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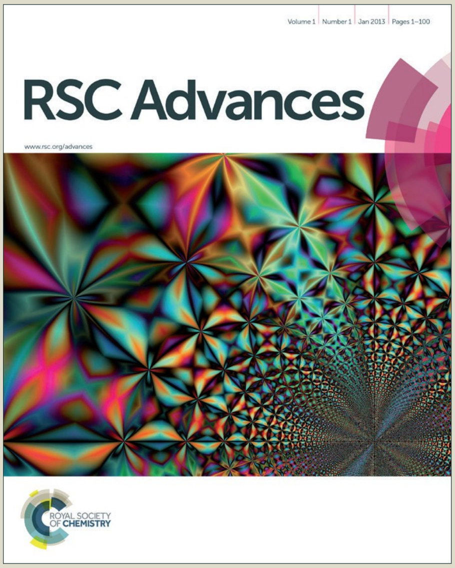

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Synthesis and Characterization of a Novel, Ditopic, Reversible and Highly Selective, “Turn-On” Fluorescent Chemosensor for Al^{3+} Ion

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We herein report a structurally characterized Schiff base ligand, L formed by the condensation of 1,1-bis-[2-hydroxy-3-acetyl-5-methylphenyl]methane with 2-picolyl amine. It utilizes the three signalling mechanisms ESIPT, chelation enhanced fluorescence (CHEF) and C=N isomerization to serve as a “Turn-On” fluorescence chemosensor for Al^{3+}. L has high selectivity for Al^{3+} in MeOH. Reversible nature of this chemosensor makes it cost effective. This joins the rare family of ditopic fluorescent chemosensor. When this Schiff-base receptor was treated with Al^{3+} salt in MeOH, the fluorescence intensity abruptly increased. Other metal ions did not show such significant effect on the fluorescence. Detection limit for this chemosensor was found to be 0.7 μM.

Introduction

Now a days people are conveniently using aluminium foils and vessels in their life style very frequently which is the main cause of increased concentration of Al in our food. The accumulation of Al^{3+} ion in the human brain tissue is proven to be one of the potential cause of Alzheimer disease and neurodemantia,[1,2] responsible for the damage to central nervous system. In spite of a non-essential element for living systems, the ionic radius (0.051 nm) and charge of Al^{3+} makes it a competitive inhibitor of several essential elements of similar characteristics like Mg^{2+}, Ca^{2+} and Fe^{3+}. Increased concentration of Al^{3+} is not only harmful for human but also to environment. Though aluminium is the third most abundant metal ion but its toxicity prevents the plant growth[3] and also it makes the soil acidic. The concentration of free Al^{3+}-ion in surface water increases due to leaching from soil during acid rain and it is dangerous for aquatic animals and plants in acidified water. Therefore it is a necessity to develop a new and effective analytical method which can detect aluminium very selectively and with very low detection limit. During the past decade, exploring the new sensing mechanisms[4] between recognition and signal reporting units in the design of new fluorescent chemosensors has been very much fascinating. Under the umbrella of supramolecular chemistry, it is an important research field and has attracted great attention because of its simplicity, high selectivity and sensitivity in fluorescent assays.[5-7] Moreover Fluorescence techniques have several advantages over other methods for metal ion monitoring inside living cells because of the non-destructive character and quick response. Recently considerable attention has been paid to the synthesis and the application of metal complexes of Schiff bases for several reasons: some of the Schiff base metal complexes are showing good antitumor properties, anti-oxidative activities and interesting electronic and photo physical properties. Schiff bases are ideal candidates for fluorescence probes[8-14] based on excited state intramolecular proton transfer (ESIPT)[15-18] or chelation enhanced fluorescence (CHEF)[19-21] or C=N isomerization.[22-24] It is well known that ESIPT-based chemosensors are suitable candidates for fluorescence probes. They generally contain a six- and/or five membered ring of hydrogen bonding and its high speed proton transfer in excited state leads to very weak or no fluorescence. After metallation, this proton is removed which leads to the inhibition of ESIPT and enhances the flurescence intensity. Compounds having C=N isomerization are often nonfluorescent because it predominantly helps in the decay process of excited states. However, the fluorescence of their metal complexes containing a metal-nitrogen bond, increases dramatically due to the suppression of C=N isomerization in the excited states. Thus it can be reasonably expected that C=N isomerization may also be inhibited through complexation with metal ions which in turn enhances the fluorescence abruptly by conformational restriction. An alternative approach to metallation could be the structural modification which may involve the introduction of an R group (Me, Et, Ar, etc.) onto the imine (R–C=N). The enhancement in the fluorescence is also attributed to the chelate ring formation due to metal complexation. This effect is referred to as the Chelation Enhanced Fluorescence (CHEF) effect. It is well known that lone pair of electrons at the C=N nitrogen of the fluorophore quenches its fluorescence. However, after complexation the lone pair is donated to the metal centre thereby enhances the fluorescence intensity through the CHEF mechanism.

