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Methionine–pyrene hybrid based fluorescent probe for trace level detection and estimation of Hg(II) in aqueous environmental samples: Experimental and computational studies

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ABSTRACT

A new fluorescent, Hg^{2+} selective chemosensor, 4-methylsulfanyl-2-[(pyren-4-ylmethylene)-amino] butyric acid methyl ester (L, MP) was synthesized by blending methionine with pyrene. It was well characterized by different analytical techniques, *viz.* ^{1}H NMR, ^{13}C NMR, QTOF mass spectra, elemental analysis, FTIR and UV–vis spectroscopy. The reaction of this ligand with Hg^{2+} was studied by steady state and time-resolved fluorescence spectroscopy. The Hg^{2+} complexation process was confirmed by comparing FTIR, UV–vis, thermal, QTOF mass spectra and ^{1}H NMR data of the product with that of the free ligand values. The composition (Hg^{2+}:L = 1:1) of the Hg^{2+} complex in solution was evaluated by fluorescence titration method. Based on the chelation assisted fluorescence quenching, a highly sensitive spectrofluorometric method was developed for the determination of trace amounts of Hg^{2+} in water. The ligand had an excitation and emission maxima at 360 nm and 455 nm, respectively. The fluorescence life times of the ligand and its Hg^{2+} complex were 1.54 ns and 0.72 ns respectively. The binding constant of the ligand, L with Hg^{2+} was calculated using Benesi–Hildebrand equation and was found to be 7.5630×10^{4}. The linear range of the method was from 0 to 16 $\mu g\,L^{-1}$ with a detection limit of 0.056 $\mu g\,L^{-1}$ for Hg^{2+}. The quantum yields of the ligand and its Hg^{2+} complex were found to be 0.1206 and 0.0757 respectively. Both the ligand and its Hg^{2+} complex have been studied computationally (*Ab-initio*, Hartree Fock method) to get their optimized structure and other related physical parameters, including bond lengths, bond angles, dipole moments, orbital interactions etc. The binding sites of the ligand to the Hg^{2+} ion as obtained from the theoretical calculations were well supported by ^{1}H NMR titration. The interference of foreign ions was negligible. This method has been successfully applied to the determination of mercury(II) in industrial waste water.

1. Introduction

Recognition of heavy metal ions by artificial receptors has received considerable attention [1,2] due to their toxic impact on environment and living systems. Hg^{2+} ion is considered as one of the most toxic cations for environment due to its wide distribution in air, water and soil. Mercury may accumulate in the human body causing a wide variety of diseases even in a low concentration: i.e. prenatal brain damage, serious cognitive and motion disorders and minamata disease [3,4]. Hence it is desirable to develop selective and sensitive assay for Hg^{2+} ion. Several techniques for the determination of mercury ions in various samples have been reported over the past few years. They include spectrophotometry [5], atomic absorption spectrometry [6], inductively coupled plasma-atomic emission spectrometry (ICP-AES) [7] and voltammetry [8]. Although these methods offer good limits of detection and wide linear ranges, most of these techniques necessitate the use of sophisticated and costly instruments and require complicated operational procedure. Chemical sensing which combines a recognition element with an optical or electronic transduction element, serves as an efficient analytical technique for the detection of particular species [9]. Amongst various chemosensory systems, the fluorescent method is very useful due to its operational simplicity, high selectivity, sensitivity, rapidity, nondestructive methodology and direct visual perception [10]. Fluorescent chemosensors consist of a receptor and a fluorophore. The receptor is responsible for the recognition of analytes, and the fluorophore converts the recognition events into optical signals. Several fluorophore-based sensors such as dansyl, rhodamine, anthracene, naphthyl, and nile blue were reported [11]. Various type of scaffolds such as crown ether, cryptand, calixarenes, steroid, and peptides have been used as receptors for the recognition of target analytes in chemical sensors

