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Research Paper

Rhodamine based chemosensor for trivalent cations: Synthesis, spectral properties, secondary complex as sensor for arsenate and molecular logic gates

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ABSTRACT

A rhodamine based chemosensor, 2-(2-(5-bromo-2-hydroxybenzylideneamino)ethyl)-3',6'-bis(diethylamino)spiro[isoindoline-1,9′-xanthen]-3-one (HL), has been explored for detection of trivalent cations, Al^{3+}, Fe^{3+} and Cr^{3+}. It has been synthesized by Schiff-base condensation and characterized by standard techniques including X-ray single crystal diffraction analysis. HL is colorless and non-fluorescent. In the presence of trivalent cations, colorless solution of HL turns pink. In UV–vis spectra, gradual addition of the cation produces gradual increment in absorption band at 528 nm in HEPES buffer in methanol:water (7:3, *v/v*) (pH 7.2). No other monovalent and divalent cation except Cu^{2+} is able to cause color change. HL is almost non-fluorescent in HEPES buffer in methanol:water (7:3, *v/v*) (pH 7.2) when it is excited at 500 nm. Emission intensity increases gradually at 552 nm in the presence of increasing concentration of trivalent cations. Intensity increases by 98, 50 and 38 fold in the presence of one equivalent of Al^{3+}, Cr^{3+} and Fe^{3+}, respectively. No other metal ion can cause an enhancement in emission intensity of HL suggesting selectivity of the probe towards these trivalent cations. Quantum yield of HL complexes with M^{3+} increases significantly compared to that of free HL. Non-fluorescent HL is a closed ring compound whereas trivalent metal ions induce ring opening of spirolactam ring and complex formation enabling strong fluorescence. Limit of detection (LOD) values of HL have been determined to be 1.18, 1.80 and 4.04 nM for Al^{3+}, Cr^{3+} and Fe^{3+}, respectively, suggesting very high sensitivity towards the cations. Job's plot analysis and mass spectral analysis shows 1:1 complex formation between HL and metal ion. AsO_4^{3-} ion quenches emission intensity of HL–Al^{3+} complex as the anion snatches Al^{3+} from its complex thereby leading to the generation of non-fluorescent spirolactam unit. DFT and TD-DFT studies have been performed to investigate different optimized structures and various spectral transitions. Al^{3+} complex with HL acts as fluorescent sensor for arsenate ion as the anion snatches Al from Al-HL complex and it returns back to its ring closed spirolactam form. Advanced level molecular logic devices e.g. different 3 and 5 input advanced level logic gates, molecular keypad lock and memory device have been constructed using these properties and interpreted.

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1. Introduction

Development of new fluorescent chemosensors for trivalent metal ions (M^{3+}), is currently of great research interest because they play very important roles in various biological systems and are directly involved in cell function [1]. Chemosensors based on ion-induced changes that resulted in alteration in fluorescence appear to be significantly important due to their facile, simple and high sensitive detection of target analytes. Even though there are a large number of chemosensors that have been developed for divalent cations, very few probes are reported for trivalent cations [2–4]. Aluminum, the third most abundant element in earth crust causes deadly effect to growing plants and can be toxic to mankind when accumulated in excessive amounts [5]. Many symptoms of Al^{3+} toxicity mimic those of Alzheimer's disease, Parkinson's disease, bone softening, chronic renal failure and osteoporosis. According to WHO, the average daily human-body intake of aluminum is 3–10 mg kg^{-1}. Intake of Al may happen through water treatment process, food additive, aluminum-based pharmaceuticals and aluminum containers [6].

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Chromium is an element which is present in major quantity in human diet and plays a crucial role on the metabolism of carbohydrates, fats, proteins and nucleic acids by activating certain enzymes and stabilizing proteins and nucleic acids [7]. Its deficiency can cause serious health problems like diabetes and cardiovascular disease [8]. Moreover, it is an environmental pollutant that causes concern in industry and agriculture.

Iron plays a crucial role in biological processes at the cellular level [9]. It is present in numerous enzymes and proteins. It is critically involved in both electron transfer reactions and oxygen transport in all tissues in the form of haemoglobin. But it is recently reported that both excess or deficiency of Fe^{3+} can cause several diseases like Alzheimer's, Huntington's and Parkinson's diseases [10]. Thus there is an urgent need to develop some probe that can monitor these trivalent species (Al^{3+}, Fe^{3+}, and Cr^{3+}).

In this aspect, the design of probes displaying changes in optical and fluorescence properties through a "turn-on" response is much preferred for designing efficient sensors than those showing a "turn-off" response. Both Cr^{3+} and Fe^{3+} are paramagnetic species which generally behave as fluorescence quenchers. So there are very few probes that have been developed for a Fe^{3+} or Cr^{3+} turn-on sensor. Rhodamine derivatives may be potential candidate for such sensing purpose. Rhodamine derivatives have received great attention of the researchers after the pioneering work of Czarnik et al. about two decades ago [11]. Rhodamine spirolactam or its derivatives are colorless and nonfluorescent, whereas spirolactam ring opening produces strong fluorescence and its color changes to pink. Generally activation of amide group in a spirolactam moiety leads to color change and strong fluorescence in acidic medium. However, design of suitable ligand based on spirolactam moiety can show a change in color and fluorescence upon interaction with appropriate metal ions under suitable conditions. There are reports of some chemosensors derived from rhodamine units [9b,12]. These rhodamine derivatives act as sensors for a variety of cations including a few for trivalent cations. But none of them have been applied for the construction of molecular logic gates so far.