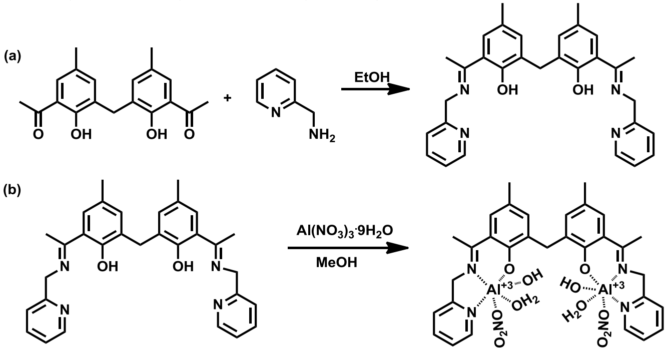
The detection of Al^{3+} has always been difficult task because of the lack of spectroscopic characteristics and poor coordination ability. Being a member of hard acid family, Al^{3+} prefers hard donor sites like N and O in its coordination sphere. As a result, most of the reported Al^{3+} sensors contain mixed nitrogen and oxygen donor sites. There are few fluorescence "turn-on" Al^{3+} sensors with high sensitivity, high selectivity, and rapid response have been reported.[3, 25-28] The present ligand L was designed because it has two binding pockets to form dinuclear Al^{3+} complex. In addition, a methyl group onto the imine has been deliberately introduced to modulate the selectivity of C=N isomerization based sensors for particular metal ions. It should also be noticed that there are potential multiple signalling mechanisms for ion sensor due to the synergistic effects of chelation between cations and the present ligand. It is noteworthy here that the formation of a 1:2 complex of L with Al^{3+} prevents the acyclic C=N isomerization and contributes to the selectivity for particular metal ion along with significant enhancement in fluorescence. Also the ligand L contains multiple "rotor" units in the structure which are frozen after the chelation with the cations and lead to enhancement in fluorescence properties. 1,1-bis-[2-hydroxy-3-acetyl-5-methylphenyl] methane and 2-picolyl amine were selected as the reactants to obtain the Schiff base ligand L as the target compound.

Experimental

Materials and Instrumentation. All reagents (analytical grade and spectroscopic grade) were obtained from Spectrochem (India) and Sigma-Aldrich (India) and used as received. Solvents were dried using standard literature method and solutions of metal ions were prepared with metal nitrate salts. ^1H NMR spectra were recorded on a Bruker AVANCE 400 NMR spectrometer. Chemical shifts (δ) are reported in ppm. Absorption spectra were recorded at 25 °C using a Perkin-Elmer model Lambda 650 UV-vis spectrophotometer. Emission spectra were recorded on Fluoromax 4P Spectrofluorometer (Horiba Jobin Mayer, Edison, NJ, USA). Fourier transform infrared (FT-IR) spectra were measured on a BRUKER ALPHA-T FT-IR spectrometer as KBr pellets. Single crystal diffractions were measured on Bruker APEX SMART D8 Venture CCD diffractometer at 110 K temperature with graphite monochromated Mo Kα radiation. Electrospray ionization mass spectrometry (ESI-MS) spectra of the compounds were recorded on a Bruker microTOF-Q II mass spectrometer.