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[12]. In most cases, it has been observed that fluorescent chemosensors required a tedious synthetic methodology, and did not work well in aqueous solution due to their low binding affinity for the target metal ions and poor solubility in water. In recent years, considerable attention has been focused on the design of fluorescent chemo sensors for Hg^{2+} ion [13–17]. Hg^{2+} is known as a fluorescent quencher via enhancement of spin–orbit coupling [18]. Various molecular systems have been reported that monitor Hg^{2+} concentration by exploiting the mechanism of complexation-induced fluorescence quenching [19–22]. Because of its long fluorescence lifetime (up to 450 ns) [23], high fluorescence quantum yield [24] and its ability to act as a donor [25–27] as well as acceptor [28,29], pyrene has often been chosen as an ideal component in a fluorescent chemosensors for Hg(II) [30,31]. Amino acids are established metal ion receptors. Fluorescent sensors having amino acid as a metal ion receptor have hardly been found in the literature. Lee et al. reported a Fe^{3+} sensor [32] having anthracene appended amino acid (L-aspartic acid or L-glutamic acid). Sulphur containing amino acids are very effective Hg^{2+} receptors as per HSAB principle [33] Hg^{2+} sensor with sulphur bearing amino acid are not available in the literature. Herein we report, the synthesis, characterization and Hg^{2+} sensory applications of a novel fluorescent compound having pyrene–methionine hybrid structure. The method developed can selectively detect as well as estimate trace level Hg^{2+} in aqueous solution and has been successively used for the analysis of Hg^{2+} in environmental samples. The ligand and its Hg^{2+} complex have been studied theoretically by *Ab-initio* (Hartee Fock) method to have some insight about the ligand–Hg^{2+} interaction.

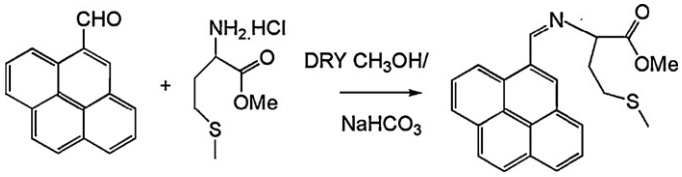
2. Experimental

2.1. Reagents

L-Methionine methyl ester hydrochloriode and pyrene aldehyde were purchased from Aldrich. Spectroscopy grade methanol (Merck, India) was used. Other chemicals are of analytical reagent grade and have been used without further purification except when specified. Milli-Q 18 Ω water was used throughout all the experiments. Real samples were collected from four different points of Tamla nala flowing through Durgapur industrial area (West Bengal, India), Station 1: main drain of Durgapur Chemicals Ltd. (DCL); station 2: junction of Tamla nala and main drain of DCL; station 3: upstream sample before meeting the main drain to Tamla nala; station 4: 50 m downstream from the junction of Tamla nala and main drain of DCL.

2.2. Instrumentation

A JASCO (model V-570) UV–vis spectrophotometer was used for measuring the UV–vis spectra of L and L–Hg^{2+} complex. FTIR spectra were recorded on a JASCO FTIR spectrophotometer (model: FTIR-H20). Mass spectrum was recorded in QTOF Micro YA 263 mass spectrometer in ES positive mode. Thermogravimetric analysis was performed on a Perkin Elmer TG/DTA lab system 1 (Technology by SII). ^{1}H NMR spectra were recorded using Bruker Avance 400 (400 MHz) in $CDCl_3$ using tetramethyl silane (TMS) as an internal standard. Elemental analysis was performed using Perkin Elmer CHN-Analyser with first 2000-Analysis kit. A VARIAN (Spectra AA 55) flame atomic absorption spectrophotometer (FAAS) (Australia) was used for measuring concentration of mercury by cold vapor technique. All measurements were performed using integrated absorbance (peak area). Hollow cathode lamp for Hg was operated at 4.0 mA in the wave length 324.7 nm and at a slit width of 0.5 nm. D2-back ground correction was performed in all the measurements. The steady-state fluorescence emission and excitation spectra were recorded with a Hitachi F-4500 spectrofluorometer equipped with a temperature controlled cell holder. Temperature was controlled to within ±0.1 K by circulating water from a constant temperature bath (Heto Holten, Denmark). The time-resolved fluorescence life time measurements of the free ligand and its Hg(II) complex were carried out using a time-correlated single photon counting (TCSPC) spectrometer from IBH (UK). To have an optimized structure of the ligand L, and its Hg(II) complex, *Ab-initio* calculations were performed by Hartree Fock method using 6-31G basis set and Gaussian '03 software package [34].



