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Selective ''naked eye'' detection of Al(III) and PPi in aqueous media on a rhodamine–isatin hybrid moiety†

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A highly selective fluorescence probe, RIH (rhodamine–isatin hybrid) for Al^{3+} has been designed and synthesized. This new dual signal (colorimetric and fluorogenic ''*off–on*'' type) chemosensing ensemble based on the complex between RIH and Al^{3+} has also been effective to selectively discriminate PPi from other anions in aqueous solution at physiological pH.

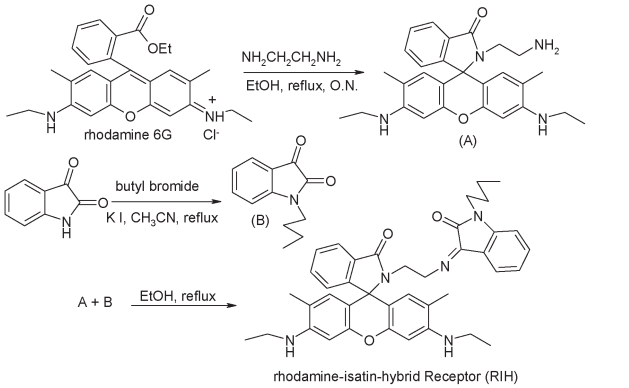
Aluminum is the third most abundant metal (after oxygen and silicon) in the earth's crust, accounting for approximately 8% of its mass. The leaching of aluminum from the soil by acid rain increases the free Al^{3+} in the environment and surface water, which is deadly to growing plants.[1] Compounds of aluminium are widely dispersed and used in the environment around us in modern society: in water treatment, in food additives, in medicines, and of course, in the production of light alloys *etc*. It is well-known that aluminium is not an essential element for biological life and its toxicity is a concern for human health. Recent advances have shed light on the biological roles of aluminium, particularly on its functions related to neurobiology. Disorders of aluminium homeostasis are implicated in a number of diseases, such as Parkinson's disease (PD),[2] Alzheimer's disease (AD),[3] and dialysis encephalopathy.[4] Therefore, detection of Al^{3+} is crucial in controlling its concentration levels in the biosphere and its direct impact on human health. Several fluorescent probes such as morin[5] and 8-hydroxyquinoline[6] derivatives have been synthesized and used for this purpose.

On the other hand, in recent years considerable efforts have been made for the development of selective and sensitive chemosensors that can detect biologically important anions using color and fluorescence responses.[7] In particular, anions such as pyrophosphate ($P_2O_7^{4-}$, PPi) which plays vital roles in several bioenergetic and metabolic processes and also in several biochemical reactions such as the hydrolysis of adenosinetriphosphate (ATP), DNA polymerization, and other metabolic processes, are significant targets that must be conventionally monitored.[8,9]

So far, only few fluorescent aluminum[10] sensors and water soluble PPi sensors[11] have been reported. Yoon and Lee *et al.* in 2010 showed a strong attraction of Al^{3+} towards PPi in aqueous media.[12] Applying this idea, we can selectively detect Al^{3+} and PPi in a single molecule and this reversible type of phenomenon can beautifully mimic logic operations (INHIBIT gate). Such basic logic gates, programmed in a single molecular switch, have possible implications in the development of electronic and photonic devices and may be further explored as a suitable analytical tool[13] to work as a tunable electronic device.

Hence, considering the above facts, we designed and synthesized a new rhodamine–isatin based sensor for the selective detection of Al^{3+} and used these receptor–Al^{3+} ensembles to detect PPi in aqueous media. The changes in fluorescence signals upon two chemical inputs and a combination of two inputs (of Al^{3+}, PPi) mimic the logic operation such as an INHIBIT logic gate (integrated by combining a NOT, a YES, and an AND gate).

The synthesis of RIH is outlined in Scheme 1. Intermediates (A)[14] and (B)[15] were synthesized according to the published procedure. The structure of the receptor was confirmed by ^1H NMR, ^{13}C NMR and ESI MS spectra (see ESI†).