Synthesis of L. To a solution of 2-picolylamine (0.450 g, 4.16 mmol) in ethanol (10 mL), ethanolic solution of 1,1-bis-[2-hydroxy-3-acetyl-5-methylphenyl]methane[29] (0.500 g, 1.6 mmol in 10 mL EtOH) was added drop wise. The reaction mixture was refluxed for 6-8 hours under nitrogen atmosphere which resulted clear orange coloured solution. The clear solution thus obtained was kept in the fridge overnight at 4 ˚C. Orange colour crystals obtained were washed with cold ethanol followed by ethar (Scheme 1a). Yield 72% (0.570g, 1.158 mmol). mp: 159˚-160 ˚C. ESI-MS m/z (Fig. S4) ($[M+H]^+$): calcd, 493.25; found, 493.24. λ_{max}, nm (ε, $dm^3mol^{-1}cm^{-1}$) in MeOH: 342 (8700), 262 (26500). IR (KBr, cm^{-1}): 3232br (ν OH), 1636s (ν C=N). ^1H NMR (Fig. S6) (DMSO-d_6, 400 MHz) δ (ppm): 8.58 (d, 2H), 7.85 (t, 2H), 7.46 (d, 2H), 7.38 (s, 2H), 7.32 (t, 2H), 6.83 (s, 2H), 4.94 (s, 4H), 3.78 (s, 2H), 2.47 (s, 3H), 2.17 (s, 3H).

Synthesis of Al^{3+} Complex of L; $[L^{-2}Al_2(H_2O)_2(NO_3)_2(OH)_2]$. To 2 mL of stirred solution of $Al(NO_3)_3$•$9H_2O$ (0.150 g, 0.4 mmol) in methanol, methanolic solution of L (0.100 g, 0.2 mmol) was added dropwise and stirring was continued for 45 min. Then solvent was removed under reduced pressure. Yellowish green solid was obtained (Scheme 1b) which was washed with water and dried in vacuo. ESI-MS m/z ($[M+H]^+$) (Fig. S5): $[L^{2-} + 2Al^{3+} + 2H_2O + 2OH^- + 2NO_3^- + H^+]$ calcd, 739.21; found, 739.28. FTIR (KBr, cm^{-1}): 1632.67, (ν C=N).



Scheme 1. Synthesis of the receptor L (**a**) and its corresponding Al^{3+} complex (**b**).

Optical Detection of Al^{3+} Using L. The receptor (10.0 μM) was mixed with different concentrations of metal ions in MeOH:H_2O (99:1, v/v) in a 1 cm cell. Solutions of metal ions were prepared using nitrate salts. After equilibrium at ambient temperature, absorption and fluorescence spectra of the mixtures were measured. Fluorescence spectra were measured at an excitation wavelength of 360 nm.

Crystallography. X-ray data were collected with a Bruker APEX SMART D8 Venture CCD diffractometer with graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation at 110(0) K. The "Bruker Saint Plus" program[30] was used for data reduction. Data were corrected for Lorentz and polarization effects; an empirical absorption correction (SADABS) was applied.[30,31] The structure was solved by direct methods with SIR-97 and refined by full-matrix least-squares methods based on F^2 by using SHELXL-97,[31] incorporated in the WinGX 2014.1 crystallographic package.[32] All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms were calculated assuming ideal geometries, but not refined.

Results and Discussion

The Schiff base probe L was synthesized easily by condensation of 1,1-bis-[2-hydroxy-3-acetyl-5-methylphenyl]methane and 2-picolylamine with 72% yield in ethanol and its Al^{3+} complex was synthesized by L and $Al(NO_3)_3 \cdot 9H_2O$ in methanol-water mixture (Scheme 1) and its fluorescence studies were done.

