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Pyrene tethered imidazole derivative for the qualitative and quantitative detection of mercury present in various matrices

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ABSTRACT

A novel pyrene tethered imidazole derivative 6-(Pyren-1-yl)-2-(1,4,5-triphenyl-1H-imidazol-2-yl)quinoline (PTIQ) is synthesized and its applicability in the selective detection of Hg^{2+} present in various matrices is explored. PTIQ is colorless in CH_3CN buffer (2:1 v/v, pH 5.0) and selectively turns to yellow with quenching its fluorescence in the presence of Hg^{2+} ions. Interaction of PTIQ with Hg^{2+} is thoroughly studied using NMR and MALDI-MS analyses. Minimum detectable limit and the limit of quantification of Hg^{2+} ions using the present method are found to be 9.8×10^{-8} M and 2.95×10^{-7} M, respectively. This method has excellent precision and recovery characteristics. Under the experimental conditions, other competitive metal ions have negligible interference in the detection ability of PTIQ. Quantification of Hg^{2+} present in various samples like Millipore water, soil, laboratory waste water, blood, urine, NaCl and dump yard waste using the present method is also described.

1. Introduction

Mercury also called as quicksilver, known from ages for its biological activity. Mercury is studied for its use in medicine and for its poisonous effects. There are case studies in history which involves mercury compounds used to treat syphilis, which eventually leads to death [1]. The excess dosage of mercury pills leads to death of the Emperor of China Qin Shi Huang on September 10, 210 BCE [2]. It's devastating, fatal poisonous effect is seen in Basra, Iraq in the year 1971, where almost 500 persons are died by the consumption of grains treated with methyl mercury fungicide [1–3]. Mercury is used in its three forms out of which inorganic and organic mercury are considered to be more hazardous than elemental mercury. Various industries like cosmetics, disinfectants, pesticides, fungicides, pharmaceutical, paper pulp and chlor-alkali production, instrumentation, mercury vapor lamps and dental amalgams are using mercury and its compounds [4]. Untreated discharges from these industries are the main source of mercury contamination of water bodies. A well quoted example of environmental contamination leading to death of nearly 600 persons in Minamata, Japan in 1950s [5]. Mercury and its compounds are also involved in accidental, suicidal and homicidal deaths [6]. Because of acute and chronic harmful effects of mercury and its compounds on central nervous system, they pose a serious threat to humans and animals [7,8]. These adverse effects of mercury and its compounds make it necessary to develop new analytical methods for the detection and determination of mercury present in various samples. Fluorescence spectrophotometry [9,10], electro-chemical methods [11,12], atomic absorption spectrophotometry [13] and inductively coupled plasma mass spectrometry [14] are useful to detect Hg^{2+} ions. Among the all, fluorescence based methodologies have gained much importance due to their high sensitivity, good selectivity and low cost procedures. Hence in the recent years, several fluorescent probes have been developed to detect mercury present in various biological and environmental samples [15–28].

Recently, we have reported a rhodamine-fluorescein conjugate for the simultaneous detection of Hg^{2+} and fluoride ions [29]. In continuation to this, herewith, we report the synthesis and metal ion detection ability of a new pyrene incorporated imidazole derivative PTIQ. Among various metal ions, PTIQ selectively binds to Hg^{2+} and changes its color from colorless to yellow with

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turning off its fluorescence. PTIQ is highly selective to Hg^{2+} and the presence of other competitive metal ions does not affect the Hg^{2+} detection ability of PTIQ. Hg^{2+} detection limit and its limit of quantification using PTIQ are estimated to be 9.8×10^{-8} M and 2.95×10^{-7} M, respectively. Moreover, applicability PTIQ in quantification of Hg^{2+} present in various samples like Millipore water, soil, laboratory waste water, blood, urine, NaCl and dump yard waste using the present method is also described.

2. Experimental section

2.1. General

All the chemicals used in this study are procured from Aldrich and Alfa Aesar chemical companies. Metal salts are commercially obtained from SD Fine-Chem Ltd. and Merck. Organic solvents are redistilled before use. Millipore water (mercury free) and HPLC grade acetonitrile are used to prepare metal ion stock solutions. Britton and Robinson Universal Buffer Solutions (pH 5.0) are prepared by adding appropriate volumes of sodium hydroxide solution (0.2 N) to the mixture of phosphoric acid (0.04 M), acetic acid (0.04 N) and boric acid (0.04 N). ^{1}H NMR and ^{13}C NMR spectra are recorded on 300 and 500 MHz (Bruker Utrashieled plus) spectrometers using TMS as internal standard in $CDCl_3$. HRMS spectra are obtained on a TOF type mass spectral analyzer. Infra-red spectra are recorded on Bruker alpha FTIR spectrophotometer. UV–vis absorption spectra are acquired at room temperature using a Cary 5000 UV–vis-NIR spectrophotometer with 10 mm path length quartz cuvettes. All the fluorescence spectra are recorded at room temperature on a Cary Eclipse fluorescence spectrophotometer with of 2.5 nm excitation and emission slit widths using 10 mm x 10 mm quartz cuvette. pH measurements are carried out on an Eco Testr Pen pH meter. Inductively coupled plasma-optical emission spectrophotometer (Thermo Fisher Scientifics, UK iCAP-6500DUO) is used to determine the metal ions present in the real samples. Metal ion stock solutions (1×10^{-2} M) are prepared from their corresponding chloride salts using Millipore water as solvent. PTIQ stock solution (1×10^{-2} M) is prepared by dissolving appropriate amount of PTIQ in HPLC grade $CHCl_3$. The working solution of PTIQ (1×10^{-5} M) is prepared by adding 3 μL of PTIQ from stock solution to HPLC grade CH_3CN: buffer (2:1 v/v, pH 5.0) and making up the volume to 3 mL. All the Hg^{2+} detection and quantification experiments are performed using CH_3CN: buffer (2:1 v/v, pH 5.0) solution.