Recently an interest has been developed to construct and interpret smart molecular logic devices based on opto-electrochemical properties of a multi-analyte sensor. In the year 1993 de Silva et al. first proposed the concept of molecular computing [13]. After that a number of scientific approaches come up to design smart functional molecular systems capable of acting as Boolean logic gates as well as several high order functions like half-adder/subtractor, [14–18] memory device,[19–23] key-pad lock,[24–29] etc. These can mimic modern Si based tools to a dimension as small as in the nanoscale order. This can be addressed successfully with the suitable design and development of molecule based operators which are able to perform a large number of complicated and integrated logic operations.

In continuation to our interest on the development of fluorescence sensing of small cations,[30] we have now designed and synthesized a rhodamine based sensor molecule, 2-(2-(5-bromo-2-hydroxybenzylideneamino)ethyl)-3′,6′-bis(diethylamino)spiro[isoindoline-1,9′-xanthen]-3-one (HL) for the differential selective detection of trivalent cations, e.g., Al^{3+}, Fe^{3+}, Cr^{3+} in mixed organic aqueous media. Rhodamine 6G has been chosen as fluorescent sensor due to its high photostability, quantum yield, good absorption and emission properties in the visible region. Apart from that, the rhodamine ethylenediamine derivative with spirolactam structure is non-fluorescent, whereas on its ring-opening, the spirolactam form gives rise to a strong fluorescence emission. This property helps to construct OFF–ON fluorescent switch sensors. HL has been synthesized following the route shown in Scheme 1 and characterized by elemental analysis, different spectroscopic techniques and X-ray single crystal diffraction analysis. Density functional theory (DFT) and time-dependent density functional theory (TD-DFT) have been applied to optimize the geometry of the probe and its Al-complex in ground as well as in the excited state and also to compute its electronic transitions for the proper assignment of the experimentally observed spectral bands of UV–vis and emission spectra. Al complex with HL acts as fluorescence sensor for arsenate ion. Arsenate ion quenches emission intensity of Al–HL complex. On the other hand, we have used our probe for construction of multi input sensing based molecular logic gates by monitoring a particular fluorescence band as the output signal. We have constructed and interpreted 3 inputs based INHIBIT and 5 inputs based OR-INHIBIT logic gates, molecular memory devices as well as Keypad lock by introduction of proper sequencing and different analytes as inputs.

2. Experimental

2.1. Materials and physical methods

Rhodamine 6G, ethylenediamine, 2-hydroxy-5-bromobenzaldehyde, metal salts such as nitrates of Al^{3+}, Fe^{3+}, Co^{2+}, Zn^{2+}, Cd^{2+}, etc. were purchased from Sigma Aldrich and used as received. Other chemicals were received from commercial sources and used as received. Solvents used during spectroscopic studies were purified and dried by standard procedures [31]. Elemental analysis was carried out in a 2400 Series-II CHN analyzer, Perkin Elmer, USA. FT-IR spectra were recorded on a Perkin Elmer spectrometer (Spectrum Two) with the samples using the attenuated total reflectance (ATR) technique. Absorption spectra were studied using a Shimadzu UV 2100 spectrophotometer. Emission spectra were recorded on a HORIBA Fluoromax-4C spectrofluorometer (S. no. 1338D-0215-FM). The ESI-MS+ (*m/z*) spectra were recorded on a QTOF Waters' HRMS spectrometer (Model: XEVO G2QTof). ^1H and ^{13}C NMR spectra were recorded in D_2O or DMSO-d_6 solvent using either a Bruker 500 MHz spectrometer or a Bruker 300 MHz spectrometer using tetramethylsilane ($\delta = 0$) as an internal standard. Luminescence lifetime measurements were performed using a TCSPC (timecorrelated single photon counting) set up from Horiba Jobin-Yvon. The luminescence decay data were recorded on a Hamamatsu MCP photomultiplier (R3809) and were analyzed using the IBH DAS6 software.

Emission quantum yields (ϕ) of HL and its M^{3+} complex were measured using the formula:

$$\Phi_{sample} = \{(OD_{standard} \times A_{sample} \times \eta^2_{sample})/(OD_{sample} \times A_{standard} \times \eta^2_{standard})\} \times \Phi_{standard}$$

where A is the area under the emission spectral curve, OD is the optical density of the compound at the excitation wavelength and η is the refractive index of the solvent. The quantum yield of the standard (here Rhodamine-6G in methanol) is 0.94.[32]

2.2. Preparation of N-(rhodamine-6G)lactam-ethylenediamine (L^1)

L^1 was synthesized following a literature method.[33]

2.3. Preparation of HL

L^1 (0.5 mmol, 0.228 g) in methanol (10 mL) was added dropwise over 30 min to a methanolic solution (30 mL) of 2-hydroxy-5-bromobenzaldehyde (0.55 mmol, 0.110 g) in the presence 1 drop of glacial acetic acid under hot (ca. 50–60 °C) conditions. Then the reaction mixture was refluxed under stirring condition for around 4 h. A yellow precipitate appeared. It was then collected by filtration and washed 3 times thoroughly with cold methanol to get HL. Single crystals suitable for X-ray diffraction analysis were obtained by recrystallization from ethanol. Yield: 0.286 g, 82%. Anal. calc. (%) for $C_{35}H_{33}BrN_4O_3$: C, 65.73; H, 5.52; N, 8.76. Found: C, 65.70;

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