Selectivity and sensitivity of L for Metal Ions. First, the metal sensing ability of L (10 μM) was examined upon treatment with various metal ions (as their nitrate salts) such as Na^+, K^+, Mg^{2+}, Ca^{2+}, Ag^+, Hg^{2+}, Pb^{2+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ga^{3+} and In^{3+} ions (20.0 μM) in methanol−water (99:1, v/v) (Fig. 1), no significant changes in the fluorescence of L were observed. The addition of Al^{3+} changed the emission signals of L remarkably (approx. 153 fold) at 472 nm which indicates that the probe is selective for Al^{3+} ion only which can be observed by naked eye under UV light (Fig. S1). Free L and Al^{3+}-nitrate individually showed no significant emission after excitation at 360 nm. Because of different binding mode with different solvent molecules, fluorescence intensity may change from solvent to solvent and it has been found that the system shows maximum fluorescence intensity in methanol as compared to other solvents (Fig. S2).

To examine the selectivity for Al^{3+} in a complex background of potentially competing species, the fluorescence enhancement of L (10 μM) with Al^{3+} (50 μM) was investigated in the presence of Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^{+}, Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Hg^{2+} and Pb^{2+} metal ions (50 μM) at 472 nm (Fig. 2). A background of most competing metal ions did not interfere with the detection of Al^{3+} by L in MeOH:H_2O (99:1, v/v), except for Cu^{2+}, which quenched the fluorescence about 70% of that obtained with Al^{3+} alone. These results indicate that L may be used as good chemosensor for Al^{3+} over competing relevant metal ions. Fluorescence quenching by Cu^{2+} may be correlated in terms of the occupancy of the frontier orbitals. We know that the HOMO→(LUMO/LUMO+n) excitations are relevant to the LMCT. These excitations correspond to charge transfer from the excited L moiety to the Cu^{2+} center (LMCT) and thus it might be providing a pathway for nonradiative deactivation of the excited state leading to fluorescence quenching.[33] As such also Cu^{2+} is well known in the literature as fluorescence quenching agent.[25a,34-36]

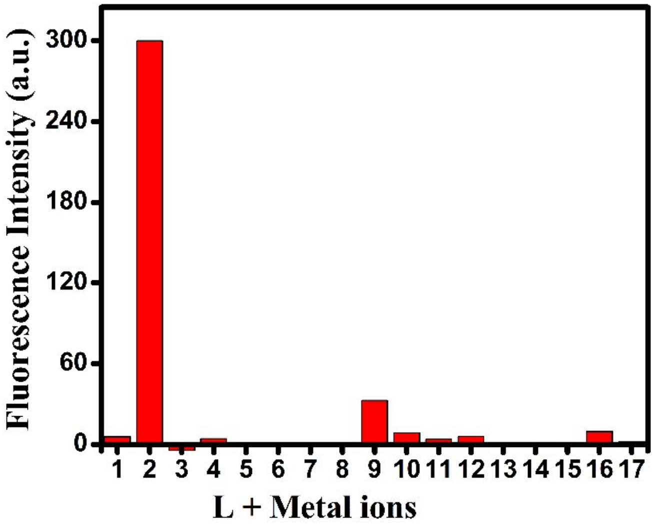


Fig. 1 Bar graph shows the relative emission intensity of L (10 μM) at 472 nm upon treatment with various metal ions (1. free L, 2. L+ Al^{3+}, 3. L+Mn^{2+}, 4. L+Hg^{2+} 5. L+Fe^{3+}, 6. L+Co^{2+}, 7. L+Ni^{2+}, 8. L+Cu^{2+}, 9. L+Zn^{2+}, 10. L+Ag^{+}, 11. L+Na^{+}, 12. L+K^{+}, 13. L+Pb^{2+}, 14. L+Mg^{2+}, 15. L+Ca^{2+}, 16. L+Ga^{3+}, 17. L+In^{3+}) (20 μM) in methanol:water (99:1).

