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FLUORESCENCE NEWS ARTICLE

Highly Efficient Colorimetric Sensor for Selective and Sensitive Detection of Arsenite Ion (III) in Aqueous Medium

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Keywords Colorimetric · Sensor · Arsenite · Aqueous medium

Introduction

Arsenic (As) is abundant in earth crust and its contamination poses a serious health problem to humans and aquatic lives. The inorganic form of As^{3+}exhibits most toxicity than the As^{5+} [1]. Arsenic originates from the mining of sulphide ores, agricultural, industrial activities and gold refining [2, 3]. The highly toxic arsenic when accumulated in water poses a major problem in many countries [4]. Intake of arsenic over the permissible limits leading to the immunogenic [5], burning and watering of eyes, malonosis, weakness, keratosis [6], cardiovascular respiratory disorder, carcinogenic [7] and black foot diseases [8]. The accessible limit of arsenic from the World Health Organization is reported to be 0.01 ppm. More than 200 million people are exposed to arsenic at higher than the permissible limit [9]. Ubiquitous arsenic contaminated groundwater used extensively to irrigate the staple food of the region in Bangladesh. In China, the maximum allowed level of the inorganic form of arsenic is $150\mu gg^{-1}$ but the accumulated arsenic level is found to be $723\mu gg^{-1}$ [10]. Inorganic arsenic can be easily absorbed through the skin and it is 60 times more toxic than a penta valent form of it [11]. Human is exposed to arsenic through the food, water and air [12]. According to IARC, in 2011 inorganic arsenic threatens million people through contaminated drinking water [13]. Thousands of hand tube well water samples have been analyzed for arsenic and more than 100,000 villagers is affected by this in West Bengal [14]. Arsenic is one of the cancer promoters rather the being cancer initiator. Arsenic exists in other forms such as arsenate (III), arsenite (IV) and arsine (0). These are the most common oxyanion found in water among them trivalent predominates [15]. In mammalian cells, the relatively high intracellular concentration of free form of glutathione would be strongly influenced by arsenite and arsenate with cysteine to form a strong As-S bond [16, 17]. This may cause more toxicity than arsenate and disrupts the activity of enzyme including thioredoxin reductase, pyruvate dehydragenase, and glutathione reductase and interrupts Kreps cycle. Mostly arsenite and arsenate have the same characteristics as to phosphite and phosphate ions, which promote the character of toxicity and hinder the conversion of ATP to ADP [18–20]. Hence, arsenite is a very severe problem to human health and global environment and thus there is a need for the detection of arsenite ion in the lowest detection limit. The most commonly used techniques for arsenic determination are chemical based which includes precipitation process, reverse osmosis, microfiltration [21], mass spectrometry [22], electroporation, atomic absorption spectroscopy [23], anodic stripping voltametry, inductively coupled plasma spectroscopy [24], ion exchange and membrane filtration [25]. Using Current methodology, most of the detection method as either generates toxic chemical [26], requires sophisticated equipment or long-time analysis. Sensors are the best key in the analysis due to the ease of real-time monitoring, low cost, good selectivity and sensitivity [27], naked eye monitoring [28]. Hence, our aim is to monitor the visualization of metal ion [29] selectively. Moreover, a high level of arsenic found in groundwater more than 0.3 mgL^{-1} is found especially in India, Cambodia, Pakistan and Bangladesh [30, 31]. Even though many papers reported are based on the hydrazones framework, 2, 4-dinitrophenyl hydrazones are of great interest as it interacts with analyst due to their strong hydrogen bonding forming ability [32]. This work based on the 2, 4-

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dinitrophenyl hydrazine framework for the visualization detection of very toxic As^{3+} in the H_2O: DMSO/ACN (9:1; *v*/v solution).

