



Fluorimetric detection of Sn^{2+} ion in aqueous medium using Salicylaldehyde based nanoparticles and application to natural samples analysis



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ABSTRACT

The fluorescent 2-[(E)-(2-phenylhydrazinylidene)methyl]phenol nanoparticles (PHPNPs) were prepared by a simple reprecipitation method. The prepared PHPNPs examined by Dynamic Light Scattering show narrower particle size distribution having an average particle size of 93.3 nm. The Scanning Electron Microphotograph shows distinct spherical shaped morphology of nanoparticles. The blue shift in UV-absorption and fluorescence spectra of PHPNPs with respect to corresponding spectra of PHP in acetone solution indicates H- aggregates and Aggregation Induced Enhanced Emission (AIEE) for nanoparticles. The nanoparticles show selective tendency towards the recognition of Sn^{2+} ions by enhancing the fluorescence intensity preference to Cu^{2+} , Fe^{3+} , Fe^{2+} , Ni^{2+} , NH_4^+ , Ca^{2+} , Pb^{2+} , Hg^{2+} and Zn^{2+} ions, which actually seem to quench the fluorescence of nanoparticles. The studies on Langmuir adsorption plot, fluorescence lifetime of PHPNPs, DLS-Zeta sizer, UV-visible and fluorescence titration with and without Sn^{2+} helped to propose a suitable mechanism of fluorescence enhancement of nanoparticles by Sn^{2+} and their binding ability during complexation. The fluorescence enhancement effect of PHPNPs induced by Sn^{2+} is further used to develop an analytical method for detection of Sn^{2+} from aqueous medium in environmental samples.

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1. Introduction

A variety of new functionalized compounds which exhibit excellent fluorescent properties are of current interest in the development of systems for detection of metal ions in aqueous media [1–3]. The design and synthesis of such compounds capable of binding and sensing metal ions selectively received more attention in recent years due to important roles of these ions in many chemical and biological processes. Although many simple fluorophores have been used for development of sensory system in the past but possibilities like narrow excitation and broad emission spectra are the hurdles in use of these fluorophores towards particular metal ion detection. However compared to these traditional fluorophores, nanoparticles based sensors are more advantageous due to their characteristics like resistance to photo bleach, broad absorption spectrum and narrow enhanced emission spectrum. Because of the size dependent, tunable photoluminescence properties of organic nanoparticles, they are evolving as promising materials for sensor development [4–7]. The sensor material should be soluble in pure water to develop an efficient method for biological and environmental sample analysis. The aqueous insolubility of the hydrophobic fluorescent chemo sensors limits the application and hence new approach encompasses to prepare

aqueous suspension of nanoparticles. Fluorescent organic nanoparticles of functionalized molecules specifically binding with certain analyte are of great importance with improved sensitivity, selectivity and low detection limit because of strong aggregation induced enhanced emission (AIEE) [8–11]. The advantage of using fluorescent organic nanoparticles is the high surface area of nanoparticles and electrostatic attraction responsible for adsorption of analyte molecule on the specifically modified surface [10,11].

In recent years, a considerable scientific approach has been drawn to devise fluorescent organic nanoparticles (FONs) based sensors which selectively recognize various metal ions [12]. Although several analytical methods such as atomic absorption spectroscopy (AAS), inductively coupled atomic emission spectroscopy and inductively coupled plasma mass spectroscopy (ICP-AES and ICP-MS) have been widely used to detect metal ions [13]. The fluorescence spectroscopy is infinitely preferable due to easy handling, less expensive, appreciating sensitivity and fast response. Despite many impressive advances in AIEE based FONs, more facile preparation method without complex synthesis and expensive reactant is still highly demanded. The reprecipitation method is one of the suitable and economic method so far widely used to prepare FONs [14]. Many of the metal ions play very important roles in living system. The excess consumption of metal ion in body may cause serious infection in human metabolism [15]. Therefore it is today's need to develop a sensitive and selective method for the detection of metal ion in