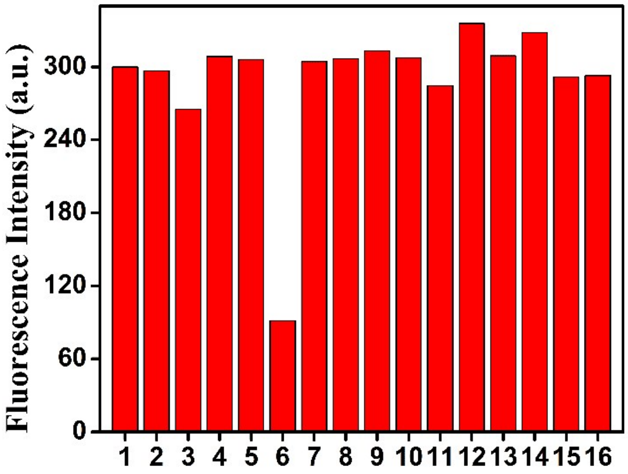


Fig. 2 Fluorescence change of the solutions containing L and 5 eq of Al^{3+} upon addition of 5 eq. of competing metal ions: 1. blank(L+Al^{3+}), 2. blank+Mn^{2+}, 3. blank+Fe^{3+}, 4. blank+Co^{2+}, 5. blank+Ni^{2+}, 6. blank+Cu^{2+}, 7. blank+Zn^{2+}, 8. blank+Ag^{+}, 9. blank+Na^{+}, 10. blank+K^{+}, 11. blank+Mg^{2+}, 12. blank+Ca^{2+}, 13. blank+Hg^{2+}, 14. blank+Pb^{2+}, 15. blank+Ga^{3+} and 16. blank+In^{3+} at λ_{ex} = 360 nm and λ_{em} = 472 nm.

To know a better insight into the fluorescence behaviour, L sensor was titrated with Al^{3+} (Fig. 3). The fluorescence intensity increased up to 10 eq. and then started decreasing.[7a]

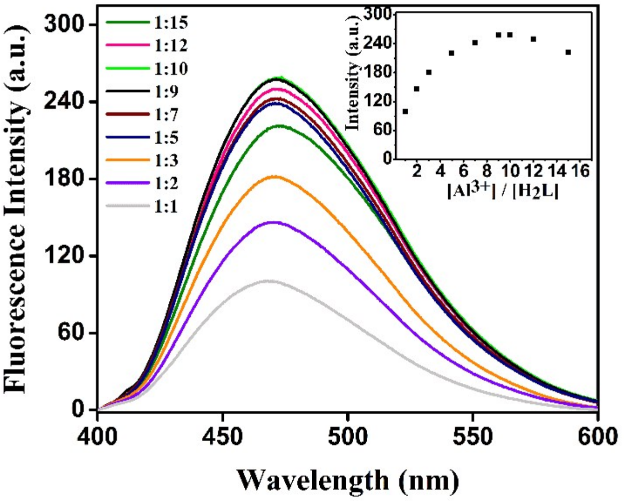


Fig. 3 Fluorescence spectra of 10 μM L (λ_{ex} = 360 nm) after addition of increasing amounts of Al^{3+} ions (10, 20, 30, 50, 70, 90, 120 and 150 μM) at room temperature. Inset graph shows the fluorescence intensity at λ_{em} = 472 nm as a function of Al^{3+} concentration.

Stoichiometry and binding property of the complex. We then measured the changes in absorbance of L upon treatment with Al^{3+} ions. Upon the gradual addition of Al^{3+}, the intensity of the absorption bands of L at 262 and 342 nm decreased with a concomitant increase in new absorption band centered at 279 and 415 nm (Fig. 4). Four well-defined isosbestic points, centered at ca. 249, 266, 303 and 369 nm are consistent with equilibrium between L and L-Al^{3+} complex in solution, indicative of a clean conversion of L into the L-Al^{3+} complex.[37]

