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Communication

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A Chemosensor Built with Rhodamine Derivatives Appended to an Aromatic Platform via 1,2,3-Triazoles: Dual Detection of Aluminum(III) and Fluoride/Acetate Ions

Shubhra B. Maity and Parimal K. Bharadwaj*

Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur 208016, India

Supporting Information

ABSTRACT: A triazole-ring-appended rhodamine dye (**L**) has been synthesized that serves as a chromogenic and fluorogenic sensor for dual sensing of aluminum(III) and fluoride or acetate ions specifically.

Aluminum is the third most abundant element in the earth's crust, accounting for almost 8.3% of its mass.[1] Regarding toxicological effects of aluminum, its primary targets are different from those of heavy metals.[2] Aluminum is alleged to interfere with the functioning of iron−sulfur proteins of the respiratory chain, and it also raises the risk of Alzheimer's disease.[3] The widespread use of aluminum in water treatment, as a food additive, and in many industrial activities including the manufacturing of cars and computers often exposes people to this metal.[1] Detection of the Al^{3+} ion in the presence of a host of other cations is, therefore, of biological as well as environmental relevance. Graphite furnace atomic absorption spectroscopy and inductively coupled plasma atomic emission spectroscopy are commonly employed methods for detection of aluminum. Both of these techniques are generally time-consuming and expensive as well. In contrast, optical detection via fluorescence is an operationally easy technique besides being highly sensitivity. Detection of anions through emission readout has attracted a lot of attention[4] because of the many recognized biological roles played by anions. The smallest anion, fluoride, with high charge density is of particular importance because of its roles in dental care and other areas.[5] The acetate ion, on the other hand, is a critical component of various metabolic processes and also plays important roles in several enzymes and antibodies.[6] The development of sensors selective for fluoride and acetate ions is, therefore, of crucial importance. Few fluorescence chemosensors or chemodosimeters for aluminum,[7] fluoride,[8] and acetate ions[9] have been reported that are operational in purely organic media, restricting their applications as sensors. When a chemosensor is operational in an aqueous medium or in a mixed aqueous−organic medium, its scope increases to a great extent.

Since Czarnik's pioneering work on the Cu^{2+}-induced ring-opening reaction of a rhodamine B derivative[10] to afford strong fluorescence, many interesting studies on rhodamine derivatives have been reported.[11] A rhodamine derivative as a dye molecule is an excellent choice as a chemosensor because the spirolactum ring does not show any emission, but once the ring is broken by an ion to afford the corresponding amide, an emission with high quantum yield is observed. In this paper, we report the synthesis and photophysical behavior of a 1,2,3-triazole-ring-appended rhodamine dye **L** for selective colorimetric as well as fluorimetric detection of the Al^{3+} ion in a methanolic aqueous medium. We show here that once the Al^{3+} ion is anchored in the dye, it can specifically detect fluoride and acetate ions in the presence of a host of other anions.

The dye **L** and a reference rhodamine derivative, **L′**, were synthesized in several steps (see the synthetic details in the Supporting Information, SI). Their molecular structures are illustrated in Figure 1. Both compounds were characterized by ^1H and ^{13}C NMR spectroscopy, electrospray ionization mass spectrometry, and elemental analysis (see the SI).

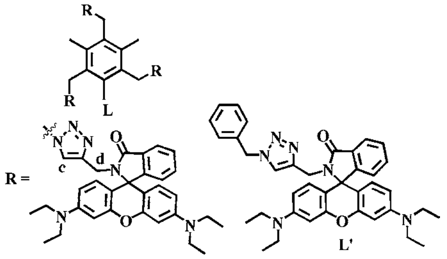

Figure 1. Molecular structures of **L** and reference dye **L′**.

Because of the lack of solubility of compound **L** in a purely aqueous medium, all absorption and emission measurements were carried out in a mixed 90% methanol−water medium. Perchlorate salts of metal ions that include Na^+, K^+, Mg^{2+}, Ca^{2+}, Al^{3+} Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ag^+, Pb^{2+}, and Fe^{3+} were used in the studies. For Ce^{3+} and Cr^{3+} ions, their nitrate salts were used. Neither metal-free **L** nor the presence of any one of the metal ions (except Al^{3+}) listed above show any absorption band of significant intensity in the visible region. Of the transition metals used, only Cr^{3+} and Fe^{3+} show slight intensity enhancement because of their higher Lewis acidic strength. In the presence of the Al^{3+} ion, however, the color of the solution changes in 30 min to pink, with a strong band appearing at 555 nm (Figure 2). This change from colorless to pink can be observed with the naked eye and is due to breaking of the spirolactum bond in the presence of the Al^{3+} ion, leading to the delocalized xanthane moiety of the rhodamine group.[12]