Scheme 1 Synthetic scheme of the receptor.

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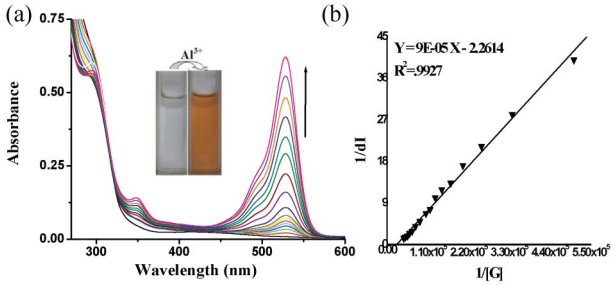

Fig. 1 (a) UV-vis absorption titration spectra of RIH ($c = 2 \times 10^{-5}$ M) in the presence of Al^{3+} ($c = 2 \times 10^{-4}$ M) in MeOH–H_2O (7 : 3, v/v, 25 °C, at pH = 7.1, 20 mM HEPES buffer); (b) Benesi–Hildebrand plot from the UV-vis titration spectral data of RIH with Al^{3+}.

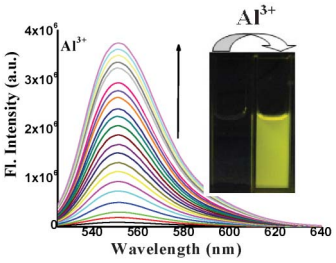

Fig. 2 (a) Fluorescence titration spectra of RIH ($c = 2 \times 10^{-5}$ M) with Al^{3+} ($c = 2 \times 10^{-4}$ M) in MeOH–H_2O (7 : 3, v/v, 25 °C, at pH = 7.1, 20 mM HEPES buffer). The naked eye fluorescence change of RIH with addition of Al^{3+} (inset).

From the observed change of fluorescence intensity at 552 nm with pH, we found the optimal condition (*i.e.* pH = 7.1) (near neutral pH) under which the receptor can work as a metal-sensing probe (Fig. S1, ESI†). The solution of the RIH in HEPES (20 mM, CH_3OH–H_2O, 7 : 3 v/v, pH 7.1) buffer solution was also nearly colorless and did not exhibit apparent absorption above 500 nm, due to the formation of the stable spirolactam ring. Addition of Al^{3+} to a solution of RIH led to an obvious absorption enhancement at 528 nm, along with an obvious color change from colorless to reddish orange (Fig. 1). Such absorption change in the UV-vis region may be ascribed to the newly formed complex between the RIH and the metal ion *i.e.* Al^{3+}.

Upon increasing the concentration of Al^{3+}, the absorbance of RIH is also increased. A Job's plot showed a 1 : 1 stoichiometry between RIH and Al^{3+} (Fig. S3, ESI†).[16] In addition, Ga^{3+} also shows an increased absorption band at 528 nm, but the intensity is less than Al^{3+} which indicates that the RIH is highly selective and sensitive for Al^{3+} as shown in a bar graph (Fig. S2, ESI†). Probably, the high positive charge density of Ga^{3+} is responsible for this interference.

Emission spectra of RIH (40 mM) in the presence of various metal ions (Ag^+, Cd^{2+}, Co^{2+}, Hg^{2+}, Cu^{2+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Fe^{3+}, Cr^{3+}, Al^{3+}, Zn^{2+}, Na^+, K^+) were measured by exciting the fluorophore at 510 nm. RIH showed only a very weak fluorescence ($\Phi fr = 0.005$) in the absence of metal ions. The addition of Al^{3+} resulted in a remarkably enhanced fluorescence intensity ($\Phi fr = 0.27$) with a red shift of the fluorescence emission wavelength to 552 nm (5 nm) (Fig. 2). From the observed change of fluorescence intensity at 552 nm with pH, we found that near neutral pH, the receptor RIH could be used as a probe for Al^{3+} (Fig. S1, ESI†).