Scheme 1.

2.3. Preparation of the ligand (IUPAC, 4-methylsulfanyl-2-[(pyren-4-ylmethylene)-amino]butyric acid methyl ester) (here after, L, MP) (Scheme 1)

To a solution of 2 g (10.01 mmol) L-methionine methyl ester hydrochloriode in 50 mL dry CH_3OH was added 2.305 g (10.01 mmol, 1 equivalent) pyrene aldehyde and excess of $NaHCO_3$ (4 equivalent). The mixture was stirred over a period of 10 min followed by reflux for 6 h. On cooling, the solution was filtered through a sintered glass gooch crucible (G4) to remove unreacted $NaHCO_3$ and the filtrate was kept overnight. The orange crystalline product was isolated and dried. Yield, 65%. M.P., 85 ± 1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (Fig. S-1), δ: 2.12 (3H, s, CH_3); 2.40 (2H, m, CH_2); 2.80 (2H, m, CH_2); 3.87 (3H, s, CH_3); 4.40 (1H, t, CH); 8.47 (1H, s, –CH=N); 8.1 (d, 4H); 8.3 (s, 1H); 9.4 (d, 2H); 8.4 (m, 2H). ^{13}C NMR (200 MHz, $CDCl_3$) (Fig. S-2), δ: 172.15 (O–C=O) 163.28 (–C=N–) 133.27–122.47 (aromatic carbon), 72.30 (–CH–N), 61.44 (O–CH_3), 32.26 (N–CH_2), 30.61 (S–CH_2), 15.4 (S–CH_3), QTOF-MS ES$^+$ (Fig. S-3): $[M+H]^+$ = 376.02; elemental analysis data as calculated for $C_{23}H_{21}NO_2S$ (%): C, 73.57; H, 5.64; N, 3.73. Found (%): C, 73.27; H, 5.54; N, 3.63. FTIR (cm^{-1}): ν(CO) 1670; ν(C=N) 1503; λ_{nm} (ε, L mol^{-1} in CH_3OH at 298 K: 392 (3056), 371 (shoulder, sh) (3700), 359 (3954), 339 sh (2670), 286 (4604), 275 sh (3691), 243 (4396).

2.4. Isolation of Hg(II) complex (Scheme 2)

Methanolic solution (10 mL) of $Hg(NO_3)_2$ (181.9 mg, 0.5319 mmol) was slowly added to a methanolic solution (10 mL) of **L** (200 mg, 0.5319 mmol) and the mixture was stirred for 1 h followed by reflux for another 2 h. On slow evaporation of the solution, pale yellow flakes of the Hg^{2+} complex was isolated in 62% yield. The complex was characterized by QTOF-MS, elemental analysis, FTIR spectra and thermal studies. Elemental analysis data was calculated for $C_{23}H_{21}N_2O_5SHg$ (%): C, 43.2; H, 3.32; N, 4.39; Hg, 31.4 Found (%): C, 42.8; H, 3.37; N, 4.36; Hg, 31.8. QTOF-MS ES$^+$ (Fig. S-4) = 563.5 ($[Hg^{2+}–L+Na+H]$. FTIR (cm^{-1}): ν(CO) 1634.38; ν(C=N) 1600.63; ν(–NO_3) 1375.96; λ_{nm} (ε, L mol^{-1} in CH_3OH at 298 K: 392 (1766), 371 (shoulder, sh) (2174), 360 (2316), 339 sh (1399), 286 (3154), 275 sh (1994), 239 sh (3221), 231 (4322), 203 (2915).

2.5. Measurement procedures

Standard solutions of Hg^{2+} were obtained by serial dilution of 1.0×10^{-2} mol L^{-1} $Hg(NO_3)_2$ solution. A 10^{-4} mol L^{-1} stock solution of L was prepared by dissolving appropriate amount of L