

Naphthaldehyde–Urea/Thiourea Conjugates as Turn-On Fluorescent Probes for Al^{3+} Based on Restricted C=N Isomerization

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Keywords: Hydrazones / Probes / Fluorescence / Aluminum / Isomerization

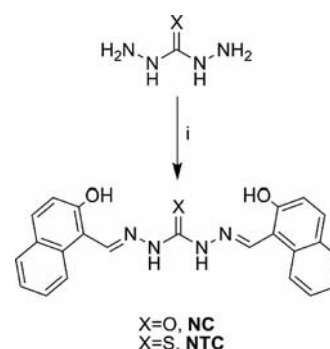
We have synthesized naphthaldehyde–carbonohydrazone (NC) and naphthaldehyde–thiocarbonohydrazone (NTC) Schiff base ligands by the condensation reaction of 2-hydroxy naphthaldehyde with urea and thiourea, respectively. Both these Schiff base ligands show blue turn-on fluorescence in the presence of aluminum(III), as a result of a restric-

ted C=N isomerization mechanism. Aluminum(III) can be detected in the presence of most of the competing metal ions by using NC and NTC. The association constant ($\log K_a$) of NC and NTC for Al^{3+} in acetonitrile was calculated to be 14.5 and 14.1, respectively.

Introduction

Aluminum is the third most abundant element in the lithosphere, accounting for approximately 8% of the earth's mass. Aluminum is used excessively in the modern world with diverse applications, because of its many unusual combinations of properties.^[1] Such widespread application of aluminum leads to its presence across a variety of domains, such as households, transportation, and industry. High concentrations of aluminum are toxic to plants, fish, algae, bacteria, and other species in aquatic ecosystems.^[2] Aluminum in its ionic form (Al^{3+}) has the ability to react with biological species by changing or suppressing their function, leading to harmful effects. Al^{3+} is neurotoxic; it causes neurofibrillary, enzymatic, and neurotransmitter changes in the central nervous system.^[3] The upper limit for the weekly dietary intake of aluminum for humans is estimated to be 7 mg/kg of body weight.^[4] Al^{3+} toxicity is also believed to be one of the main causes of neurological disorders such as Parkinson's disease, Alzheimer's disease, and dialysis encephalopathy.^[3] The design of fluorescent chemosensors for the selective recognition and sensing of specific cations has attracted considerable interest due to their importance in biological and environmental applications. The detection of Al^{3+} has always been problematic because of its lack of spectroscopic characteristics and poor coordination ability, in comparison to transition metals. The presence of H^+ , alkali, or alkaline earth metal ions does not allow for the reduction of Al^{3+} .^[5] Therefore, the development of fluorescent probes is critical in the environmental and biological

monitoring of aluminum(III) ions. Recently, we have reported on pyrrolidine-constrained fluoroionophores for selective Al^{3+} detection.^[6] Metal complexes of Schiff base ligands have several properties like selective extraction,^[7] antitumor activity,^[8] antioxidative activity,^[9] and attractive electronic and photophysical properties.^[10] In addition, Schiff base derivatives having a fluorescent moiety are appealing tools for designing optical probes for metal ions.^[11] Only a few fluorescent probes have been reported for the detection of Al^{3+} .^[6,12] We have recently reported simple Schiff base conjugates of urea or thiourea and salicylaldehyde or julolidinal, which serve as chemosensors for the selective detection of copper(II).^[13] Employing a similar strategy, we have designed Schiff base conjugates of 2-hydroxy-1-naphthaldehyde and urea or thiourea (Scheme 1) and used them as fluorescent chemosensors for the selective detection of Al^{3+} , which is based on the restriction of the isomerization of the C=N bonds upon complexation with the cation.^[14] Therefore, the metal ion receptor formed by a simple one-step condensation reaction of aldehyde and amine detects Al^{3+} by means of an enhanced fluorescence



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Scheme 1. Synthesis of ligands NC and NTC. (i) 2-hydroxy-1-naphthaldehyde, EtOH/H₂O (1:1), reflux (94% yield).

response and is important from the viewpoint of its potential use as a sensing reagent for environmental applications. In this article, we report on the synthesis and fluorescence properties of naphthaldehyde conjugates of carbohydrazide and thiocarbohydrazide and on their utilization for the selective detection of Al^{3+} on the basis of the restricted isomerization of $\text{C}=\text{N}$ bonds, which results from their complexation with the aluminum(III) ion. To the best of our knowledge, this is the first method that exploits $\text{C}=\text{N}$ isomerization as a signal transduction mechanism for the recognition of Al^{3+} .