This result indicates that the spirolactam ring (non-fluorescent) of the rhodamine based receptor is opened by complexation with Al^{3+}. The increased emission intensity was due to the complexation of Al^{3+} and RIH. Due to the oxophilic nature and high charge density of Al^{3+}, strong binding happens with RIH and opens the spirolactum ring of rhodamine, followed by a large CHEF effect.[17] Interestingly, RIH showed a more sensitive response to the low concentration of Al^{3+} in 20 mM HEPES buffer solution at pH 7.1. The association constant was estimated to be 2.51×10^4 M^{-1} (error < 10%) by UV-vis titration (Fig. 1b) and 8×10^4 M^{-1} by the fluorescence titration method (Fig. S4, ESI†) for the sensor RIH with Al^{3+} using the Benesi–Hildebrand equation.[18] The calculated detection limit is 0.86 μM based on $K \times Sb1/S$,[19] where Sb1 is the standard deviation of blank measurements and S is the slope of the calibration curve (Fig. S4, ESI†).

As discussed in the Introduction, phosphate compounds form stable complexes with Al^{3+} in aqueous solution at physiological pH.[20] Thus, it is possible that these compounds will remove Al^{3+} from the complex between the sensor and Al^{3+} and the opened spirolactam ring will then close. If the ring-closure reaction occurs in the presence of the phosphate compounds, the complex (RIH–Al^{3+}) can be used as a new chemosensing ensemble. To test this possibility, we prepared ensembles based on the complex (RIH–Al^{3+}) by mixing RIH (40 μM) with Al^{3+} (400 μM) and then measured the fluorescence and absorbance spectra of the solution in the presence of various anions.

The reddish orange color of the RIH–Al^{3+} vanished upon the addition of an increasing concentration of PPi (Fig. 3a). The absorbance at 528 nm decreased upon the addition of an increased concentration of PPi. The addition of 12 equiv. of PPi to RIH–Al^{3+} turned the original reddish orange colored solution into a colorless solution *i.e.* the UV-vis absorption changes were completely saturated, whereas the addition of the same amount of other anions to the solution did not affect the original reddish orange color. The decrease of reddish orange color of the solution containing the RIH–Al^{3+} complex strongly suggested that the ring-opened amide form of RIH–Al^{3+} was converted to the spirolactam form of RIH in the presence of PPi.

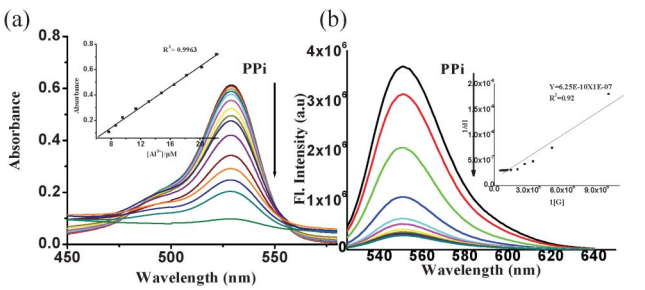

Fig. 3 (a) Absorbance spectra and (b) fluorescence emission spectra of ensemble (RIH–Al^{3+}, 400 μM) upon the addition of pyrophosphate in 20 mM HEPES buffer at pH 7.1 (λ_{ex} = 510).

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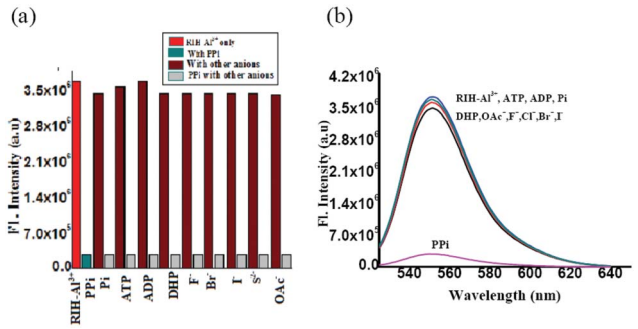

Fig. 4 (a) Fluorescence response of ensemble (RIH–Al^{3+},400 μM) in the presence of pyrophosphate (400 μM) and additional various anions (10 equiv.) in 20 mM HEPES buffer at pH = 7.1; (b) fluorescence emission spectra of RIH (40 μM) with Al^{3+} (400 μM) upon the addition of various anions (400 μM) in 20 mM HEPES buffer at pH = 7.1.