Experimental Techniques

Chemicals and Instrumental Method

All the chemicals and reagents were purchased from Aldrich and used without further purification. Metal chlorides salts are collected from Merck chemicals India and were used as a source for the study of metal ions. Here, the absorption spectra using double beam of JASCO-UV-VIS spectrophotometer. The ^{1}H and ^{13}C-NMR spectra were performed on a Brukar (Avance) 300 MHz NMR instrument using DMSO-d_6 as a solvent. HRMS spectrum was recorded on a JEOL GC Mate-II spectrometer. LC-MS mass were recorded on a Waters–Xevo- TQD mass spectrometry. Vibrational spectra were recorded on a thermo fisher (NICOLET 6700) FT-IR spectrophotometer. Sodium salts of arsenite were used for recognition of arsenite metal.

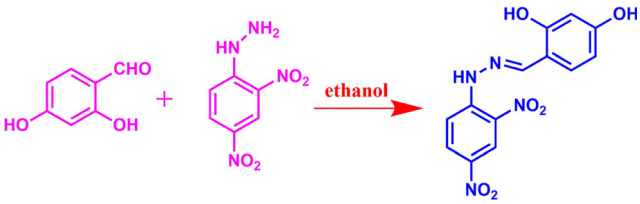
Synthetic Route of PHTH

Probe PHTH (E) – 4- [{2-(2, 4 –dinitrophenyl) hydrazono} benzene 1, 3-diol] was synthesized by earlier reported procedure [32]. A condensation reaction of 2, 4-dinitrophenylhydrazine (1 mmol), 2, 4-dihydroxy benzaldehyde and ethanol (5 ml) was taken in a round bottom flask. The reaction mixture was refluxed for 4 h to obtained red color crystalline product. The resulting product was filtered, dried and recrystallized in ethanol. The synthesized probe (PHTH) is as shown in Scheme 1.

The synthesized compound was characterized using ^{1}H, ^{13}C, FT-IR, LC-MS Mass and HRMS are shown in Figures (Figure S1 to S4a).

Procedure for Preparation of Stock Solutions

Stock solution of metal ions (1.0×10^{-2} M) such as Cu^{2+}, Hg^{2+}, Fe^{2+}, Fe^{3+}, Zn^{2+}, Pb^{2+}, Ni^{2+}, Co^{2+} were prepared from the chloride salt of metal and 100 ml of double distilled water. The 1.0×10^{-2} M concentration of sodium arsenite (III) stock solution was prepared by similar procedure. The adequate working stock solutions were obtained by the further dilution with double distilled water [33].



Scheme 1 Synthesis of probe PHTH

Colorimetric Titration Experiments

The probe (PHTH) was dissolved in appropriate quantity of DMSO and ACN afforded a required concentration of (1×10^{-2}M) stock solution, which was then diluted to adequate concentration with the solution of H_2O: DMSO/ACN (1×10^{-3}M, 9:1 *v*/v). Sodium salt of arsenite stock solution (1×10^{-2}M) was prepared with double distilled water for colorimetric titration studies. The intensity changes upon the addition of As^{3+} and were recorded using absorption spectrometer.

Results and Discussion

Hydrazine based framework of PHTH was easily synthesized by Schiff base condensation reaction as mentioned in Scheme 1. Further the probe was characterized by ^{1}H-NMR, ^{13}C NMR and FT-IR. The binding interactions of PHTH with As^{3+} ion were studied by ^{1}H-NMR titration, mass analysis and FT-IR analysis. Most favorable preliminary test for the detection of As^{3+} under naked eye was performed on the concentration (1×10^{-5}M) of probe with favorable concentration of 240 mM As^{3+} in H_2O:DMSO, 9:1 *v*/v, there was suddenly color change from orange to purple shown in Fig. 1.