Results and Discussion

Synthesis

A solution of 2-hydroxy-1-naphthaldehyde in ethanol was added slowly to a solution of thiocarbohydrazide or carbohydrazide in water (Scheme 1). The reaction mixture was heated at reflux with stirring for 24 h. The reaction mixture was then cooled to room temperature, and the precipitate that had formed was filtered off. The precipitate was washed with ethanol and dried under vacuum to obtain naphthaldehyde-carbohydrazide (NC) or naphthaldehyde-thiocarbohydrazide (NTC) in quantitative yield.^[13] These compounds were characterized by NMR spectroscopy, mass spectrometry, and elemental analysis.^[15]

Photophysical Studies

The photophysical properties of NC and NTC were investigated by monitoring their absorption and emission spectra upon addition of metal ions, such as Li^+ , Na^+ , K^+ , Ba^{2+} , Sr^{2+} , Mg^{2+} , Ca^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Ag^+ , Hg^{2+} , Pb^{2+} , In^{3+} , and Al^{3+} in $\text{CH}_3\text{CN}/\text{DMSO}$ (99.5:0.5). The absorption spectrum of NTC exhibits a band centered around 380 nm, which remains unchanged upon addition of Li^+ , Na^+ , K^+ , Ba^{2+} , Sr^{2+} , Mg^{2+} , Ca^{2+} , Mn^{2+} , or Pb^{2+} . The addition of Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Ag^+ , Hg^{2+} , In^{3+} , or Al^{3+} leads to a redshift of the absorption maxima to different extents (see Figure S1 in the Supporting Information). In the case of Al^{3+} , the absorbance slightly decreases around 380 nm, and a new band appears around 440 nm.^[15] The absorption spectrum of NC shows a band centered around 370 nm, which remains unchanged upon addition of Li^+ , Na^+ , K^+ , Ba^{2+} , Sr^{2+} , Mg^{2+} , Ca^{2+} , Mn^{2+} , Ag^+ , or Pb^{2+} . The addition of Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Hg^{2+} , In^{3+} , or Al^{3+} leads to a redshift of the absorption maxima to different extents (see Figure S3 in the Supporting Information). The absorption band around 370 nm gradually decreases upon addition of 1 equiv. of Al^{3+} . Absorbance at 370 nm decreases sharply to its limiting value upon addition of one more equivalent of Al^{3+} , and a new prominent band appears at 400 nm with an isosbestic point at 378 nm.^[15] The color of the solution changes from colorless to light green.

Upon excitation at 395 nm, NTC does not show any significant fluorescence (quantum yield $\Phi = 0.00035$). The addition of Li^+ , Na^+ , K^+ , Ba^{2+} , Sr^{2+} , Mg^{2+} , Ca^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Ag^+ , Hg^{2+} , or Pb^{2+} has no effect on the fluorescence, whereas the addition of Zn^{2+} , Cd^{2+} , or In^{3+} results in a little enhancement of emission intensity and a redshift in the fluorescence spectrum. In contrast, the addition of Al^{3+} results in turn-on fluorescence with a 33-fold enhancement (quantum yield $\Phi = 0.0115$) of emission intensity around 458 nm, as shown in Figure 1. Fluorometric titrations were performed by adding different amounts of Al^{3+} to a solution of NTC, as shown in Figure 2. Simi-

