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Rhodamine-based molecular clips for highly selective recognition of Al³⁺ ions: synthesis, crystal structure and spectroscopic properties

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Abstract

A novel fluorescent chemosensor based on rhodamine derivative (**L**) was designed, synthesized, and used as selective Al³⁺ ion sensor. Upon addition of Al³⁺ to an aqueous-acetonitrile solution of **L**, the development of a strong fluorescence signal by chelation-enhanced fluorescence (CHEF) process was observed with an attractive glowing orange emission. This sensor was high selectivity towards Al³⁺ ions in presence of other competing metal ions. The fluorescence quantum yield of **L**-Al³⁺ ($\Phi_f = 0.30$) was found to be very high compared to the bare ligand. The limit of detection (LOD) of Al³⁺ ions was calculated to be 2×10^{-8} M according to fluorescence titration. The 1:1 binding stoichiometry of the metal complex was established by combined UV-vis, fluorescence and TOF-MS spectroscopy.

Introduction

The recognition and sensing of biologically and environmentally important species have emerged as a significant goal in the field of chemical sensors in recent years, since they allow nondestructive and prompt detection of the species (cations or anions) by a simple fluorescence

enhancement (turn-on) or quenching (turn-off) response.¹ Aluminum is the third most abundant metallic element in the earth's crust, which is found in waters and most biological tissues in its ionic form Al^{3+} . The amount of free Al^{3+} in the surface water is increased by leaching from soil due to acid rain. It is toxic to plants and kills fish in acidified water.² The World Health Organization (WHO) recommended the average daily human intake of Al^{3+} is around 3–10 mg and weekly tolerable dietary intake as 7 mg kg^{-1} body weight.³ The widespread use of aluminum around us in the modern society are in water treatment, food additives, medicines, of course the production of cooking utensils, aluminums foil etc. Al^{3+} toxicity causes microcytic hypochromic anemia, Al-related bone disease (ARBD), encephalopathy; neuronal disorder leading to dementia, myopathy, and also affects the absorption of iron in blood, causing anemia. In addition, the toxicity of aluminum causes damage to the central nervous system, is suspected to be involved in neurodegenerative diseases such as Alzheimer's and Parkinson's and is responsible for intoxication in hemodialysis patients.⁴ In the biosphere, the detection and estimation of Al^{3+} levels have significant importance on human health. Recently, the design and construction of chemosensors with high selectivity and sensitivity towards Al^{3+} have become the focus in numerous studies in the field of supramolecular chemistry. The poor coordination ability, strong hydration ability, and the lack of spectroscopic characteristics of Al^{3+} have hindered development of a suitable fluorescence sensor compared to other metal ions.⁵ Practically, Al^{3+} is a hard-acid; it is found that Al^{3+} prefers a coordination sphere containing N and O as hard-base donor sites.⁶ As a result, most of the reported Al^{3+} sensors contain mixed nitrogen and oxygen donor sites. So, the design and synthesis of highly sensitive and selective fluorescent chemosensors for Al^{3+} is still a great demand.

The rhodamine moiety has been used widely in the field of chemosensors, especially as a chemodosimeter, given its fluorescence OFF-ON behavior results from the unique structural architecture and properties. In general, spiro lactam form of rhodamine derivatives is found to be nonfluorescent, whereas its ring opened amide system gives rise to a strong fluorescence emission.⁷ Furthermore, the rhodamine fluorophore exhibits a longer wavelength emission (over 550 nm), often serving as a sensor for the analyte to avoid the influence of background fluorescence (below 500 nm).⁸ Rhodamine spiro lactam based chemosensors are attractive because of their excellent photophysical properties, such as long absorption and emission wavelengths elongated to visible region, high fluorescence quantum yield, and large absorption coefficient.⁹

Here, we report a novel rhodamine-based spiro lactam derivative (**L**) as a chemosensor for Al^{3+} ^{6,10} where the binding phenomena could be probed through binding induced changes in the electronic spectral pattern via chelation enhanced fluorescence (CHEF)^{6,10(d)} effect in presence of Al^{3+} ions. Interestingly, binding of these metal ions to **L** causes color changes, which could also be detected by the “naked eye”. Most interestingly, the fluorescence emission at 581 nm for rhodamine is relatively unaffected in the pH range between 4.8 and 9.2. Therefore, we have speculated that the introduction of the dihydroxybenzaldehyde receptor to a rhodamine-based probe would (1) increase its affinity towards Al^{3+} ion in aqueous-acetonitrile media, (2) quickly induce the fluorescent and color responses, that is, realize the real-time detection, (3) improve the selectivity, and (4) recognize reversible binding to Al^{3+} and hence can be useful as a potential chemosensor material. To the best of our knowledge, there are very few reports on aluminum sensor based on rhodamine dyes through spirocyclic ring-opening mechanism.¹¹ In this work we

report a new molecule for selective detection of Al^{3+} ion fluorogenically as well as colorimetrically.

