the receptor 1 in the presence of a few most interfering anions (such as F^-, CH_3COO^- and $H_2PO_4^-$) on the addition of Al^{3+} (Fig. 3a) proved no obvious interference by anions also. In the DMSO-H_2O (95:5, v/v), the detection limit of Al^{3+} ion is 25–50 μM level with receptor concentration 5×10^{-5} M. Between these concentration limit of Al^{3+} ion the visible color change is observable through naked-eye.

2.2. ^1H NMR titration studies

To further look into the nature of host–guest interactions, ^1H NMR titration experiments (see ESI) were performed by adding

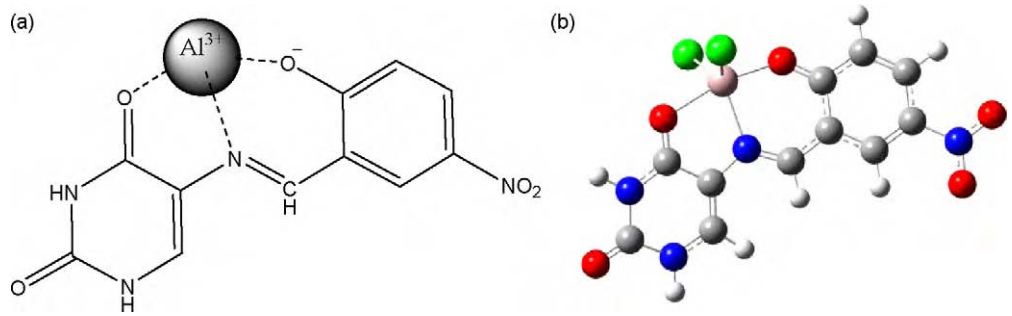

Fig. 5. (a) Possible mode of interaction of Al^{3+} with receptor 1. (b) Energy-minimized structure of receptor 1 + Al^{3+} complex calculated by B3LYP method with the 6-31G** basis set.

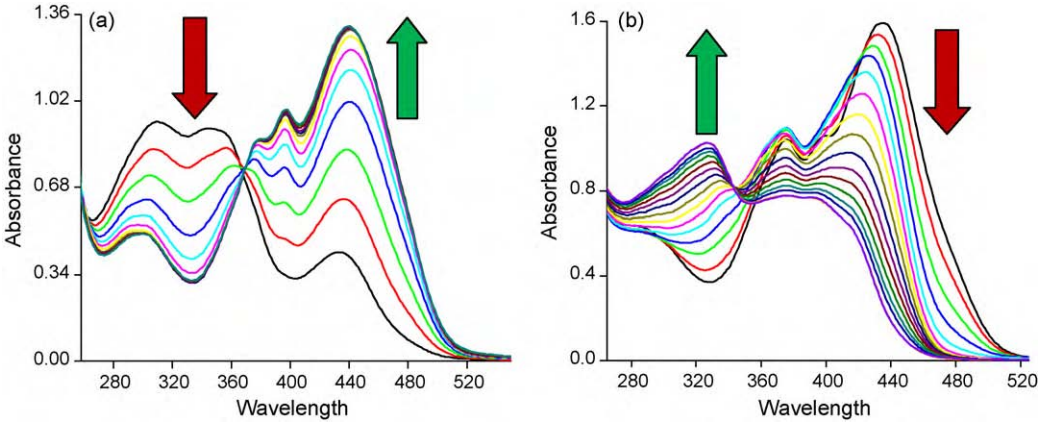

Fig. 6. (a) UV–visible spectral pattern of receptor 1 upon concomitant additions of anion. (b) UV–visible spectral pattern of receptor 1 upon concomitant additions of Al^{3+} to the receptor-anion solution.