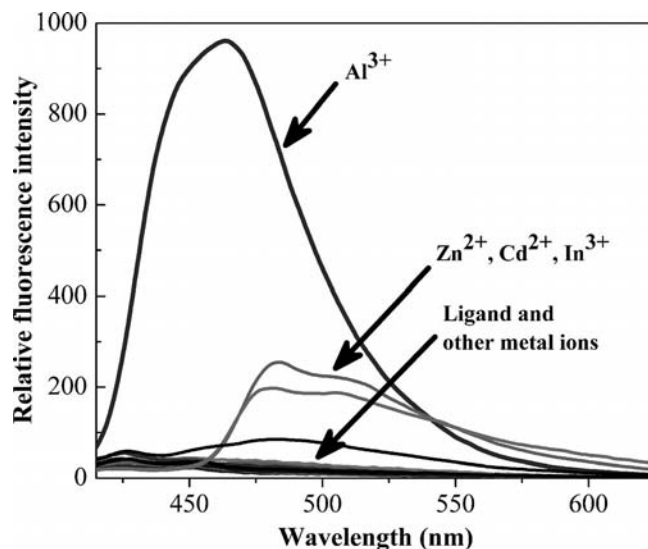


Figure 1. Fluorescence spectra (excitation at 395 nm) of a pure NTC solution (10 μM) and of solutions to which metal ions (50 equiv. Li^+ , Na^+ , K^+ , Ba^{2+} , Sr^{2+} , Mg^{2+} , Ca^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Ag^+ , Hg^{2+} , Pb^{2+} , In^{3+} , or Al^{3+}) were added.

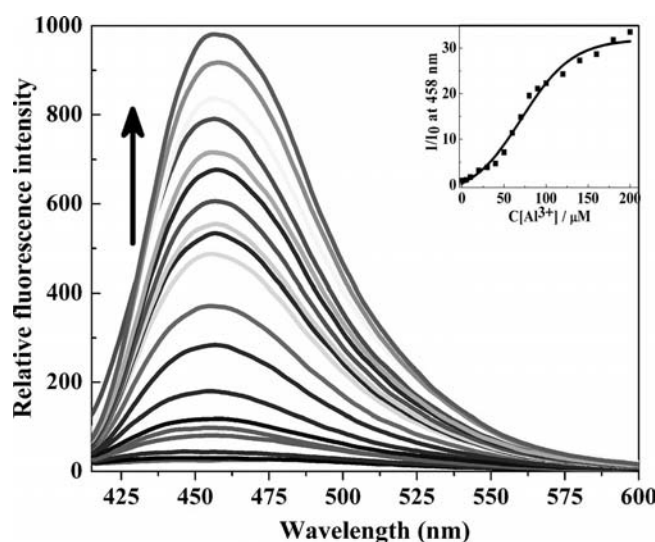


Figure 2. Fluorescence spectra (excitation at 395 nm) of a NTC solution (10 μM) recorded upon the sequential addition of Al^{3+} (0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 120, 140, 160, 180, 200, 300, and 400 μM). Inset: Emission intensity at 458 nm as a function of $[\text{Al}^{3+}]$.

larly, ligand NC does not show appreciable fluorescence emission (quantum yield $\Phi = 0.00026$) with excitation at 390 nm. The addition of Li^+ , Na^+ , K^+ , Ba^{2+} , Sr^{2+} , Mg^{2+} , Ca^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Ag^+ , Hg^{2+} , Pb^{2+} , or In^{3+} has no effect on the fluorescence. In contrast, the addition of Al^{3+} results in turn-on fluorescence with 700-fold enhancement of the emission intensity (quantum yield $\Phi = 0.1813$) around 450 nm, as shown in Figure 3. Changes in the fluorescence of NC upon sequential addition of increasing amounts of Al^{3+} are shown in Figure 4. A minimum of 2 equiv. and 1 equiv. of Al^{3+} can be easily detected by using 10 μM solutions of NTC and NC, respectively.

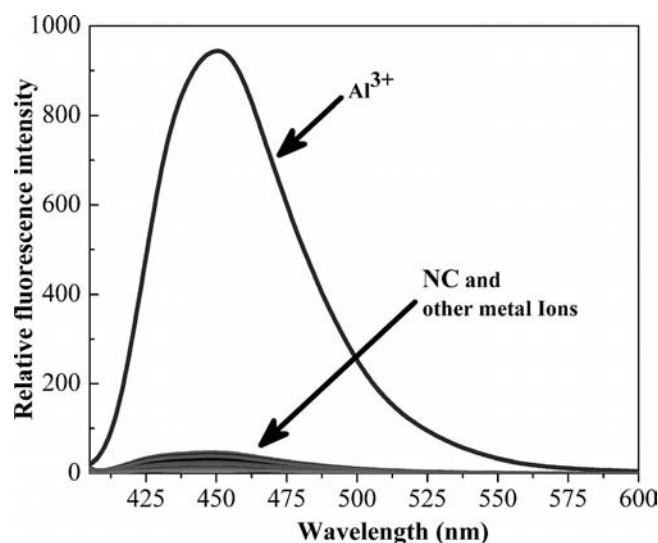


Figure 3. Fluorescence spectra (excitation at 390 nm) of a pure NC solution (10 μM) and of solutions to which metal ions (50 equiv. Li^+ , Na^+ , K^+ , Ba^{2+} , Sr^{2+} , Mg^{2+} , Ca^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Ag^+ , Hg^{2+} , Pb^{2+} , In^{3+} or Al^{3+}) were added.