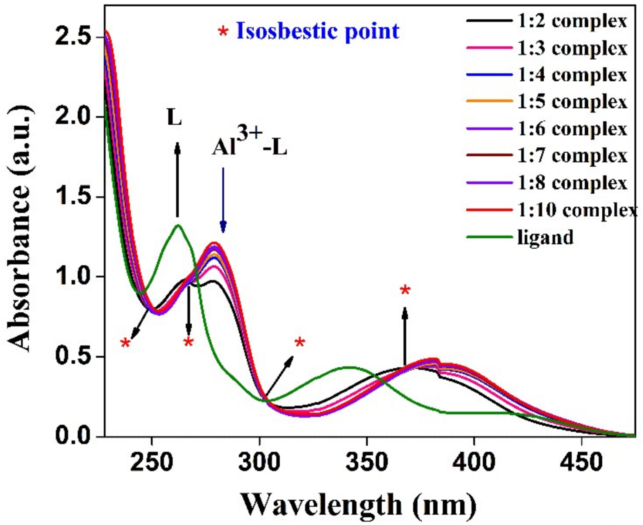


Fig. 4 UV−vis spectral changes of 50 μM L after addition of Al^{3+} ions (2, 3, 4, 5, 6, 7, 8 and 10 eq.) in MeOH−H_2O (99:1).

To determine the stoichiometry of the L-Al^{3+} complex, the method of continuous variations (Job's plot) was used. The stoichiometry for the L-Al^{3+} complex was determined as 1:2 from Job's plot (Fig. 5a). This 1:2 stoichiometry of L-Al^{3+} is again confirmed by the following eqn (1) which is used to calculate the stability constant for the complex.[38]

$$\log\left[\frac{F_{max}-F}{F-F_{min}}\right] = n\log C_M + \log K_a \qquad \text{eqn (1)}$$

Here, F_{max} and F_{min} represents the fluorescence intensity at the respective wavelength, n denotes the stoichiometry and K_a is the apparent stability constant of the complex. According to fluorescence data at λ_{ex}=360 nm and λ_{em}=472 nm, stability constant was calculated as 3.61×10^9 M^{-1} (Fig. 5b).

To further study the coordination of L with Al^{3+}, ESI mass spectra were recorded. The positive-ion mass spectrum of L upon addition of 2.0 eq. of Al^{3+} exhibited two intense peak at m/z 739.28 and 871.30, corresponding to the [L^{2-} + 2 Al^{3+} + $2H_2O$ + $2OH^-$ + $2NO_3^-$] (calcd m/z 739.21) and [L^{2-} + $2Al^{3+}$ + $2H_2O$ + $2OH^-$ + $2NO_3^-$ + 3MeOH + $2H_2O$] (calcd m/z 871.31), respectively (Fig. S5).

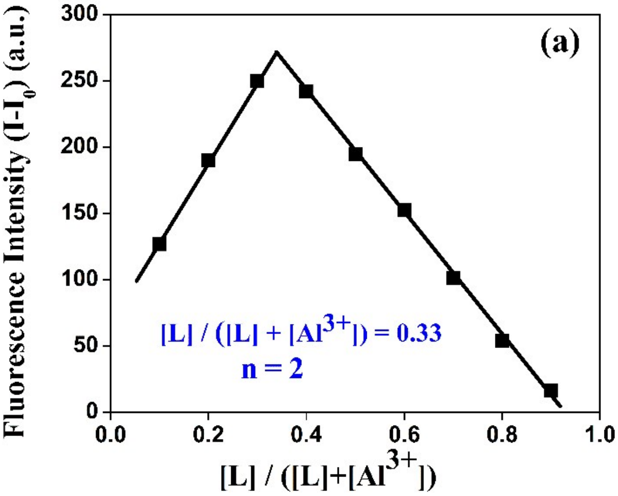


Fig. (5a) Job's plot for the binding of L with Al^{3+} emission intensity at 472 nm was plotted as a function of the molar ratio [L] / ([L] + [Al^{3+}]).