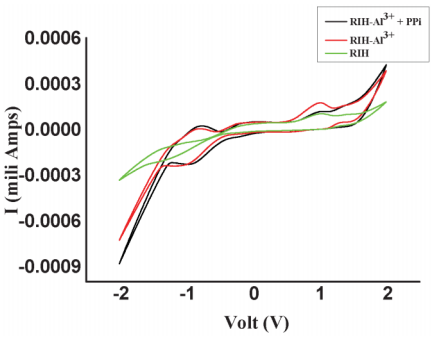

Fig. 6 Cyclic voltammetry of RIH, RIH + Al^{3+} and RIH–Al^{3+} + PPi.

The selectivity of the fluorescence response of RIH–Al^{3+} was verified in the presence of different anions such as Br^-, Cl^-, I^-, F^-, ADP, ATP, PPi, OAc^-, Pi, *etc.* (Fig. 4). Interestingly, only the addition of PPi instantly caused a sensitive fluorescence change as well as a colorimetric change. In all these cases, the reddish orange color and yellow fluorescence of RIH–Al^{3+} is retained without any change upon the addition of other anions. The fluorescence titration was conducted using the ensemble (RIH–Al^{3+}) upon addition of various anions in HEPES buffer solution at pH 7.1 (Fig. 3b).

An increased concentration of PPi resulted in decreased emission intensity. When we added 12 equivalents of PPi to the ensemble (RIH–Al^{3+}), it resulted in a complete decrease of the emission intensity. This process is reversible, *i.e.* the addition of Al^{3+} to this solution regenerated its reddish orange color and yellow fluorescence (Fig. 5). These processes could be repeated several times thereby making the probe recyclable. The probe was found to be able to detect PPi in micromolar concentration. The selectivity of the probe was checked by quantitatively recording the fluorescence intensity of the RIH–Al^{3+} complex in the presence of a 10 fold excess of different anions (Fig. 4 and 5). Thus, this ensemble was more selective for PPi in aqueous solution than the previously reported PPi sensors because most PPi sensors working in aqueous solution showed some response to Pi or ATP.[21]

From these plots, it is clear that all of the anions, except PPi, are practically insensitive to the fluorescence of the RIH–Al^{3+} complex. The sensitivity for PPi was calculated on the basis of the linear relationship between the emission intensity at 552 nm and the PPi concentration. The RIH–Al^{3+} has a detection limit of 2.19 μM for PPi. The equilibrium competition constant[12,22] was 165 M^{-1} on the basis of the fluorescence titration data (Fig. 3b) in HEPES buffer solution at pH 7.1. The data fit to a displacement model that provides an equilibrium competition constant (Fig. S5, ESI†).

To further look into the nature of the interaction between the RIH–Al^{3+} complex and PPi, ESI mass spectrometric experiments were carried out. When 1.2 equiv. of PPi was added to this complex, the peak at *m/z* 668.57 corresponding to $[RIH–Al^{3+}]^+$ disappeared and only the peak at *m/z* 642.58 corresponding to $[RIH + H]^+$ was observed. This suggests that the binding affinity of PPi towards Al^{3+} is much more than that of RIH towards Al^{3+} and the removal of Al^{3+} from the complex proceeds by the PPi induced ring-closure reaction (Fig. 7). The binding of Al^{3+} with RIH and RIH–Al^{3+} with PPi is further supported by cyclic voltammetry. On addition of Al^{3+} to a solution of RIH in MeOH, a reversible one electron oxidation[23] is observed and a clear evolution of an oxidation wave at $E_{1/2}$ = 1.01 V *vs.* $Hg/HgCl_2$ with 1 equiv. of added Al^{3+} probably corresponds to the oxidation of the NH group of the rhodamine moiety in the complex (Fig. S6, ESI†). Then, with addition of 1 equivalent of PPi, the complete disappearance of the oxidation wave strongly suggests it proceeds *via* the decomplexation process (Fig. 6).

