



Dual emission and pH based naphthalimide derivative fluorescent sensor for the detection of Bi^{3+}



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ABSTRACT

This paper describes a novel dual emission N-hydroxy 1,8-naphthalimide (NHN) sensor for selective determination of Bi^{3+} ion and pH. This chemosensor displayed a red shift in absorption spectra and fluorescence enhancement towards highly selective Bi^{3+} ion in neutral aqueous solution. The binding stoichiometry of NHN with Bi^{3+} have been determined to be 1:1 by the job's plot and the binding constant is calculated by Benesi-Hildebrand relation. The effect of β -cyclodextrin (β -CD) on NHN is also studied at $\text{pH} \sim 7$. The binding mode of NHN with Bi^{3+} through carbonyl and the hydroxyl group of NHN is confirmed by FT-IR spectra. The influence of hydroxyl group in naphthalimide as a function of pH and metal ions was studied by UV-vis and fluorescence spectroscopy. Fluorescence emission of naphthalimide varied in a narrow range of pH (5–9) and was only slightly influenced by the addition of metal ions in aqueous solution.

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1. Introduction

In the last decade, much attention has been paid to supramolecular fluorescent systems for the sensing and reporting of cations which may be of importance for chemical, biological and environmental sciences [1–5]. The determination of pH has great interest in different areas such as environmental monitoring, clinical analysis, control and monitoring of biochemical reactions, industrial processes, development of new pharmaceutical products and scientific researches [6–10]. Different methods have been developed to monitor and to determine pH values, including electrochemistry [11], nuclear magnetic resonance [12], absorbance spectroscopy [13] and fluorescence probe analysis [14]. Among all of these methods, measurement of pH by fluorescence-based techniques has important implications in analytical and biological chemistry. Development of fluorescent pH sensing probes for both imaging and sensing applications has received much attention in the current literature [15]. A handful of detection schemes exploiting proton binding induced perturbations of de-excitation pathways such as photo induced electron transfer (PET) [15a,b], intramolecular charge transfer (ICT) [15e], Forster resonance energy transfer (FRET) [15c,d] have been used for the development of pH sensing

probes. The photo induced electron transfer (PET) process has been widely exploited for the sensing of cations as well as anions [16]. Generally, PET sensors based on nitrogen donors are highly sensitive to environmental pH stimuli, because the degree of nitrogen protonation is strongly pH dependent.

On the other hand, the heightened concern for environmentally and biologically relevant species such as Bi^{3+} , Al^{3+} , Pb^{2+} , Hg^{2+} and Cu^{2+} , has been active research on the potential impact of their toxic effects. In particular, bismuth compounds have application in semiconductors, cosmetic preparations, metallurgy and alloy industry, iron castings, electronics, lubricating oils and greases, pigments, medicines for treatment of helicobacter pyloric- induced gastritis, contact lens cleaning solution, nuclear reactor cooling fluids and reagent for purification of sugar [17–19]. On the other hand, a number of toxic effects in humans have been attributed to bismuth compounds such as nephropathy, osteoarthropathy, hepatitis and neuropathology [20].

As the use of bismuth in medicine increases, it has spread in the environment and the chance of exposure of organisms to bismuth has increased. Various methods have been evolved for the determination of bismuth. These include hydride generation inductively-coupled plasma (HG-ICPAES), electro thermal vaporization ICP mass spectrometry (ETV-ICP-MS), atomic absorption spectrometry (AAS), potentiometric stripping analysis (PSA), anodic stripping voltammetry and cathodic stripping voltammetry (CSV) [21–26]. However, most of these methods suffer from either widespread availability of instrumentation, prohibitive cost,

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or technical. Because of these considerations, spectrofluorometric seems attractive for the determination of bismuth in several samples.

The number of special fluorophores sensitive to pH or metal ions with dual excitation or emission wavelength is limited. Derivatives of naphthalimides have attracted the attention for this purpose by their fluorescent characteristics. Naphthalimides and their derivatives are well-known, and they demonstrate a wide variety of applications due to properties such as fluorescence, electro activity and photo stability. The 1,8-naphthalimide moiety has also been used to design fluorescent molecular probe sensitive to variation in pH or metal ion concentration [27]. Meanwhile, the photoreactions of naphthalimide have been investigated in the past decade by Kubo and coworkers [28]. Now a day the new sensors based on naphthalimide have been reported for the determination of cations [29–31], metal ions and protons [32], pH [33–35] and anions [36–39]. Sensors for the determination of metal ions and pH based on mono and bis-1,8-naphthalimides showing PET (photo induced electron transfer) effect also have been developed [40,41]. To our knowledge, there are no reports on the development of N-hydroxy1,8-naphthalimide sensor based on the measurement of fluorescence intensity in function of pH and metal ion. Based on these considerations, we present in this article a novel dual emission sensor towards pH and metal ion based on PET mechanism. The pH detection with this kind of probe in the literature are generally troubled with the insufficient water solubility and the inference from the coexist cations. To overcome the poor solubility of the probe, it is used along with β -Cyclodextrin, which enhances the solubility of the probe. The precise structure of β -cyclodextrin (CD) makes the probe readily soluble in aqueous solution and prepares it to undergo host-guest interaction with β -Cyclodextrin [42]. This important property of CD is utilized in our research to convert the probe to operate in an aqueous system by the formation of the inclusion complex with β -CD. The results show that the inclusion complex displays a highly selective and sensitive response towards Bi^{3+} cation in neutral/aqueous solution. The binding properties of the compound NHN with Bi^{3+} cation were investigated by UV–vis and fluorescence spectroscopy. A novel spectrofluorometric method for the determination of Bi^{3+} with high selectivity and sensitivity was proposed.