As the same concentration of probe was carried out in acetonitrile solution sudden color change from yellow to red was observed during the addition of As^{3+} ion. As the same equivalent of different metal ions with PHTH probe was added there was no color changes in DMSO as well as in ACN solvent (Fig.S5). The probe suddenly changed color from yellow to red and orange to purple due to the formation of hydrogen bond with the As^{3+} and simultaneous deprotonation of hydroxy group of PHTH. The Fig.S1 shows the IR spectrum of probe PHTH, the sharp peak at 3412 and 3265 cm^{-1} corresponds to the stretching vibration of O-H and N-H group of PHTH. The strong absorption peak 1614 cm^{-1} is confirms the formation of imine bond (-C=N) of PHTH. A simple condensation of 2, 4-dihydroxy benzaldehyde and 2, 4-dinitrophenylhydrazine resulted in the formation of PHTH. Further, the binding interaction of probe PHTH with As^{3+} is demonstrated by the IR spectrum Fig.S6. After

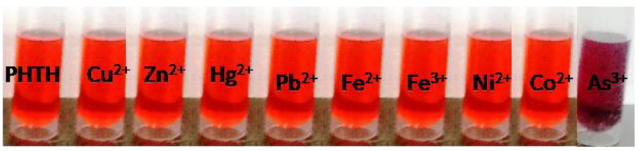


Fig. 1 Color changes of PHTH (1×10^{-5}M) from orange to purple in DMSO with As^{3+} (240 mM)

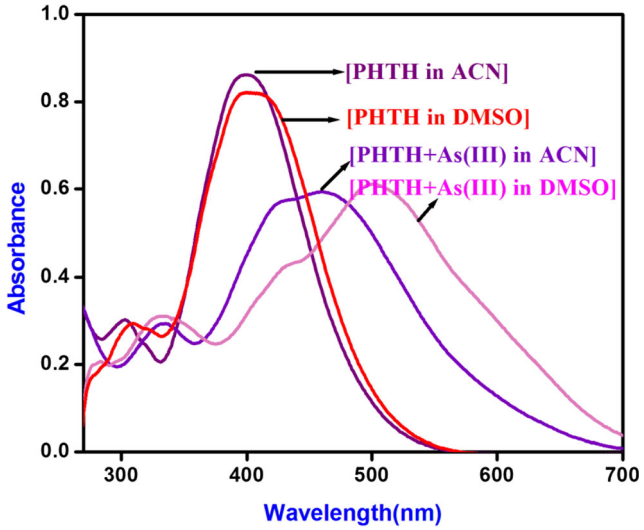


Fig. 2 Absorption spectrum of PHTH (10 μM) using both ACN & DMSO solvents with As^{3+} ion (240 mM)

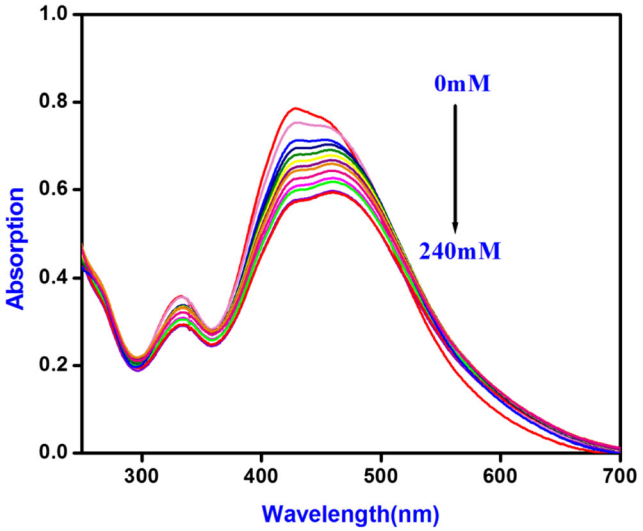


Fig. 4 Absorption spectrum of PHTH (10 μM) with addition of As^{3+} (0–240 mM) in ACN solvent

the complex formation, there will be disappearance of OH peak (3412 cm^{-1}) confirms the deprotonation.