In order to strengthen our conclusion based on the finding through UV-vis and fluorescence titration, we have performed ^1H NMR spectral studies by the addition of 1 equv. of Al^{3+} to RIH and 1 equiv. of PPi to the RIH–Al^{3+} ensemble (see ESI†). When we added Al^{3+} to RIH, the 'N–H' proton is shifted upfield (δ 4.808 ppm to 4.488 ppm), and returns to its old position (δ 4.488 ppm to 4.804 ppm) with the addition of PPi. The aromatic protons of RIH

Fig. 5 Naked eye color change of the ensemble (RIH–Al^{3+}, 40 μM) upon the addition of various anions (400 μM) in MeOH–H_2O (7 : 3, v/v, 25 °C) at pH 7.1 by using 20 mM HEPES buffer (colorless with PPi).

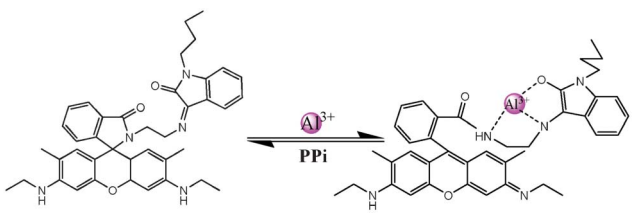

Fig. 7 Probable binding of Al(III) and PPi towards RIH.

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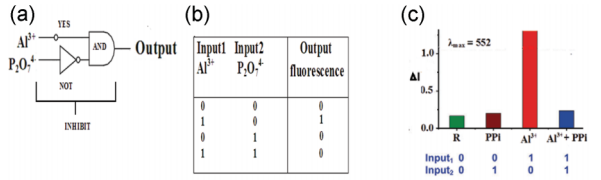

Scheme 2 (a) General representation of the symbol of an INHIBIT gate (formal combination of a NOT, YES and AND gate); (b) the corresponding truth table of this logic gate; (c) the output signals of this logic gate in the presence of different inputs.

also showed a reversible shift (upfield to downfield) with the addition of Al^{3+} and then PPi. From this study we concluded that RIH has a strong affinity towards the Al^{3+} ion and RIH–Al^{3+} behaves as a good ensemble for the selective recognition of PPi.

In this case, the behavior of RIH mimics the INHIBIT gate which can be integrated[24] by combining a NOT, a YES, and an AND gate (Scheme 2). In this logic gate, Al^{3+} and PPi are used as inputs. For the input, the presence of Al^{3+} and PPi are defined as a "1" state and the absence of the molecules define the "0" state. One of them *i.e.* Al^{3+} in this case, should lead to absorption and fluorescence in its occupied state, equivalent to a YES operation (input 1, Scheme 2). The interaction of the other input *i.e.* PPi in this case (input 2, Scheme 2) with its corresponding receptor should lead to absorption and fluorescence quenching, thereby implementing the necessary NOT gate. The receptor *i.e.* RIH (occupied or free) acts in parallel on the absorption and fluorescence output signal, which implements the required AND function. In the presence of both inputs, the quenching (by input 2) should override the absorption and fluorescence enhancement by input 1, in accordance with the truth table shown in Scheme 2.

In conclusion, a new rhodamine probe bearing an isatin moiety (RIH) has been synthesized for the selective detection of Al^{3+} in aqueous solution. The RIH–Al^{3+} complex was utilized as a fluorescence chemosensor for PPi. The "*off–on–off*" behavior of the RIH towards Al^{3+} and PPi is also mimicking the INHIBIT logic gate.

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