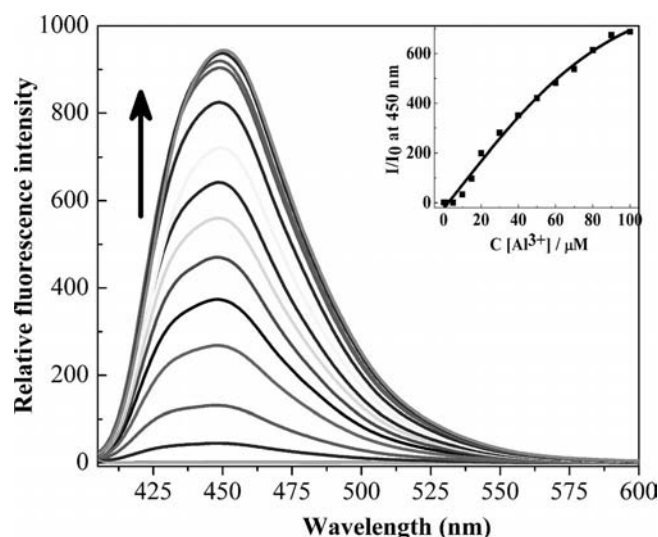


Figure 4. Fluorescence spectra (excitation at 390 nm) of a NC solution (10 μM) upon the addition of Al^{3+} (0, 1, 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 90, 100, 150, and 200 μM). Inset: Emission intensity at 450 nm as a function of $[\text{Al}^{3+}]$.

Competitive Detection of Al^{3+}

The selectivity of NC and NTC as fluorescent chemosensors for the detection of Al^{3+} was studied in the presence of various competing metal ions. For this purpose, NTC was treated with 10 equiv. of Al^{3+} in the presence of 10 equiv. of other metal ions (Figure 5a). There was no interference for the detection of Al^{3+} in the presence of Li^+ , Na^+ , K^+ , Ba^{2+} , Sr^{2+} , Ca^{2+} , Mg^{2+} , Mn^{2+} , Cd^{2+} , Ag^+ , or Pb^{2+} . A relatively low but clearly detectable response was observed in the presence of Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Hg^{2+} , or In^{3+} . Similarly, NC was treated with 10 equiv. of Al^{3+} in the presence of 10 equiv. of other metal ions. The data in Figure 5b show that there is no interference for detection of Al^{3+} in the presence of all other metal ions tested except for Cu^{2+} and Hg^{2+} . In the case of Cu^{2+} and Hg^{2+} , quenching of fluorescence was observed. The NC responses for Al^{3+} in the presence of Fe^{2+} , Co^{2+} , Ni^{2+} , or Zn^{2+} are relatively low but clearly detectable. Thus, NC can be used