Further, the sensing property of the probe PHTH with As^{3+} were characterized by UV studies are shown in Fig. 2**.** The probe PHTH (1×10^{-5}M) was dissolved in DMSO, the absorption bands exhibited at 415 nm with addition of As^{3+} were observed at 509 nm. It indicates the addition of As^{3+} into the probe resulted in red shifts from 415 to 509 nm. Similarly, the intensity was gradually quenching for every addition of As^{3+} into the probe due to the formation of hydrogen bonding is shown in Fig. 3. During the addition of As^{3+} color changes from orange to purple were observed at UV titration (H_2O: DMSO, 9:1 *v*/v) in aqueous medium.

The probe PHTH (1×10^{-5}M) was dissolved in appropriate quantity of ACN and absorption was measured with 397 nm, while the addition of As^{3+} into the probe exhibited peak at 470 nm. Meanwhile, addition of As^{3+} into the probe (H_2O: ACN, 9:1 v/v) shows yellow to red color. When the gradual addition of As^{3+} to the probe intensity was quenching in ACN medium are shown in Fig. 4.

The various metal ions like (Cu^{2+}, Hg^{2+}, Fe^{3+}, Fe^{2+}, Zn^{2+}, Pb^{2+}, Ni^{2+} and $Co2^{+}$) were used in the form of chloride salts in aqueous medium. The absorption band at 415 nm shifted to 509 nm by the addition of 240 mm solution of As^{3+}. The other metals (Cu^{2+}, Hg^{2+}, Fe^{3+}, Fe^{2+}, Zn^{2+}, Pb^{2+}, Ni^{2+}, Co^{2+}) do not change their wavelength resulting in selective detection of As^{3+} as shown in Fig. 5 The linear plots obtained from various concentration vs intensity of As^{3+} solution gives straight line as shown in Fig.S7. From the linear plot, linearity on the addition of various concentrations are obtained with linear

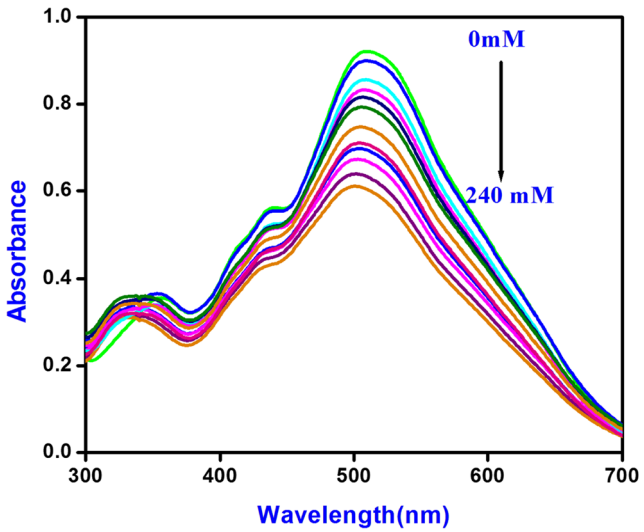


Fig. 3 UV-Visible spectrum of PHTH (10 μM) with increasing concentration of As^{3+} ions (0-240 mM) in (H_2O: DMSO, 9:1 *v*/v)

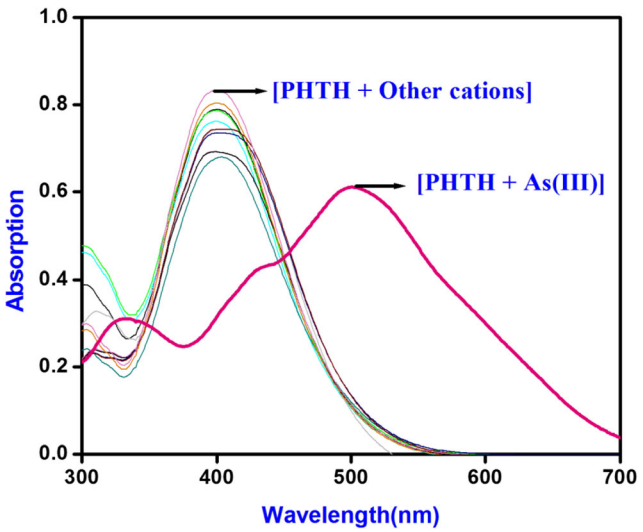


Fig. 5 Comparative studies between various metals like Cu^{2+}, Hg^{2+}, Fe^{3+}, Fe^{2+}, Zn^{2+}, Pb^{2+}, Ni^{2+}, Co^{2+} (240 mM) and As^{3+} (240 mM) with PHTH (1×10^{-5}M) in DMSO