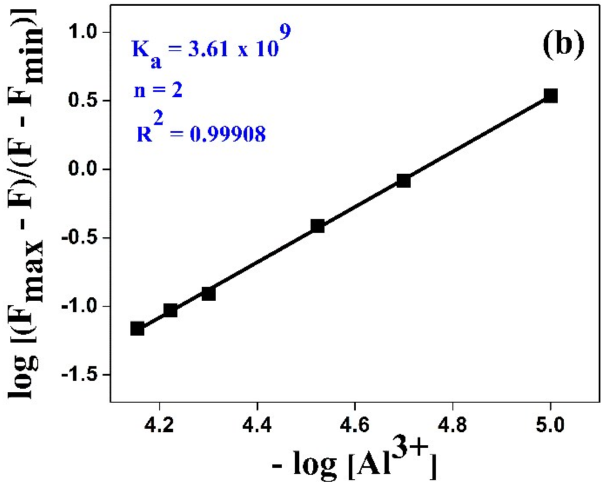


Fig. (5b) Plot for calculation of apparent stability constant of L (10 μM) with Al^{3+} (1.0 to 10.0 eq.).

Detection limit. From the titration results, the detection limit of L for Al^{3+} was estimated to be 0.7 μM at 472 nm in 99% methanol (Fig. S3). The detection limit is very low and it is much lower than US EPA limit (7.41 μM) to detect Al^{3+} ion in drinking water. The excellent detection limit of this fluorescent chemosensor L would be useful in the detection of a trace quantity of Al^{3+} in biological and environmental samples. The detection limit was calculated using the following eqn (2).[39]

$$\text{Detection limit} = 10^{-\left[\frac{\text{slope}}{\text{intercept}}\right]} \qquad \text{eqn (2)}$$

Reversibility. Reversible usage is an important feature for optical chemosensors. The reversibility of the recognition process of receptor (L) was tested by adding an Al^{3+} binding agent, EDTA (Fig. 6). The addition of EDTA to a mixture of (L) and Al^{3+} resulted decrease in the fluorescence intensity at 472 nm, which clearly indicated the regeneration of the free L. Fluorescence was recovered by the addition of excess Al^{3+} to the previous mixture. These phenomena indicate the reversible nature of L as a chemosensor for Al^{3+} ion.[38a,40]

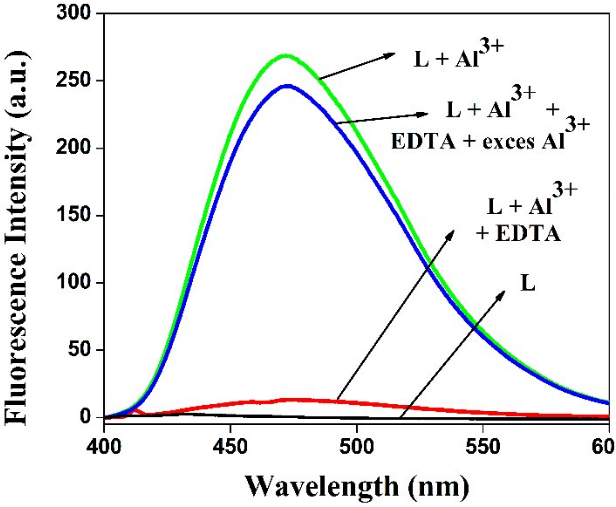


Fig. 6 Reversible fluorescence response of L to Al^{3+} ions.

Photoluminescence Quantum Yield. All the fluorescence spectra of reference, ligand and complex were taken at excitation wavelength 366 nm. The stock solutions of quinine sulphate were prepared in 0.05M H_2SO_4 but the stock solutions of ligand and Al^{3+}-complex were prepared in methanol. Photoluminescence quantum yields were calculated according to the following eqn (3).[41]

$$\Phi_X = \Phi_S \times \left(\frac{Grad_X}{Grad_S}\right) \times \left(\frac{\eta_X^2}{\eta_S^2}\right) \qquad \text{eqn (3)}$$

Subscript S represents the standard samples and Subscript X represents the test samples, Φ represents the photoluminescence quantum yield, η represents the refractive index of the solvent, Grad represents the gradient of the respective curves. The photoluminescence quantum yields (Φ_F) of the ligand (L) and its aluminum complex have been measured using Quinine sulfate as the reference. The quantum yield of L in the absence of Al^{3+} is