Upon excitation at 540 nm, no noticeable emission is observed with the dye ($\Phi = 0.002$) in a metal-free state or in

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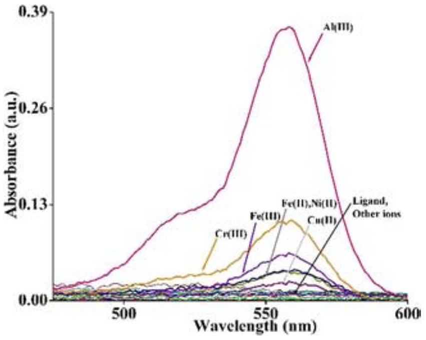


Figure 2. Absorption spectra of **L** (20 μM) and that of **L** in the presence of 10 equiv of various metal ions in a mixed aqueous medium [CH_3OH-H_2O, 9:1 (v/v)].

the presence of the mono- and divalent metal ions listed above. Among the trivalent metal ions, both Cr^{3+} and Fe^{3+} exhibit a weak and broad emission band around 570 nm with a slight increase of the emission quantum yield (Φ = 0.12 and 0.09, respectively). However, in the presence of the Al^{3+} ion, a strong emission band centering at 577 nm (quantum yield, Φ = 0.43) is observed with almost 200 times fluorescence enhancement compared to the metal-free **L** (Figure 3). This is assignable[11] to the delocalized xanthane moiety of the rhodamine group that results from breaking of the spirolactum ring in the presence of the Al^{3+} ion.

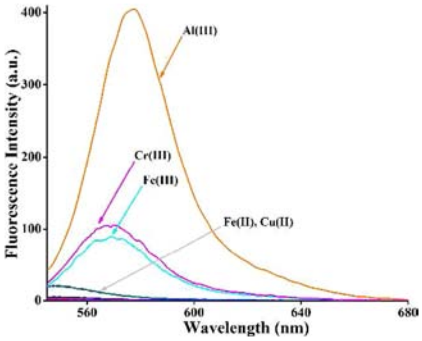


Figure 3. Emission spectra of **L** (4 μM) in the presence of 10 equiv of various metal ions in a mixed aqueous medium [CH_3OH-H_2O, 9:1 (v/v); excitation at 540 nm; slit, 3 nm/3 nm].

The reference compound **L′** bearing a single triazole moiety was prepared to probe whether the tripodal moiety present in **L** is necessary for the selective detection of Al^{3+}. Under identical conditions of measurements, the reference rhodamine derivative **L′** behaved differently compared to that of **L**. In the case of **L′**, the selectivity for the Al^{3+} ion is lost. Most of the transition-metal ions exhibit absorption and emission characteristics similar to those of Al^{3+} (see Figures S7 and S8 in the SI). This suggests that the tripodal platform is necessary for selectivity of the Al^{3+} ion.

To investigate the binding stoichiometry between **L** and the Al^{3+} ion, both Job's plot and Benesi–Hildebrand plot experiments[13] (see Figures S9 and S10 in the SI) were carried out, with the results showing a 1:1 complexation. Such 1:1 complex formation of a tripodal dye molecule with a Cu^{II} ion is available in the literature.[14] The 1:1 complexation is also supported from mass spectral studies, which show a prominent peak at 589.3210 (60%) due to $[L + Al^{3+} + H_2O]^{3+}$ (Figure S11 in the SI). The binding constant between **L** and the Al^{3+} ion was calculated from the absorption titration result and was found to be 2.55×10^4 (see Figure S12 in the SI).

The selectivity of the dye for the Al^{3+} ion over other metal ions was probed by competition experiments in which the dye was first mixed with 30 equiv of a metal ion, followed by the addition of 10 equiv of Al^{3+}. Emission spectroscopy was used to monitor these competition events.

As can be seen from Figure 4, the presence of background metal ions has either no or a small effect on the emission response of the dye to the Al^{3+} ion. Therefore, **L** is shown to be a promising selective fluorescence sensor for Al^{3+} in the presence of most competing metal ions.