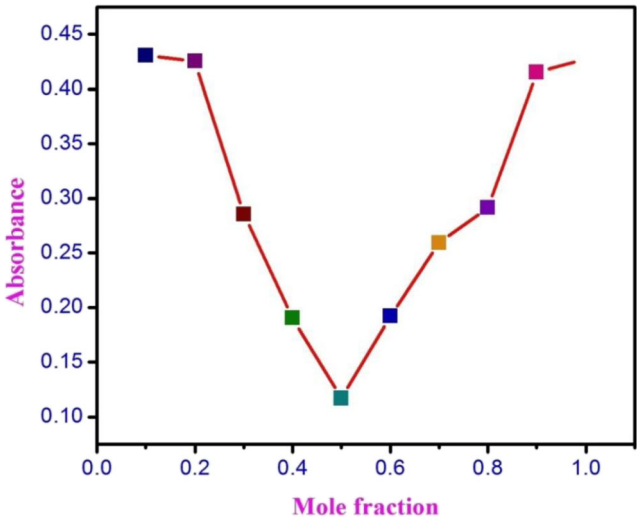


Fig. 6 Job's plot between the absorption intensity vs mole fraction within same concentration (1×10^{-3} M) in H_2O: DMSO (9:1 *v*/v)

co- efficient ($R^2 = 0.99531$). The detection limit of various concentration of As^{3+} was determined to be 0.35×10^{-6} M [33, 34]. The binding constant of As^{3+} with probe were calculated from the absorption titration i.e. 3.96×10^6 M^{-1} respectively for As^{3+} as shown in Fig.S8 [19].

The stoichiometry 1:1 binding ratio of probe with As^{3+} was calculated using Job's plot as shown in Fig. 6. To analyze interaction between the As^{3+} to probe PHTH was carried out on NMR titration used d_6-DMSO as a solvent are shown in Fig. 7. In PHTH, NH proton appeared at 11.58 ppm, OH appeared at 9.95, 10.12 respectively. When the addition of 100 mM As^{3+} solution to the PHTH resulted in NH signal to be shifted towards up field at 11.64, simultaneously and OH signal diminished. Hence, these results indicate that interaction of probe PHTH with As^{3+} through the hydrogen bonding and removal of OH proton. The photo physical property of PHTH and PHTH+As^{3+} was studied by using density functional theory calculation (DFT) with Gaussian 09 program [35].

In HOMO density functional theory of PHTH spread over the benzene-1, 3- diol while that in the LUMO density was localized on the 2, 4-dinitrophenyl hydrazono unit. However, the energy level gap between HOMO and LUMO of PHTH was 0.10535 eV. The electron densities of PHTH in HOMO and LUMO were affected by the addition of As^{3+}. As a result, the energy gap between HOMO and LUMO diminished from 0.10535 eV to 0.05126 eV while binding of As^{3+} with PHTH shown in Fig. 8. The PHTH + As^{3+} of electron distribution around the HOMO in benzene-1, 3- diol while that in LUMO was around the 2, 4-dinitrophenyl hydrazono unit.