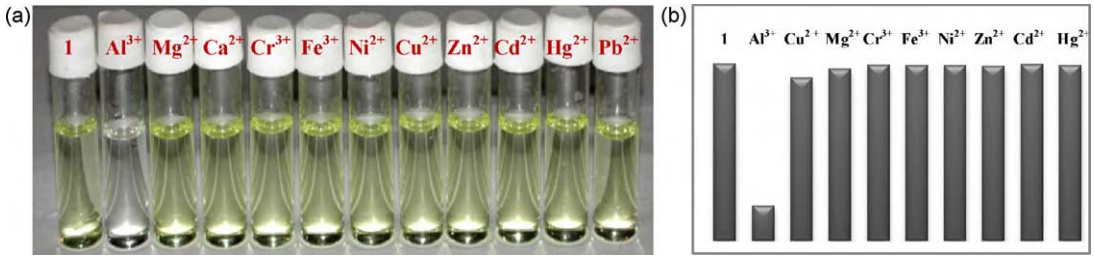

Fig. 7. (a) Color changes of receptor 1 with various metal ions (1 equivalent each). (b) Effect of various metal ions on the 434 nm band of receptor 1; from left to right: 1, Al^{3+}, Cu^{2+}, Mg^{2+}, Cr^{3+}, Fe^{3+}, Ni^{2+}, Zn^{2+}, Cd^{2+} and Hg^{2+}.

Table 1
Changes in chemical shifts (δ ppm) of receptor 1 during ^{1}H NMR titration experiment upon concomitant addition of $AlCl_3$.

Equiv.	–OH	$-N_3H$	$-N_1H$	–CH=N–	$-C_6H$	Ar–H_a	Ar–H_b	Ar–H_c
0.0	13.840	11.513	11.388	9.596	7.976	8.531	8.216	7.096
0.1	13.840	11.515	11.408	9.595	7.974	8.532	8.216	7.100
0.5	13.857	11.518	11.420	9.592	7.963	8.533	8.216	7.106
1.0	–	11.513	11.396	9.586	7.956	8.531	8.217	7.107
2.0	–	11.518	11.410	9.578	7.950	–	–	7.108

varying equivalents of Al^{3+} (0.1–2 equivalents) as its chloride salt to the 5×10^{-3} M DMSO-d_6 solution of receptor 1. The chemical shifts in δ ppm for various protons have been given in Table 1.

A perusal of Table 1 clearly proved the deprotonation of phenolic moiety along with downfield shifting of $-N_1H$, $-N_3H$ and H_c protons (Fig. 8). The rest of the protons experienced upfield shifting. The downfield shifting of $-N_1H$ and $-N_3H$ may be understood in terms of chelate formation of Al^{3+} with aldimine N atom and one of the carbonyl of the pyrimidine ring (Fig. 8). Moreover, the deprotonation of the phenolic proton facilitated its coordination with the Al^{3+} leading to fulfilment of its electronic and stereochemical requirement. Hence, ^{1}H NMR titration nicely supported our speculation regarding the chemical structure image of the species formed by the interaction of Al^{3+} with the receptor 1 (Fig. 5a). Although the extent of the chemical shifts in various proton absorptions of the receptor 1 on the concomitant addition of Al^{3+} is very small ones but they are well within the range observed earlier by us [5] and other workers [26–28].

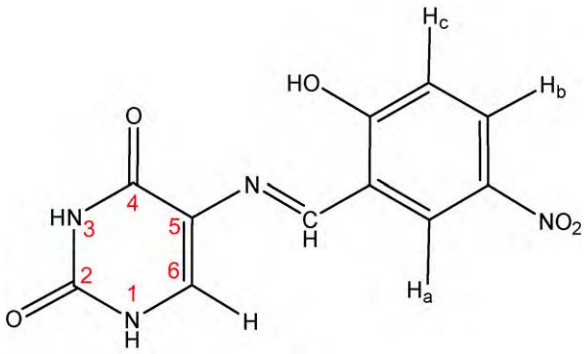

Fig. 8. Partial labeling of receptor 1.

3. Conclusion

We have demonstrated a pyrimidine based colorimetric receptor for Al^{3+} in aqueous DMSO. The recognition of Al^{3+} gave an obvious color change from olive green to colorless. Moreover, the competition experiments showed the interferences from other ions were minimal. As the synthetic protocol of receptor 1 is quite simple one but its selectivity for Al^{3+} is very high. Hence, the present receptor is a good tool based on optical changes for the detection of Al^{3+} in aqueous DMSO. Although the very high percentage of DMSO (95%) in the reaction medium will be restricting its potential use for biological samples. In spite of that receptor 1 has a high potential for its practical application towards a large number of industrial effluents having Al^{3+} as one of the component. The further efforts for making

receptor 1 soluble in water are still undergoing in our laboratory.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2010.05.003.

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