2. Experimental

2.1. Chemicals and instruments

β -Cyclodextrin (β -CD, were obtained from Hi-media chemical Company} and used without further purification. N-hydroxy1,8-naphthalimide (NHN) purchased from Hi-media Chemical Reagents Company. Solutions of metal ions were prepared from perchlorate salts of metal ions used in this study and were dissolved in distilled water. Triply distilled water was used to prepare all solutions. All reactants were commercially available and used without further purification. The UV–vis spectra (absorption spectral measurements) were carried out with Shimadzu UV-2401PC double-beam spectrophotometer (range 1100–200 nm) with scan speed at 400 nm min⁻¹, Fluorescence measurements were made using a Jasco FP-880 spectrofluorimeter and the pH values in the range 1.0–12.0 were measured on Elico pH meter LI-120, ¹H NMR spectra were taken by BRUKER-NMR 500 MHz in DMSO-*d*₆ solvent, FT-IR was recorded using Nicolet 380 and solids of the metal complex grown from the aqueous solution are used. Two-dimensional rotating-frame Overhauser effect spectroscopy (ROESY) experiments were performed using BRUKER-NMR 400 MHz instrument operating at 300 K and the standard Bruker program was used,

Table 1

Various Prototropic maxima (Absorption & emission spectra) and pKa, pKa* values of NHN with β -CD medium.

Species (pH/pKa)	Without β -CD		With β -CD	
	λ^{max} (nm)	λ_{Flu} (nm)	λ^{max} (nm)	λ_{Flu} (nm)
Neutral (pH ~ 1–7)	342.5	383.0	340.0	383.0
	233.0		237.0	
Monoanion (>pH ~ 7)	406.5	382.5	406.5	382.5
	338.0		338.0	
	234.5		235.5	
pKa/pKa*	6.9	4.8	6.8	4.9

DMSO-*d*₆ was used as a solvent, relaxation delay of 1 s and mixing time 300 ms under the spin lock conditions.

2.2. Preparation of stock solutions for UV–vis and fluorescence studies

The stock solution of β -CD (12×10^{-3} mol dm⁻³) was prepared using pH ~ 7 (0.1 M KH₂PO₄ + 0.1 M NaOH) buffer solutions. From the stock solution 2, 4, 6, 8, 10 and 12×10^{-3} M of β -CD were prepared using pH ~ 7 buffers. 1×10^{-2} M concentration of stock solution of NHN was prepared using ethanol and appropriate volume of this stock solution were added into 10 ml volumetric flasks and made up to the mark using following concentrations of β -CD solutions 0, 2, 4, 6, 8, 10 and 12×10^{-3} M respectively and shaken thoroughly. So, the final concentration of NHN in each flask becomes 2×10^{-5} M. Solutions in the pH range 1.0–12.0 were prepared by adding the appropriate amount of NaOH and H₃PO₄. A modified Hammett's acidity scale (H₀) [43] for the solutions below pH ~ 2 (using a H₂SO₄–H₂O mixture) and Yagil basicity scale (H₋) [44] for solutions above pH ~ 12 (using a NaOH–H₂O mixture) were employed. The solutions were prepared just before taking measurements. The recognition between Naphthalimide and different metal cations were investigated by UV–vis spectroscopy in aqueous solution. The stock solution of NHN and metal ions were in a concentration of 1×10^{-2} M. All absorption spectral studies were carried out in pure triply distilled water at room temperature. For colorimetric titrations, the stock solutions (5×10^{-5} M) of all metal ions were prepared in aqueous solution and used. To analyze the effect of metal through UV–vis and Fluorescence spectra, various concentrations of Bi^{3+} (5×10^{-9} – 5×10^{-5} M) were prepared in 10 ml volumetric flask and shaken thoroughly. All the absorption and emission spectra were recorded at 30 ± 1 °C.

3. Results and discussion

3.1. Effect of pH

Influence of pH on the absorbance and fluorescence behavior of naphthalimide was recorded in a pH range 1.0–12.0. The absorption and fluorescence spectra of different prototropic species of naphthalimide were recorded and the relevant data are given in Table 1 and Fig. 1. In absorption spectra, the two bands of NHN at 342.5 nm and 233.0 nm are due to n- π^* and π - π^* transition [45]. It can be observed from the UV–vis absorption spectra that the absorption intensity of two bands increased with an increase in pH value from 1.0 to 7.0. In the pH range 1.0–7.0, observed absorption maxima resembles the spectra observed in aqueous solvent (e.g. in Water at ~342.5 nm) and thus can be assigned to neutral species. The absorption maximum at 342.5 nm was observed, could be due to exists of the neutral form of NHN. In alkali medium, i.e. above pH ~ 7. 0 to pH ~ 12. 0, NHN gives a newly red shifted peak with the maxima at 406.5 nm and the peak at 342.5 nm is slightly blue shifted to 338.0 nm and besides the color of the solution is changed

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