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TO WHOM IT MAY CONCERN

This is to certify that the following activities were conducted under the Collaborative Research Activities signed between Government General Degree College, Mangalkote, Panchanantala, Khudrun Dighi, P.O: Majhigram, Block – Mangalkote, Dist: Purba Bardhaman (W.B.) INDIA, PIN-713132 and Dr. Partha Roy, Professor, Department of Chemistry, Jadavpur University, Kolkata 700032, West Bengal, India for a period of five years with effect from 11/01/2022.

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Short communication

Turning a fluorescent probe for Al^{3+} into a pH sensor by introducing Cl-substitution

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ABSTRACT

Here we report a new Schiff-base molecule, 4,4′-sulfonylbis(2-(5-chloro-2- hydroxybenzylideneamino)phenol) (**H_4L^{Cl}**) as a colorimetric and fluorescent probe for pH. On increase in pH from 2.0 to 12.0, the fluorescence intensity of **H_4L^{Cl}** increases by 45-fold at 509 nm in Britton-Robinson buffer (λ_{ex} = 380 nm). Quantum yield of the probe also increases on increase in pH of the media. This enhancement of fluorescence intensity is mainly due to the deprotonation of the phenolic OH groups in the sensor molecule. The pK_a of the probe has been determined to be 7.18. Theoritical studies show that the increment in intensity occurs via ICT-AIE controlled pathway. Naked eye detection is possible by noting the color change of the solutions observed under visible and UV light. Several cations and anions do not interfere in the pH sensing properties of **H_4L^{Cl}**. It is to mention that the compound without Cl-substituion, namely, 4,4′-sulfonylbis(2-(-2-hydroxybenzylideneamino)phenol), was reported earlier as a chemosensor for Al^{3+} ion (New J. Chem. 41 (2017) 10677). Introduction of Cl changes sensing preference of the Schiff-base from Al^{3+} to pH. **H_4L^{Cl}** has been used for pH detection of river water.

1. Introduction

It is well known that several biological transformations, which occur at a particular pH, frequently involve protonation and deprotonation of biomolecules, and alteration in pH may hamper the processes. So, extracellular and intracellular pH detection is of great importance because of its connection with biological processes like cell growth, endocytosis, ion transport, etc. [1–4]. pH is the negative logarithm of $[H^+]$ (pH = $-\log[H^+]$). It is an important parameter employed in many areas of research such as chemical, environmental and medical sciences, and industries as well [5–9]. Water is one of the basic needs for all living organisms. World Health Organization (WHO) recommends that pH of drinking water should be in the range of 6.5–8.5 [10,11]. If the pH of the water is altered, it can affect greatly *in vivo* functions and different activities in the human body [12]. In recent years, rapid urbanization, development of industries, household activities, acid rain, and huge plastic uses are causing water pollution which in turn changes the pH of the water [13,14]. Thus, pH plays a key role in monitoring the quality of water.

Generally, potentiometric pH glass electrodes are applied to determine the pH in laboratory. Although this technique is successful to measure pH but has several limitations such as frequent calibration, electrical interference, etc. Moreover, this technique could not be employed during intracellular pH measurements [5,15,16]. On the contrary, optical-based fluorescent pH sensors have no such shortcomings. In addition, fluorescent pH sensors have drawn special interest to researchers because of their high sensitivity, selectivity, ease to handle, low cost, and harmless applications in living cells, etc. [17]. In recent years, great efforts have been devoted to the development of efficient fluorescent chemosensors for the detection of pH in environmental samples [18–22]. Different fluorophoric platforms such as rhodamine, 4-methyl-2,6-diformylphenol (DFP), etc. have been used to develop chemosensors for pH [23–25]. We have been working on the development of fluorescent sensors including probes for pH based on DFP for quite a time [26–30]. It has been learnt that substitution(s) on aromatic ring or increase in decolalization by introducing aromatic ring(s) has significant effect on pH sensing properties. However, the design of efficient fluorescent probes for monitoring pH has remained challenging for real samples. Till date, only few fluorescent probes containing sulfone moiety have been reported for various ions [31,32]. But reports on pH sensors containing sulfone moiety are rare.

In this context, here we report the synthesis, characterization and pH

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Modulation of aluminum sensing properties of a sulphone group containing chemosensor and its biological applications

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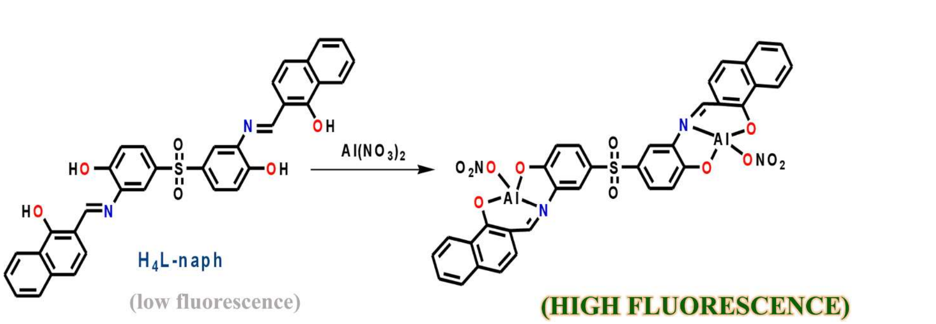
HIGHLIGHTS

- A sulfone based chemosensor, 2,2′-(1E)-(5,5′-sulfonylbis(2-hydroxy-5,1-phenylene))bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)dinaphthalen-1-ol (H_4L-naph), was synthesized.
- H_4L-naph with two binding pockets explored for selective Al^{3+} sensing in DMF- HEPES buffer (1:4, v/v, pH 7.4).
- In comparison to an analogous probe having phenyl, it showed fluorescence in longer wavelength.
- It was applied in living cell imaging studies.

GRAPHICAL ABSTRACT



ARTICLE INFO

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ABSTRACT

A chemosensor with two binding pockets facilitates binding of one metal ion in either of the pockets providing a better chance for the interaction and hence recognition of the cation. We report here a chemosensor, namely 2,2′-(1E)-(5,5′-sulfonylbis(2-hydroxy-5,1-phenylene))bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)dinaphthalen-1-ol (H_4L-naph), for selective sensing of Al^{3+} in DMF- HEPES buffer (1:4, v/v, pH 7.4). It shows almost 100-fold fluorescence enhancement at 532 nm (λ_{ex} = 482 nm) in the presence of Al^{3+}. Its quantum yield and excited state lifetime enhances significantly with the cations. H_4L-naph forms a 1:2 complex with Al^{3+} with an association constant value of 2.18×10^4 M^{-2}. Fluorescence enhancement may be attributed to CHEFF mechanism and restriction of >C=N isomerization. Effect of the presence of naphthyl rings instead phenyl ring of a previously reported probe has resulted shifting of excitation/emission peak towards longer wavelength. The probe has been applied to image Al^{3+} in L6 cells with no significant cytotoxicity.

1. Introduction

Some of the research groups are actively engaged in the development of chemosensors for Al^{3+} ions [1–3]. It is not essential for biological functions but its excess deposit on human body may create some health issues. Surplus accumulation of aluminum is related to some nerve related issues, Parkinson's disease. osteomalacia, etc. There is debate on its role on Alzheimer's disease (AD) [4]. Few groups believe that it has no role in AD [5]. However, some groups mentioned its role in AD. As aluminum is widely used in food industries, textile industries, domestic

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