0.0007. After 1:2 complexation with Al^{3+} quantum yield increases ~153 fold (Φ_F of complex=0.106).

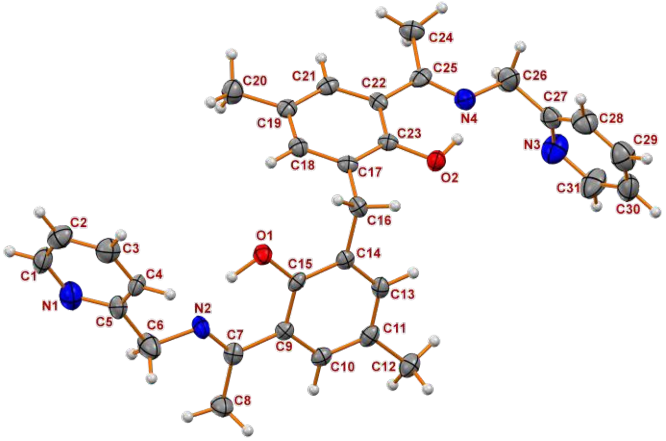


Fig. 7 ORTEP view of the L at 110 K. Displacement ellipsoids are drawn at the 50% probability level. Single crystal was obtained by recrystallization of L from ethanol.

Structure of the ligand was determined by X-ray crystallography. ORTEP diagram has been shown in Fig. 7. Its purity was checked by ^1H NMR in protic (Methanol-d_4) as well as aprotic solvent ($CDCl_3$) and DMSO-d_6 and it was found that the phenolic OH peak which was observed at δ=12.5 ppm in aprotic solvent $CDCl_3$ was missing in protic solvent (Methanol-d_4) because of proton exchange with solvent (Fig. S8).

Conclusion

In conclusion, a ditopic Schiff base ligand as turn-on fluorescent chemosensor for the Al^{3+} ion based on GSIPT/ESIPT, CHEF and C=N isomerization was obtained. The receptor L displayed dramatic enhancement in the fluorescence intensity selectively for Al^{3+} over other ions investigated in MeOH-H_2O solution. The detection limit is insufficiently low to detect micromolar concentration of Al^{3+}. The addition of EDTA quenches the fluorescence of the receptor-Al^{3+} complex however on successive addition of excess amount of Al^{3+}, the fluorescence intensity again recovers which clearly indicates that L serves as a reversible chemosensor. The quantum yield for Al^{3+} complex of L increases 153 fold than that of the pure ligand L. Thus we conclude that the receptor L has the ability to serve as a practical detection sensor for Al^{3+} in the environment.

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Notes and references

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Electronic Supplementary Information (ESI) available: Crytallographic information file (CIF) for X-ray crystallographic data, ^1H NMR of L in different solvents, ESI Mass of L and its corresponding Al^{3+} complex, Detection limit, Optimized Cartesian coordinates and energies and frequencies for L.

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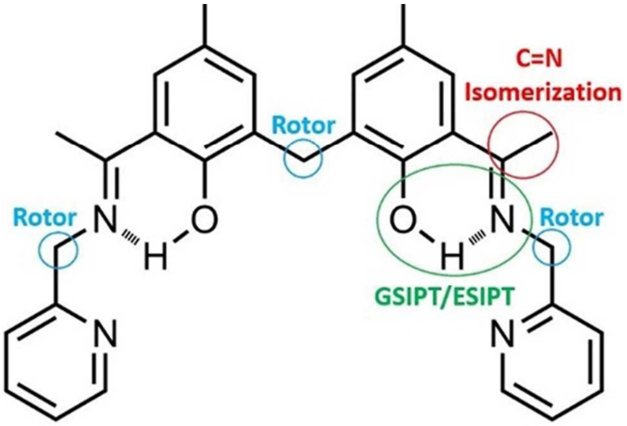

A ditopic Schiff base fluorescent chemosensor L (OFF state), selectively senses Al^{3+} by inhibition of ESIPT/GSIPT, C=N isomerization and chelate-enhanced fluorescence (ON state).