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aqueous medium. Fluorescence probes based on Schiff base units have been developed and applied in the field of metal ion recognition in recent years. The development and application of Schiff base compounds with –N and –O as hard-base donor sites provide a facile pathway for binding towards metal ion in aqueous media [16–18]. We believe that the development of Schiff base centered nanoparticles based sensory system with controlled and regulation in properties can be used to detect metal ions and explored in field applications. Schiff base derivatives are known to coordinate with metal ions and exhibit enhanced optical properties of probe. In contrast to fluorescence quenching, the optical probes based on fluorescence enhancement effect are more advantages due to strong output signal arising from the system [19,20]. Therefore, it is proposed to synthesize Schiff base 2-[(E)-(2-phenylhydrazinylidene)methyl]phenol (PHP) to explore its use in the form of nanoparticles in sensing of metal ion. The metal ion recognition test performed using aqueous suspension of nanoparticles of PHP showed that presence of tin (Sn^{2+}) ion solution enhances the fluorescence of PHP nanoparticles while other ions namely Cu^{2+} , Fe^{3+} , Fe^{2+} , Ni^{2+} , NH_4^+ , Ca^{2+} , Pb^{2+} , Hg^{2+} and Zn^{2+} actually quench the fluorescence. The selective sensing and detection of tin ion from aqueous solution by fluorescence change of organic nanoparticles are discussed in this present paper.

Tin is a soft, white, silvery metal that is insoluble in water. Tin is a metal that can combine with other chemicals to form various compounds which are water soluble. Tin poisoning refers to the toxic effects of tin and its compounds. Tin can enter human body when food or drinks with contaminated water is consumed which has tin in it [21]. The University of Medical Sciences in Iran investigated in vitro effects of several metals, including tin, on sperm creatine kinase. Reduced sperm metabolism was observed which is believed to be a cause of infertility in men. The water soluble tin complex can irritate the skin and delicate tissue, particularly the eyes and respiratory system. The contaminated water with tin content was found to be extremely toxic to human embryonic kidney cells, energy metabolism and brain function by interfering with neurotransmitters. Therefore it is a current need to develop a highly selective and sensitive method for the determination of Sn^{2+} in aqueous medium. In this paper, we report a synthesis and characterization of Schiff-base compound for preparation of its nanoparticles by reprecipitation method. Further, nanoparticles that are explored as novel nano probe for the detection of Sn^{2+} in aqueous media depend on fluorescence enhancement studies. The present method was successfully applied to quantitative determination of Sn^{2+} in collected environmental samples.

2. Experimental

2.1. Materials

Salicylaldehyde and Phenyl hydrazine were obtained from Sigma Aldrich (India). The required metal salts viz. SnCl_2 , CuCl_2 , FeCl_3 , FeCl_2 , NiCl_2 , NH_4Cl , CaCl_2 , PbCl_2 , HgCl_2 and ZnCl_2 used as sources were procured from Spectrochem Pvt. Ltd. Mumbai, (India) and were used as received. Analytical grade acetone and ethanol (S. D. Fine Chemicals, Mumbai, India) were used after distillation. Ultrapure water was obtained by passing distilled water through a Millipore unit (India) and used in preparation of solution required for fluorescence experiments.

2.2. Instruments for Characterization

^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded in CDCl_3 on Bruker Avance 300 NMR spectrophotometer. Chemical shifts were reported using tetramethylsilane (TMS) as an internal standard. Infrared spectrum was recorded in KBr pallets on a Perkin Elmer FT-IR spectrophotometer in the 4000–400 cm^{-1} region. Mass spectrum was recorded using Agilent 1200 series LC and 6130 series Single Quadrupole MS systems instrument. UV–visible spectra and Fluorescence spectra of the solutions were recorded on a Shimadzu

spectrophotometer and on a JASCO FP-750 spectrofluorometer, respectively. The size and zeta potential of the PHPNPs were measured using a Malvern Zetasizer (nano ZS-90) equipped with a 4 mW, 633 nm He–Ne Laser (U.K.) at 25 °C under the fixed angle of 90° in disposable polystyrene cuvettes. The morphology of PHPNPs was assessed by Scanning Electron Microscope (SEM), (JEON-6360 Japan), operated at an accelerating voltage of 20 kV. The pH of the aqueous suspension of nanoparticles was measured on LI120 digital pH meter instrument. The fluorescence lifetimes measured by time correlated single photon counting method for which a time resolved fluorescence spectrometer (Horiba Jobin Yvon IBH) was used equipped with nanosecond LEDs (420 nm).