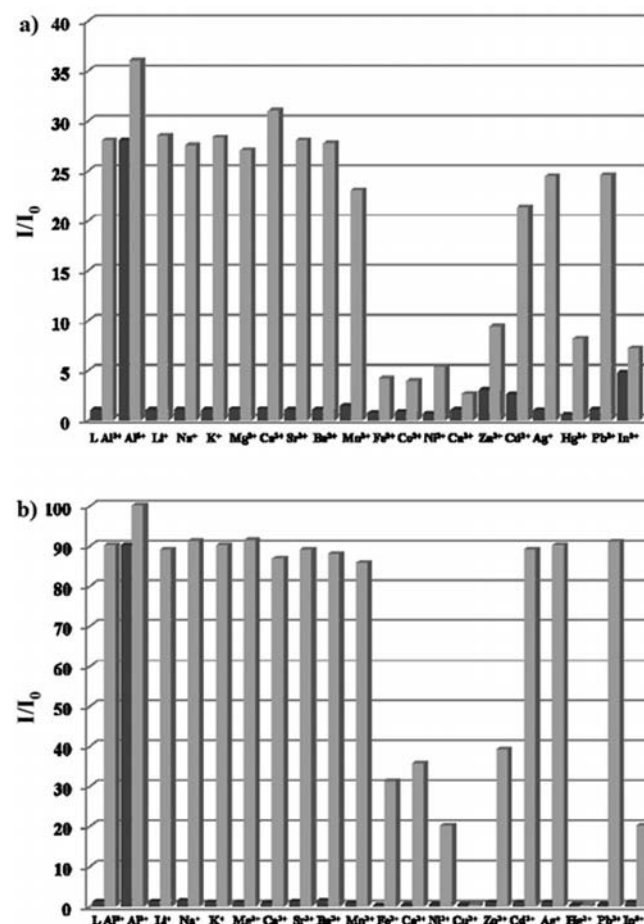
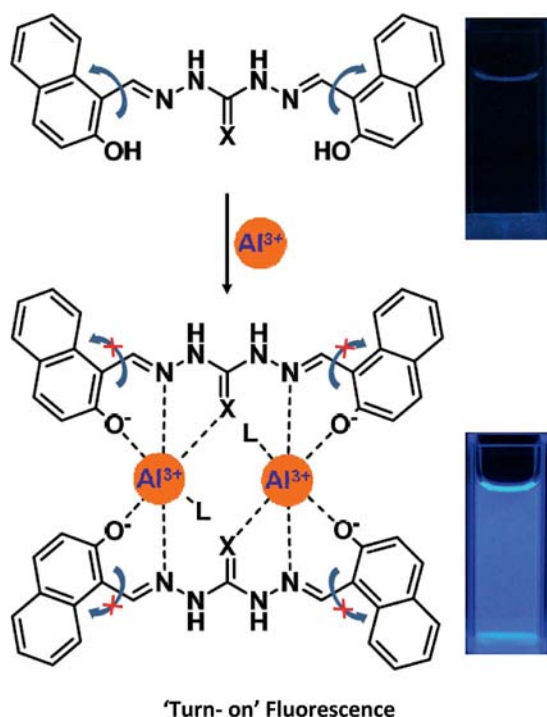


Figure 5. Relative fluorescence of (a) NTC (emission intensity at 458 nm) and (b) NC (emission intensity at 450 nm) and their $\text{Al}(\text{III})$ complexes in the presence of various metal ions. Dark gray bar: (a) NTC (10 μM) and (b) NC (10 μM) with 10 equiv. of the metal ion stated. Light gray bar: Solutions (10 μM) of (a) NTC and (b) NC with 10 equiv. of Al^{3+} and 10 equiv. of the metal ion stated. The relative fluorescence intensities of (a) NTC and (b) NC solutions (10 μM) without Al^{3+} (dark gray bar, L) and with 10 equiv. of Al^{3+} (light gray bar, L) are included as controls.

as a selective fluorescent probe for Al^{3+} detection in the presence of most competing metal ions except for Cu^{2+} and Hg^{2+} . With NTC and NC, Al^{3+} can be selectively detected in the presence of millimolar concentrations of Li^+ , Na^+ , K^+ , Ba^{2+} , Sr^{2+} , Ca^{2+} , or Mg^{2+} (Figure S7 and Figure S8 in the Supporting Information).

Stoichiometry of Al(III) Binding

Job plots obtained from the absorbance data show a 1:1 stoichiometry for the complexation of Al^{3+} with both NC and NTC.^[15] The 1:1 binding stoichiometry of NC with Al^{3+} was also supported by ^1H NMR spectra of NC in CD_3CN recorded upon addition of various amounts of Al^{3+} .^[15] The coordination of NC with Al^{3+} did not lead to significant changes in the chemical shifts of aromatic and imine protons. Interestingly, deprotonation of all the phenolic hydroxy groups ($\delta = 11.87$ ppm) was observed upon the addition of 1 equiv. of Al^{3+} . Deprotonation of the naphthol moieties followed by the coordination of naphthoxy groups to Al^{3+} is depicted in Scheme 2. These data were further confirmed by mass spectrometric detection of a doubly deprotonated NC: Al^{3+} complex.^[15] MALDI/TOF-MS data show the formation of a complex containing two molecules of doubly deprotonated NC and two aluminum(III) ions (MS: calcd. for $\text{C}_{46}\text{H}_{32}\text{Al}_2\text{N}_8\text{O}_6$ 845.75; found 846.21). A complex containing two molecules of doubly deprotonated



Scheme 2. Proposed mechanism of formation of a $2\text{L}:2\text{Al}^{3+}$ complex ($\text{L} = \text{NC}$ or NTC). Restricted isomerization of $\text{C}=\text{N}$ is indicated by crossed arrows. Turn-on fluorescence of ligands upon complexation with Al^{3+} is shown (right). $\text{X} = \text{O}$ or S ; $\text{L} = \text{H}_2\text{O}$ or ClO_4^- .