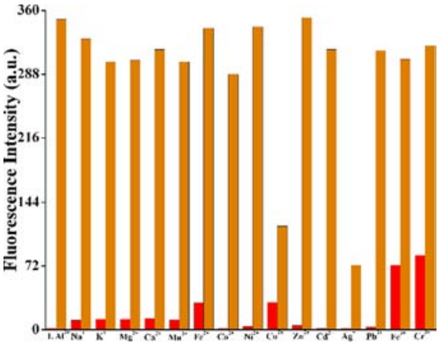


Figure 4. Selectivity of the dye **L** for the Al^{3+} ion in a methanolic aqueous medium [CH_3OH-H_2O, 9:1 (v/v)]. Red bars indicate the fluorometric response of the dye with 30 equiv of the metal ion of interest, and orange bars represent the final integrated fluorescence response after the addition of 10 equiv of Al^{3+} to each solution containing other metals over the initial integrated emission. Dye concentration = 4 μM.

^1H NMR titration of **L** in the presence of different equivalent amounts of Al^{3+} ions was conducted in a $CDCl_3-CD_3OD$ [1:1 (v/v)] medium. The complexation mode of **L** toward the Al^{3+} ion, with spectral differences upon binding of the metal to the dye, is depicted in Figure S13 in the SI. The signals of H_c and H_d (Figure 1 shows c and d protons) shifted downfield by 0.62 and 0.11 ppm, respectively, upon the addition of 1.0 equiv of Al^{3+} salt. These signals remain unaltered after the addition of up to 5 equiv of Al^{3+} salt, indicating 1:1 complexation. In addition, IR spectra of **L** and its Al^{3+} complex were also recorded. It is observed that, upon addition of the Al^{3+} ion, the characteristic carbonyl amide stretching frequency shifts from 1692 cm^{-1} in **L** to 1677 cm^{-1} in the complex (see Figures S14 and S15 in the SI).

Interestingly, when the Al^{3+} complex of the dye is treated with a sodium salt of either F^- or AcO^-, the color of the solution changes from pink to colorless and the emission is completely quenched within 10 min (Figure 5), while other anions such as Cl^-, Br^-, I^-, NO_3^-, SO_4^{2-}, ClO_3^-, PF_6^-, and BF_4^- do not show any change.

This observation suggests that the dye, while acting as a sensor for the Al^{3+} ion, could serve as a sensor for F^- and AcO^- anions as well. Once the Al^{III} ion interacts with the dye, the spirolactum ring is broken, giving high fluorescence. In the presence of F^- or AcO^-, the metal ion is abstracted and the spirolactum ring closes (Scheme 1), leading to the absence of fluorescence.[15] We get almost all of the dye **L** back along with minute amounts of other products after fluoride/acetate is added to the aluminum complex.

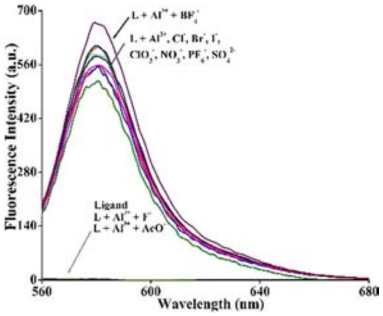
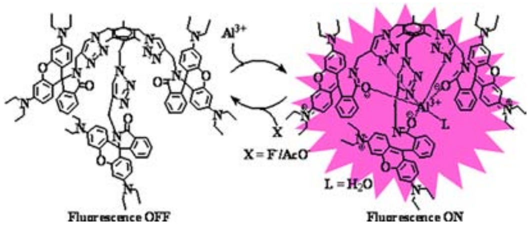


Figure 5. Emission responses of the aluminum complex of ligand **L** (10 μM) toward various anions (100 μM) in a mixed aqueous medium [CH_3OH-H_2O, 9:1 (v/v); excitation at 540 nm; slit, 3 nm/3 nm].

Scheme 1. Proposed Mechanistic Pathway for Sensing



In conclusion, we have developed a tripodal ligand, **L**, generated from the click reaction between an alkyne derivative of rhodamine B and an azide derivative of mesitylene. It serves as a colorimetric and fluorimetric sensor for Al^{3+} as well as F^- and AcO^- ions without interference from other cations and anions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detail experimental procedures, NMR and mass spectra, and additional UV−visible and fluorescence spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: pkb@iitk.ac.in.

Notes

The authors declare no competing financial interest.

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