Results and discussion

Rhodamine B hydrazide was synthesized following a literature method¹² and characterized by ^1H NMR spectra, mass data, and FT-IR. It was then condensed with 2,3-dihydroxybenzaldehyde in methanol to form **L** in 71% yield (Scheme 1). The structure of compound **L** was confirmed by its spectroscopic, analytical data (^1H NMR, ^{13}C NMR, ESI-MS, FT-IR, and Fig. S1-S4, ESI †) and X-ray crystal structure analysis (Fig. 1). Single crystal of **L** was obtained by slow evaporation of the methanol solution (Table 1 and 2).

We have carried out UV-vis titration experiments to understand the nature of binding of **L** with Al^{3+} . The chemosensor **L** (10 μM) in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (8:2, v/v) buffered with 2-[4-(2-hydroxyethyl)piperazin-1-yl]ethanesulfonic acid (HEPES), pH = 7.2 showed an absorption maximum at 347 nm, suggesting the spirolactam ring of rhodamine B unit preferred its ring-closed state at this condition. The selectivity of **L** has been checked with different biologically important metal ions eg, Na^+ , Mg^{2+} , Hg^{2+} , Cu^{2+} , Pb^{2+} , Zn^{2+} , Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cd^{2+} , Cr^{3+} , In^{3+} , Ga^{3+} and Al^{3+} in $\text{CH}_3\text{CN}/\text{aqueous}$ (8:2, v/v) buffered with HEPES, pH = 7.2. A significant change in the UV-vis spectral pattern was observed only in the presence of Al^{3+} among all the other metal ions used (Fig. S7, ESI †). Upon gradual addition of Al^{3+} ions (0-100 μM) to chemosensor **L** (10 μM) in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (8:2, v/v), a concomitant red shift in the spectral position at 554 nm was observed along with an increase in the absorption intensity. The emergence of the absorption band at 554 nm was due to the opening of spirolactam ring of the rhodamine moiety along with a color change from colorless to deep magenta (Fig. 2). As

depicted in inset of Fig. 2, the absorbance at 554 nm band as a function of Al^{3+} concentration predicted 1:1 stoichiometric complex between **L** with Al^{3+} ion. The association constant¹³ between **L** and the Al^{3+} ion was calculated from the absorption titration result and was found to be $2.11 \times 10^3 \text{ M}^{-1}$ at 25 °C (Fig. 3). Under the same condition, additions of other metal ions did not cause any discernible changes. This unique selectivity of **L** towards Al^{3+} can be explained in terms of the absolute hardness (η), defined as $\eta = (I + A)/2$, where I and A are the ionization potential and proton affinity, respectively. Namely, it was reported by Paar and Pearson that Al^{3+} is the hardest acid among all the cations considered in this study¹⁴ (Scheme 2). The color of the solution was significantly changed from deep magenta to bright orange when illuminated with a hand-held UV lamp (Fig. 4). So it could easily be detected by the “naked-eye” without the need of any other instrumental assistance.

The fluorescence spectrum of **L** (10 μM) in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (8:2, v/v) buffered with HEPES, pH = 7.2, exhibited emission band at 542 nm when excited at 554 nm. Upon interaction with various metal ions eg, Al^{3+} , Cr^{3+} , In^{3+} , Ga^{3+} , Na^+ , Mg^{2+} , Pb^{2+} , Hg^{2+} , Fe^{3+} , Cu^{2+} , Ni^{2+} , Co^{2+} , Mn^{2+} , Cd^{2+} and Zn^{2+} a much weaker spectral response was observed relative to Al^{3+} at the same concentration (Fig. 5a). During sequential titration (0-100 μM of Al^{3+}), the emission band was peaked up at 581 nm which was attributed to delocalization in the xanthene moiety of the rhodamine and hence emission intensity was increased significantly (Fig. 6). The observed fluorescence occurred due to the metal binding event induced an electronic rearrangement within the dye that opened the spirolactam and yielded a fully conjugated rhodamine dye. The solution showed an intense orange fluorescence, with an approximately 15-fold enhancement in the fluorescence intensity at 581 nm. The inset in Fig. 6 showed the dependence of the emission intensity at 581 nm with increase of Al^{3+} ion concentration. This fact means that **L** could be used