NTC and two aluminum(III) ions was also detected (MS: calcd. for $\text{C}_{46}\text{H}_{32}\text{Al}_2\text{N}_8\text{NaO}_4\text{S}_2$ [$2\text{NTC} + 2\text{Al}^{3+} + \text{Na}^+ - 4\text{H}^+$] 901.15; found 901.18).

Response Parameter and Binding Constants

The response parameter α , which is defined as the ratio of the free ligand concentration to the initial concentration of the ligand, is plotted as a function of the logarithm of the Al^{3+} concentration (Figure 6).

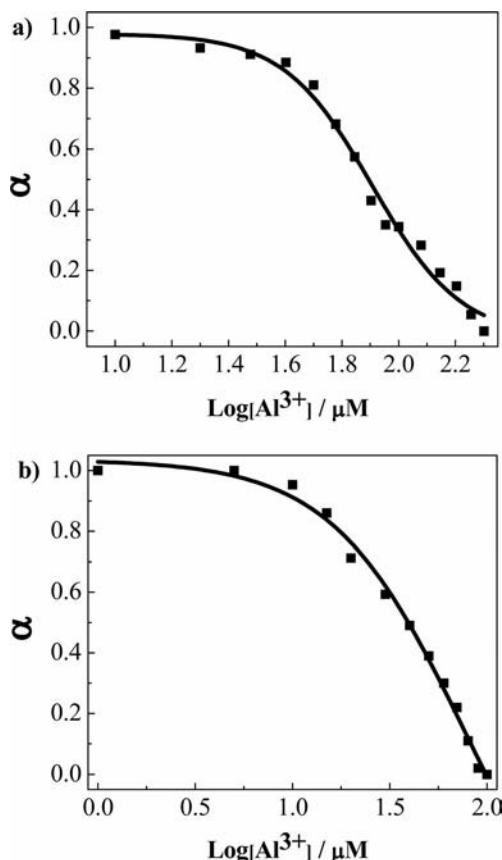


Figure 6. Response parameter values (α) plotted as a function of the logarithm of the Al^{3+} concentration for (a) NTC and (b) NC. Parameter α is defined as the ratio between the free ligand concentration and the initial concentration of the ligand.

This plot can serve as the calibration curve for detection of Al^{3+} . The association constants ($\log K_a$) of NC and NTC for Al^{3+} were calculated to be 14.5 and 14.1, respectively, by using Li's equations.^[16]

NC and NTC ligands have no appreciable fluorescence emission in their free form and show bright fluorescence on complexation with Al^{3+} . This phenomenon of turn-on fluorescence can be explained by considering the restricted $\text{C}=\text{N}$ isomerization mechanism. Rapid $\text{C}=\text{N}$ isomerization of imine double bonds in the ligands NC and NTC is responsible for nonradiative deactivation of the fluorophore in the excited state. Hence, these ligands exhibit very poor fluorescence quantum yields in their unbound form. To

support this mechanistic proposal, we synthesized two control compounds by condensing 1-naphthaldehyde with thiocarbohydrazide or carbohydrazide in aqueous ethanol (Supporting Information). We then studied the emission behavior of these two Schiff bases in the presence of Al³⁺. Both compounds are nonfluorescent and do not show any fluorescent turn-on behavior in the presence of Al³⁺. Presumably, this is due to the absence of phenolic OH groups in the control compounds. The control compounds cannot coordinate properly with Al³⁺, and hence free rotation around C=N is not restricted. Therefore, the control ligands exhibit very poor fluorescence quantum yields in their unbound form as well as in the presence of Al³⁺. Thus, control studies have confirmed that the turn-on fluorescent behavior of NC and NTC in the presence of Al³⁺ is based on restricted C=N isomerization. There are some reports in the recent past describing the specific detection of various metal ions with Schiff base receptors, based on the C=N isomerization mechanism.^[14]