2.3. Synthesis of 2-[(E)-(2-phenylhydrazinylidene)methyl]phenol: (PHP)

PHP was synthesized using reported procedure [22,23]. The synthesis route performed is shown in Scheme 1. Salicylaldehyde (0.1 mmol) was dissolved in 20 mL ethanol and a solution 0.1 mmol phenyl hydrazine was added. The resulting mixture was stirred on a magnetic stirrer for 30 min. The pale yellow solid thus obtained was filtered, washed with distilled water and dried. The final product was recrystallized from hot ethanol solution and was characterized to be used further for preparation of nanoparticles in aqueous suspension.

2.4. Spectral Characterization of PHP

The formation of product was confirmed by spectral techniques viz. IR, ^1H , ^{13}C NMR and MS analysis. Pale yellow powder; IR (Fig. S1, ES $^+$): 3290 cm^{-1} , Presence of –NH, 1602 indicates the presence of $\text{C}=\text{N}$; ^1H NMR (300 MHz, CDCl_3 , Fig. S2, ES $^+$): δ 10.88 (1H, s, –NH), δ 7.90 (1H, s, –OH), δ 7.53–7.59 (1H, d, J = 18 Hz, –CH), δ 6.90–7.35 (9H, m, Ar–H); ^{13}C NMR (75 MHz, CDCl_3 , Fig. S3, ES $^+$): $\text{C}=\text{O}$, δ 157.06 (C – 1); δ 143.40 (C – 11), δ 143.20 (C – 8) 112.65–130.4 (Ar – C); MS (EI) (Fig. S4, ES $^+$): 213.9 [M] $^+$ m/z. The IR spectrum exhibited bands at 3290 cm^{-1} for NH stretching, while band detected at 1602 cm^{-1} are due to stretching of $>\text{C}=\text{N}$. In ^1H NMR spectrum, a significant singlet at δ 10.88 ppm confirmed the presence of –NH protons. Singlet depicted at δ 7.90 ppm highlighted presence of –OH, and doublet at δ 7.56 ppm is due to –CH protons. In ^{13}C NMR –C=N carbon appeared at δ 143.20 ppm while the carbon adjacent to OH appeared at 157.06 ppm. Mass spectrum that displayed a strong peak at 213.9 m/z for [M] $^+$ is also in good agreement with the molecular ion peak of proposed structure.

2.5. Preparation of PHPNPs

Nanoparticles of PHP were prepared using simple and efficient reprecipitation method [15] developed in the laboratory. 5 mL solution of PHP in acetone (5 mM) was injected into 250 mL water (Millipore) by using micro syringe. The whole solution was vigorously stirred by magnetic stirrer for 1 h and sonicated for 30 min to disperse the nanoparticles in aqueous medium. Pale yellow colored transparent suspension of nanoparticles was then undertaken for particle size distribution analysis and surface morphology examination.

3. Results and Discussion

3.1. Particle Size and Morphology of PHPNPs

Fig. 1 shows particle size distribution histogram of PHPNPs taken on the Malvern Zetasizer (nano ZS-90) based on dynamic light scattering (DLS) technique. The histogram shows narrow particle size distribution and the average particle diameter of 93.3 nm indicating that the aggregates are of nanoscale size. In order to obtain monodispersed aqueous suspension of nanoparticles with narrower particle size distribution the parameters like concentration of the solution, sonication time and temperature were optimized. The optimum values are i) concentration

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