Conclusion

In this context, the synthesized chemosensor PHTH by the simple synthetic route for naked eye detection of the most toxic inorganic form of As^{3+} in aqueous medium. The experimental studies clearly demonstrate the selectivity of probe towards As^{3+} when compared to other competitative metal ions. The NMR studies clearly show that the formation of hydrogen bond and deprotonation of OH unit of the PHTH probe with As^{3+}. The binding mode of As^{3+} with probe PHTH was clearly demonstrated by FT-IR studies and NMR titration. Furthermore, the addition of As^{3+} with the probe resulted in the color change of PHTH solution from orange to purple under the UV lamp in DMSO solvent. Further, the binding

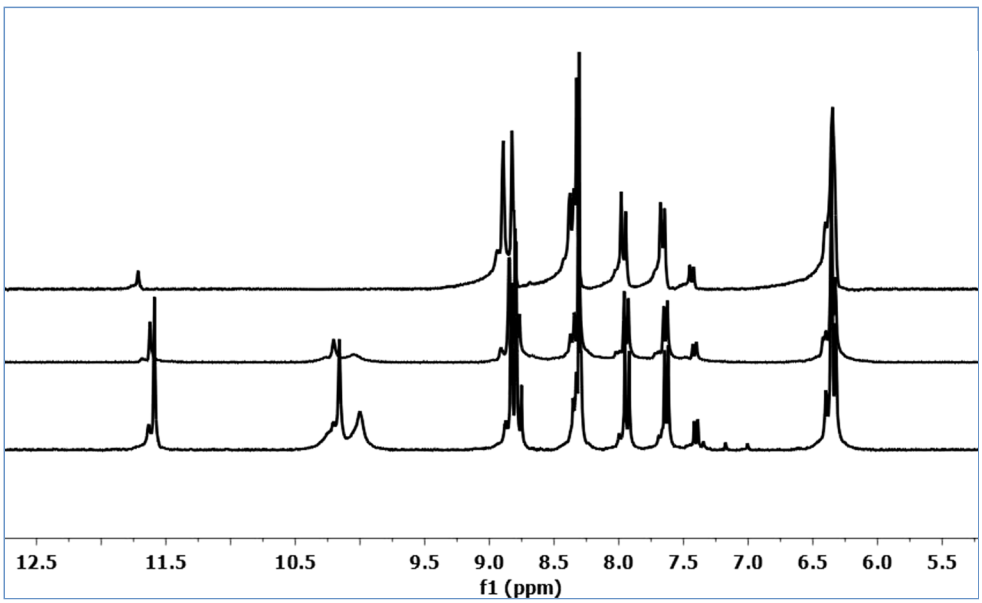


Fig. 7 NMR titration carried PHTH with addition of As^{3+} in d_6 –DMSO

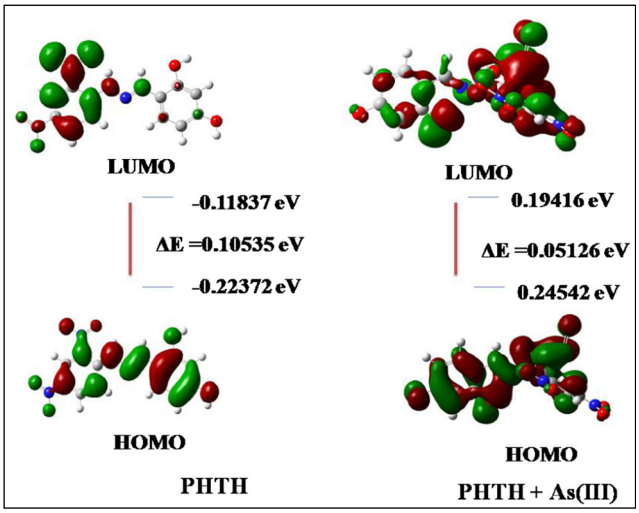


Fig. 8 Frontier molecular orbital diagram of PHTH and PHTH + As^{3+} calculated from DFT calculation using Gaussian09 program

mode of As^{3+} was clarified by binding constant and detection limit. The binding constant of As^{3+} was found to be 3.96×10^6 and detection limit 0.35×10^{-6} M in aqueous medium. Hence, we developed sensor having advantages such as low detection limit, colorimetric in nature, low cost and in aqueous medium compared to other reports.

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