Conclusions

We have demonstrated that Schiff base derivatives naphthaldehyde–carbonohydrazone (NC) and naphthaldehyde–thiocarbonohydrazone (NTC) can serve as selective fluorometric chemosensors for Al³⁺. The work presented here provides access to Al³⁺ probes through a highly economical, simple, and straightforward synthetic route. We have exploited two signal transduction mechanisms, namely, chelation-enhanced fluorescence and restricted C=N isomerization, to design NC and NTC ligands as turn-on fluorescent chemosensors for aluminum(III) ions. Al³⁺ can be detected in the presence of most of the competing metal ions by using NC and NTC. Investigations towards the development of more sophisticated chemosensor systems based on the design principle reported here for recognition of cations and anions are in progress in our laboratory.

Experimental Section

Materials and Instruments: All the solvents and reagents were obtained from Sigma–Aldrich and used as received unless otherwise mentioned. The solutions of metal ions were prepared from Al(ClO₄)₃·9H₂O, LiClO₄·3H₂O, NaClO₄, KClO₄, Ca(ClO₄)₂·4H₂O, Mg(ClO₄)₂, Sr(NO₃)₂, Ba(ClO₄)₂, Mn(ClO₄)₂·6H₂O, Fe(ClO₄)₂·H₂O, Co(ClO₄)₂·6H₂O, Ni(ClO₄)₂·6H₂O, Cd(ClO₄)₂·H₂O, Ag(ClO₄)₂, Hg(ClO₄)₂, Pb(ClO₄)₂, Cu(ClO₄)₂·6H₂O, Zn(ClO₄)₂·6H₂O, and In(NO₃)₃ in CH₃CN. ¹H and ¹³C NMR spectroscopic data were recorded with a Bruker AV-400 spectrometer (in [D₆]-DMSO, tetramethylsilane was used as an internal standard). Mass spectra were obtained with a Shimadzu 2020 LC-MS and a Bruker Ultraflex II MALDI/TOF spectrometer. IR spectra were recorded with a Bruker IFS 66/V spectrometer with KBr discs. Elemental analyses were carried out with a ThermoScientific FLASH 2000 Organic Element Analyzer. UV/Vis spectra were recorded with a Perkin–Elmer Lambda 900 spectrophotometer. Fluorescence spectra were recorded with a Perkin–Elmer LS 55 spectrophotometer.

General Procedure for the Synthesis of NC and NTC: A solution of 2-hydroxy-1-naphthaldehyde (1.0 g, 6 mmol) in ethanol (40 mL) was added slowly to a solution of thiocarbohydrazide or carbohydrazide (3 mmol) in water (40 mL). Initially, the solution turned turbid, and after complete addition the solution became clear. The reaction mixture was heated at reflux with stirring for 24 h. The reaction mixture was then cooled to room temperature, and a precipitate was filtered off, washed with ethanol, and dried under vacuum to obtain naphthaldehyde–carbonohydrazone (NC) or naphthaldehyde–thiocarbonohydrazone (NTC) in quantitative yield.

Bis[(2-hydroxynaphthyl)methylene] Carbonic Dihydrazide [Naphthaldehyde–Carbonohydrazone (NC)]: Yield 94%. ¹H NMR (400 MHz, [D₆]DMSO): δ = 7.22–7.24 (d, *J* = 8.8 Hz, 2 H), 7.38–7.42 (m, 2 H), 7.58–7.62 (m, 2 H), 7.87–7.90 (m, 4 H), 8.33–8.35 (d, *J* = 8.4 Hz, 2 H), 9.19 (s, 2 H), 11.00 (s, 2 H), 11.87 (br, 2 H) ppm. ¹³C NMR (400 MHz, [D₆]DMSO): δ = 109.4, 118.6, 121.6, 123.3, 127.6, 127.9, 128.7, 131.5, 131.9, 143.2, 151.6, 156.7 ppm. MS (EI): calcd. for C₂₃H₁₈N₄O₃ [M]⁺ 398.14; found 399.2 [M + H]⁺.