2.2. Job plot

A series of PTIQ-Hg^{2+} complex solutions (10 μM in total) with various ligand/metal concentration ratios are prepared and measured for their emission profiles. Obtained intensity at its emission maximum is plotted against the mole fraction of Hg^{2+} ions to get the Job plot.

2.3. ^{1}H NMR studies of PTIQ-Hg^{2+} complex

To the solution of PTIQ (100 μM) in $CDCl_3$, various concentrations of Hg^{2+} (0-0.6 mM) are added and the resulting solutions are subjected to ^{1}H NMR analysis.

2.4. Precision and recovery studies

The precision of the proposed method is experimentally determined by estimating the corresponding spectrophotometer responses for five repeated analysis of a known quantity of Hg^{2+} from working solution and these values are plotted to get precision values. Recovery studies are carried out by measuring the spectrophotometric response of PTIQ solution with different concentrations of Hg^{2+}. All these experiments are performed in triplicates and the mean value for each concentration is plotted to get recovery values.

2.5. Analytical applications

Real samples with different matrices like laboratory waste water, Millipore water, blood and urine are spiked with 13.5 mg of $HgCl_2$. Soil sampled added 13.5 mg of $HgCl_2$ is dissolved ion Millipore water (5 mL) and filtered to remove insoluble residue. NaCl (0.6 M, the concentration normally seen in marine water) samples are prepared by dissolving the $HgCl_2$ (0.001 M) in NaCl solution prepared by dissolving NaCl (35.1 mg) in Millipore water (1 mL). The final volume of each sample is adjusted to 5 mL to get 1×10^{-2} M Hg^{2+} concentration. This solution is diluted to 5×10^{-5} M and analyzed for Hg^{2+} using ICP-OES. Further samples with Hg^{2+} concentration of 2×10^{-5} M and 5×10^{-5} M are prepared and analyzed for Hg^{2+} using the present method. Dump yard waste samples are collected from Jawahar nagar dump yard, Hyderabad. Dump yard soil is sampled from the place using dump tubelights and cfl bulbs and these soil samples are air dried, digested with H_2O_2 and HCl [30]. The resulting solution is filtered through Whatman filter paper and the pH of the filtrate is adjusted to 5 with ammonia solution and subjected to spectrophotometric and ICP-OES analyses.

2.6. Synthesis of PTIQ

2.6.1. 6-Bromo-2-(1, 4, 5-triphenyl-1H-imidazol-2-yl) quinoline (1)

To a round bottom flask, benzil (1.00 g, 4.75 mmol), ammonium acetate (3.66 g, 47.50 mmol), 6-bromoquinoline-2-carbaldehyde (1.12 g, 4.75 mmol), aniline (663 mg, 7.12 mmol) and glacial acetic acid (100 mL) are added and the resulting solution is refluxed for 12 h under nitrogen atmosphere. The precipitate formed upon cooling the reaction mixture is filtered and the filtrate is extracted thrice with chloroform (3×100 mL) and the combined organic extract is washed with brine (100 mL), dried over anhydrous Na_2SO_4 and filtered. The filtrate obtained is concentrated and purified on silica gel column with hexane/ethyl acetate (10:2) as eluent to obtain **1** as white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 7.59-7.56 (m, 2H), 7.38-7.35 (m, 2H), 7.32-7.18 (m, 12H), 7.13-7.10 (m, 2H), 7.05-7.02 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm: 149.48, 145.56, 144.79, 138.88, 138.31, 134.80, 134.22, 133.11, 132.68, 131.09, 130.22, 129.87, 129.38, 129.01, 128.93, 128.69, 128.39, 128.30, 128.26, 128.17, 128.05, 127.92, 127.81, 127.37, 127.31, 126.96, 126.77, 126.58, 121.79, 120.23.

ESI-HRMS $[M+H]^+$ (m/z): Calculated for $C_{30}H_{21}BrN_3$ is 502.0919; found 502.0968.

2.6.2. 4,4,5,5-Tetramethyl-2-(pyren-1-yl)-1,3,2-dioxaborolane (3)

To a stirred solution of **2** [31] (6.00 g, 21.4 mmol) in anhydrous THF (100 mL), *n*-BuLi (11.7 mL, 23.5 mmol, 2.0 M in hexane) is added slowly at −78 °C under nitrogen atmosphere. The mixture is stirred for 1 h at the same temperature and 2-isopropoxy-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (6.40 g, 34.2 mmol) is added and allowed to reach room temperature. Reaction mixture is stirred at RT for 3 h and water (30 mL) is added to quench the reaction. Reaction mixture is extracted with DCM (3×60 mL) and the combined organic extract is dried over anhydrous Na_2SO_4, filtered and the solvent was removed under vacuum. The residue obtained is subjected to column chromatography (60–120 mesh size silica) using