as an 'off-on' fluorescent chemosensor for Al^{3+} . Relative fluorescence enhancement of **L** in the absence and presence of various other metal ions and thereby its selectivity for Al^{3+} was shown in Fig. 5b.

To investigate the recognition ability between **L** and the Al^{3+} ion, both Job's plot¹⁵ and Benesi-Hildebrand plot¹³ experiments were carried out to determine the binding stoichiometry of the **L**- Al^{3+} complex. The absorption intensity varies through a maximum at a molar fraction of about 0.5 of Al^{3+} , indicating a 1:1 stoichiometry and this is the most possible case of binding of Al^{3+} with **L** (Fig. 7). To confirm further the stoichiometry between **L** and Al^{3+} ion, TOF-MS analysis was conducted (Fig. S5, ESI[†]). Mass peak at m/z 729.09 corresponding to **L**. $\text{Al}(\text{SO}_4)(\text{OMe})$ is the indicative for the formation of a 1:1 complex. From the emission intensity data, the association constant (K)¹³ of **L** with Al^{3+} was observed to be $2.56 \times 10^3 \text{ M}^{-1}$, indicating strong binding of **L** with Al^{3+} ion with 1: 1 stoichiometry (Fig. 8). Values thus evaluated using two different spectroscopic techniques were in good agreement.

To check the practical ability of chemosensor **L** as a selective Al^{3+} ion fluorescent chemosensor, we have carried out competitive experiments in the presence of Al^{3+} ion mixed with other different metal ions (Cr^{3+} , In^{3+} , Ga^{3+} , Na^+ , Mg^{2+} , Pb^{2+} , Hg^{2+} , Fe^{3+} , Cu^{2+} , Ni^{2+} , Co^{2+} , Mn^{2+} , Cd^{2+} and Zn^{2+}). The fluorescence response of **L**- Al^{3+} system remains the same by comparison with or without the other metal ions (Fig. 9). These findings confirmed the selectivity and effective interaction of probe **L** with Al^{3+} . For practical application, the detection limit of **L** was also estimated. The fluorescence titration profile of **L** (10 μM) with Al^{3+} demonstrated that the detection limit¹⁶ of Al^{3+} is $2 \times 10^{-8} \text{ M}$ which is far below the WHO acceptable limit (0.05 mg L^{-1} or 1.85 μM of Al^{3+}) in the drinking water (Fig. 10).

In order to gain insight into the sensing mechanism, ^1H NMR titration has been performed by 1 equiv addition of Al^{3+} to the $\text{DMSO}-d_6$ solution of **L** (Fig. 11). Upon addition of 1 equiv of Al^{3+} , i proton of **L** has gradually shifted downfield from 8.85 (free **L**) to 9.03 ppm. Downfield shifts of both a and b in N, N-diethyl group of **L** clearly indicate that Al^{3+} induces the formation of delocalised xanthene moiety of rhodamine B. All other protons of **L** viz. c, d, e, f, g, and h have been shifted downfield after interaction with Al^{3+} . Further, IR spectra of chemosensor **L** with Al^{3+} ion also confirms the proposed mechanism (Fig. S6, ESI †). Upon addition of 1 equiv of Al^{3+} , the characteristic carbonyl amide stretching frequency shifts from 1690 cm^{-1} in **L** to 1662 cm^{-1} in the complex, indicating coordination of carbonyl oxygen with Al^{3+} . These findings clearly support the ring-opening mechanism.

Reversible binding of Al^{3+} to **L** was also established through spectral studies in presence of Na_2EDTA in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ solution. Upon addition of EDTA (excess) to the mixture of **L** (10 μM) and Al^{3+} in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (8:2, v/v), the color of the solution was disappeared instantly. If Al^{3+} was added to the system again, the signal is almost completely recovered with turning solution from colorless to pink (Fig. S8, ESI†). These findings indicate that **L** was a reversible fluorescent probe for Al^{3+} . Fluorescence quantum yield (Φ_{fs})¹⁷ of **L** in the free and Al^{3+} -bound state was found to be 0.02 and 0.30 respectively.