Bis[(2-hydroxynaphthyl)methylene] Carbonothioic Dihydrazide [Naphthaldehyde–Thiocarbonohydrazone (NTC)]: Yield 94%. ¹H NMR (400 MHz, [D₆]DMSO): δ = 7.23–7.25 (d, *J* = 9.2 Hz, 2 H), 7.39–7.43 (m, 2 H), 7.59–7.63 (m, 2 H), 7.88–7.95 (m, 4 H), 8.24–8.52 (br, 2 H), 9.16–9.64 (br, 2 H), 10.61 (br, 1 H), 12.07 (s, 2 H), 12.88 (br, 1 H) ppm. ¹³C NMR (400 MHz, [D₆]DMSO): δ = 109.3, 118.7, 121.0, 123.5, 127.8, 127.9, 128.7, 131.7, 132.6, 145.8, 157.1, 174.0 ppm. MS (EI): calcd. for C₂₃H₁₈N₄O₂S [M]⁺ 414.12; found 415.4 [M + H]⁺. C₂₃H₁₈N₄O₂S (414.48): calcd. C 66.65, H 4.38, N 13.52, S 7.74; found C 66.7, H 4.39, N 13.51, S 7.72.

Measurements of Photophysical Properties: Cells with a diameter of 1 cm were used for absorption and emission titrations. For UV/Vis and fluorescence titrations, stock solutions of NC and NTC were prepared (*c* = 2 mM) in DMSO. The solutions of guest cations were prepared in CH₃CN with concentrations in the order of 1 mM. Samples of NC, NTC, and metal ions were prepared from the stock solutions. The excitation wavelengths were 390 and 395 nm for NC and NTC, respectively, with 15 nm excitation and 5 nm emission slit widths.

Job Plot by the UV/Vis Method: A series of solutions containing NC or NTC and Al(ClO₄)₃ were prepared in such a way that the sum of the total concentration of metal ions and ligand remained constant (100 μM). The mole fraction *x* of Al³⁺ was varied from 0.1 to 1.0. The corrected absorbance ([A – A₀]/[A₀]) at 440 nm for NTC and at 400 nm for NC was plotted against the mole fraction of the Al³⁺ solution.

Determination of Binding Constants: The response parameter *a* is defined as the ratio of the free ligand concentration to the initial concentration of the ligand. When *a* is defined as the ratio between the free ligand concentration [L] and the total concentration of ligand [L]_T:

$$\alpha = \frac{[L]}{[L]_T}$$

a can be determined from the emission changes in the presence of different concentrations of Mⁿ⁺:

$$\alpha = \frac{[I - I_0]}{[I_1 - I_0]}$$

where *I*₁ and *I*₀ are the limiting emission values for *a* = 1 (in the absence of Mⁿ⁺) and *a* = 0 (when the probe completely coordinates to Mⁿ⁺), respectively.

Li et al.^[16] converted the Tse equation^[17] to the following equation that can be used for any stoichiometric ratio between the ligand and the analyte:

$$[M^{n+}]^m = \frac{1}{n \cdot K} \cdot \frac{1}{[L]^n} \cdot \frac{1-\alpha}{\alpha^n}$$

Here, K is the equilibrium constant of complex formation, M_nL_n is the complex, L is the ligand, $[L]$, $[M^{n+}]$, and $[M_nL_n]$ are the concentrations of the respective species. Parameter α is the ratio between free ligand concentration, $[L]$, and the initial concentration of ligand, $[L]_T$. In our case, the stoichiometric ratio of Al^{3+} and fluoroionophore is 1:1. So, this equation can be written as:

$$[Al^{3+}] = \frac{1}{3KL^2} \cdot \frac{1-\alpha}{\alpha^2}$$

Calculation of Quantum Yields: Fluorescence quantum yields were determined by using perylene ($\Phi = 0.94$) in cyclohexane as reference.^[18] The quantum yields of NC, NTC, and their Al^{3+} complexes with excitation at 395 nm were calculated according to the following equation.

$$\Phi_x = \Phi_s(A_s S_x)/(A_x S_s)(n_x/n_s)$$

Here, A_x is the absorbance of the NC- Al^{3+} or NTC- Al^{3+} complex and A_s is the absorbance of the perylene standard. S_x is the integrated fluorescence emission corresponding to Al^{3+} complexes and S_s is that of the perylene standard. The parameters n_x and n_s are the refractive indexes of the solvents used for the complex and standard sample measurements, respectively.

Supporting Information (see footnote on the first page of this article): UV/Vis spectra, Job plots, mass, IR, and NMR spectra.

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