The enhancement of fluorescence of **L** upon binding with Al^{3+} has been supported by the results obtained from fluorescence decay measurement, using Time Correlated Single Photon Counting (TCSPC) technique (Fig. 12). The fluorescence decay of **L** was fitted with triexponential function with time constant (τ_1) 1.2 ns (15.5%), (τ_2) 4.38 ns (4.5%) and (τ_3) 0.49 ns (80%). Upon binding with Al^{3+} ion the same fluorescence decay was observed to (τ_1) 3.05 ns (20%), (τ_2) 1.63 ns (3%) and (τ_3) 0.04 ns (76%) ($\chi^2 = 1.08$ and 1.30) in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (8:2 v/v)

using HEPES buffer, pH = 7.2 at 25⁰C. The average fluorescence lifetime for the bare molecules (2.66 ns) was decreased in the complex (2.07 ns); this was due to the opening of spiroactum ring formation. (Table S1, ESI †). Upon addition of Al³⁺ to chemosensor (**L**) formation of tight binding complex (as observed from higher binding constant) along with the opening of spiroactum ring to convert free (hanging) rhodamine B part of the complex, thereby increased of non-radiative decay channels and as a result average lifetime decreased.

To study the practical applicability, the effect of pH on the fluorescence response of the new chemosensor **L** towards Al³⁺ has also been investigated. Experimental results shows that for free **L**, at acidic conditions (pH < 3), an obvious fluorescence off-on (Fig. S9, ESI †) situation appears due to the formation of the open-ring state because of the strong protonation, and it shows a fluorescence quenching effect upon addition of Al³⁺. In the pH range from 4.8 to 9.2, neither the color nor the fluorescence (excited at 554 nm) characteristics of rhodamine could be observed for **L**, suggesting that the spirocyclic form was still preferred in this range.

Conclusion

In summary, we have developed a novel turn-on fluorescent chemosensor based on a rhodamine–dihydroxybenzaldehyde conjugate. The sensor **L** displays an excellent selectivity and high sensitivity toward the detection of Al³⁺ in CH₃CN/H₂O over a wide range of tested metal ions with remarkably enhanced fluorescent intensity and also shows clear color change from colorless to deep magenta. A comparison of the present probe with other existing Al³⁺ sensitive “turn-on” fluorescent probes reveals that it is very competitive and somewhat better than others in respect of all the parameters. The present probe is relatively cheap as it involves a facile two step reactions with the commercially available much cheaper chemicals. Under UV light

illumination, one can visually detect even 2×10^{-8} M Al^{3+} in aqueous-acetonitrile buffer solution by this sensor without the aid of any sophisticated instruments. Thus the chemosensor **L** is able to serve as a 'naked eye' chemosensor for Al^{3+} ion. We believe that **L** can be used for many practical applications in chemical, environmental and biological systems.

Experimental Section

General information

The solvents and reagents were purchased from Sigma-Aldrich commercial sources and were used without any further purification. The solvents were distilled prior to use. The rhodamine B hydrazide was prepared by literature methods. Elemental analyses (carbon, hydrogen and nitrogen) were done with a Perkin–Elmer CHN analyzer 2400. Melting points were determined using a Buchi 530 melting apparatus. ^1H and ^{13}C NMR spectra were recorded on Bruker Avance II 500 MHz and Bruker Avance 300 MHz Spectrometer in $\text{DMSO-}d_6$ and CDCl_3 . Mass spectra were recorded in methanol solvent in Qtof Micro YA263. The electronic spectra were recorded in $\text{CH}_3\text{CN-H}_2\text{O}$ solution on a Hitachi model U-3501 spectrophotometer. IR spectra (KBr pellet, $400\text{--}4000\text{ cm}^{-1}$) were recorded on a Perkin–Elmer model 883 infrared spectrophotometer. Emission spectra were measured Perkin Elmer (Model LS-50B) fluorimeter.

Time resolved spectral measurement

Fluorescence lifetimes were measured by the method of Time Correlated Single-Photon counting (TCSPC) using a HORIBA Jobin Yvon Fluorocube-01-NL fluorescence lifetime spectrometer. The sample was excited using a nanosecond laser diode at 340 nm and 450 nm and the signals were collected at the magic angle of 54.7° ¹⁸. The typical time resolution of our experimental set-up is ~ 800 ps. The decays were deconvoluted using DAS-6 decay analysis software. The acceptability of the fits was judged by χ^2 criteria and visual inspection of the

residuals of the fitted function to the data. Mean (average) fluorescence lifetimes were calculated using the following equation (1):

$$\tau_{av} = \frac{\sum \alpha_i \tau_i^2}{\sum \alpha_i \tau_i} \quad (1)$$

in which α_i is the pre-exponential factor corresponding to the i^{th} decay time constant, τ_i .

Fluorimetric Analysis

For measurement of the quantum yields (Φ) of **L** and its complex, we recorded the absorbance of the compounds in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ solution. The emission spectra were recorded using the maximal excitation wavelengths, and the integrated areas of the fluorescence-corrected spectra were measured. The standard used for the measurement of the fluorescence quantum yield was rhodamine 6G ($\Phi = 0.95$ in ethanol) as the reference¹⁹ using the following equation²⁰:

$$\Phi_X = \Phi_S \times (I_X/I_S) \times (A_S/A_X) \times (\eta_X/\eta_S)^2 \quad (2)$$

Where, X & S indicates the unknown and standard solution respectively, Φ is the quantum yield, I is the integrated area under the fluorescence spectra, A is the absorbance and η is the refractive index of the solvent.

Association Constant

(i) Calculation for the association constant using spectrophotometric titration data

The association constant for the formation of the complex, $[\text{Al}^{3+}\text{-L}]$ was evaluated using the Benesi–Hildebrand (B–H) plot

$$1/(A - A_0) = 1/\{K(A_{\text{max}} - A_0)C\} + 1/(A_{\text{max}} - A_0) \quad (3)$$

A_0 is the absorbance of **L** at absorbance maxima ($\lambda = 554$ nm), A is the observed absorbance at

that particular wavelength in the presence of a certain concentration of the metal ion (C), A_{\max} is the maximum absorbance value that was obtained at $\lambda = 554$ nm (for Al^{3+}) during titration with varying [C], K is the association constant (M^{-1}) and was determined from the slope of the linear plot, and [C] is the concentration of the Al^{3+} ion added during titration studies. The goodness of the linear fit of the B–H plot of $1/(A - A_0)$ vs $1/[\text{Al}^{3+}]$ for 1:1 complex formation confirms the binding stoichiometry between **L** and Al^{3+} .

(ii) Calculation for the association constant using emission titration data

Association constant was calculated using the Benesi-Hildebrand equation:

$$1/\Delta F = 1/\Delta F_{\max} + (1/K[\text{C}]) (1/\Delta F_{\max}) \quad (4)$$

Here $\Delta F = F_x - F_0$ and $\Delta F_{\max} = F - F_0$, where F_0 , F_x , and F are the emission intensities of **L** considered in the absence of Al^{3+} , at an intermediate Al^{3+} concentration, and at a concentration of complete interaction, respectively, at 581 nm and where K is the binding constant and [C] the Al^{3+} concentration. The plot of $(F - F_0)/(F_x - F_0)$ against $[\text{C}]^{-1}$ and the association constant (K) was obtained by the ratio intercept/slope.

Calculation of the detection limit

The detection limit (DL) of **L** for Al^{3+} was determined using the following equation:

$$\text{DL} = K \times \text{Sb}/S \quad (5)$$

Where $K = 2$ or 3 (we take 3 in this case), Sb is the standard deviation of the blank solution and S is the slope of the calibration curve.

General procedures of spectra detection

Stock solution (2×10^{-3} M) of different metal ions as, Al^{3+} , Cr^{3+} , In^{3+} , Ga^{3+} , Na^+ , Mg^{2+} , Pb^{2+} , Hg^{2+} , Fe^{3+} , Cu^{2+} , Ni^{2+} , Co^{2+} , Mn^{2+} , Cd^{2+} and Zn^{2+} were prepared. High concentration of the stock solutions chemosensor **L** ($10 \mu\text{M}$) was prepared in acetonitrile. Before spectroscopic

measurements, the solution of **L** was freshly prepared by diluting the high concentration stock solution to the concentrations of desirable solution. The suspension solutions of **L** were prepared by dispersing the fine powder in water. Each time a 2 mL solution of **L** was filled in a quartz cell of 1 cm optical path length, and different stock solutions of cations were added into the quartz cell gradually by using a micro-pipette. The volume of cationic stock solution added was less than 100 μ L with the purpose of keeping the total volume of testing solution without obvious change. All the spectroscopic measurements were performed at least in triplicate and averaged.

Synthesis of chemosensor **L**

Rhodamine B hydrazide was synthesized following a literature procedure.¹² To a solution of 2,3-dihydroxybenzaldehyde (0.151 gm, 1.095 mmol) in methanol (10 mL) was added rhodamine B hydrazide (0.5 gm, 1.095 mmol) in methanol (10 mL). The resulting was heated to reflux at 100 °C in oil bath using a fused CaCl₂ guard tube for 15 h. A reddish brown crystalline solid which was precipitated out after 30 min of stirring was isolated by filtration. The isolated product was washed with cold methanol several times and dried under vacuum. Reddish brown crystalline solid was obtained. Yield: 0.45 g, 71%. M.P. - 232 °C (decomp.). FT-IR (KBr, cm⁻¹): ν = 2971, 1690, 1661, 1617, 1546, 1516, 1467, 1428, 1373, 1269, 1220, 1119, 1020, 867, 815, 782, 700. ¹H-NMR (500 MHz, DMSO-*d*₆): δ (ppm), 1.09 (t, 12H, NCH₂CH₃, *J* = 5 Hz), 3.35 (q, 8H, NCH₂CH₃), 6.37-6.35 (q, 2H, xanthene-H, *J* = 5 Hz), 6.46-6.43 (q, 4H, xanthene-H), 6.67 (d, 1H, phen-H, *J* = 8 Hz), 6.79 (d, 1H, Ar-H *J* = 8Hz), 7.12 (d, 1H, benzo-dioxole-H), 6.79 (d, *J* = 8 Hz, 1H), 7.12 (d, *J* = 7.5 Hz, 1H), 7.63-7.59 (q, 2H), 7.93 (d, *J* = 7.5 Hz, 1H), 9.06 (s, 1H, N=C-H), 9.19 (s, 1H), 10.29 (s, 1H). ¹³C-NMR (300 MHz, CDCl₃+DMSO-*d*₆) δ (ppm): 12.87, 44.12, 65.94, 97.84, 105.17, 108.70, 118.23, 119.26, 119.72, 120.74, 123.51, 124.28, 128.14, 129.34, 134.44, 146.00, 146.41, 149.07, 151.65, 153.14, 164.03; ESI-MS: *m/z* calculated for

$C_{35}H_{37}N_4O_4$ $[M+H]^+$ (m/z): 577.28, found 577.6. Anal. Calc. for $C_{35}H_{36}N_4O_4$: C, 73.02; H, 6.36; N, 9.76; Found: C, 72.90; H, 6.29; N, 9.72.

Synthesis of L-Al³⁺ complex

A 5 mL methanolic solution of $Al_2(SO_4)_3 \cdot 16H_2O$ (0.054 g, 0.0867 mmol) was added drop wise to a magnetically stirred solution (5 mL) of **L** (0.05 g, 0.0867 mmol) in methanol. The color of the ligand solution was changed from almost colorless to deep magenta upon addition $Al_2(SO_4)_3 \cdot 16H_2O$. After two hours of stirring at room temperature, the solution was dried using rotary evaporator which yielded a magenta L-Al³⁺ complex. The complex was characterized by mass spectral studies, FT-IR and ¹H NMR studies.

Crystallographic measurements

Measurements were done on a Bruker SMART APEX II CCD area detector equipped with graphite monochromated Mo K α radiation ($k = 0.71073 \text{ \AA}$) source in ω scan mode at 293 K. Cell parameters refinement and data reduction were carried out using the Bruker SMART and Bruker SAINT softwares for **L**. All non-hydrogen atoms were refined anisotropically. Positions of hydrogen atoms attached to carbon atoms were fixed at their ideal position

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Rhodamine-based molecular clips for highly selective recognition of Al^{3+} ions: synthesis, crystal structure and spectroscopic properties

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Graphical Abstract

