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Research Paper

Mercaptobenzoheterocyclic compounds functionalized silver nanoparticle, an ultrasensitive colorimetric probe for Hg(II) detection in water with picomolar precision: A correlation between sensitivity and binding affinity

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ABSTRACT

Toxic heavy metal ions, specially Hg(II) pose lethal threat to the environment and human beings. To this end, there is a strong need to establish a simple, inexpensive method for the detection of Hg(II) ions with high selectivity and sensitivity in aqueous medium. Herein, we report an ultra-sensitive colorimetric detection of Hg(II) ions following a simple protocol by synthesizing silver nanoparticles functionalized with mercaptobenzoheterocyclic compounds (viz. mercaptobenzooxazole (MBO), mercaptobenzoimidazole (MBI) and mercaptobenzothiazole (MBT). These nanoparticles are found to show a limit of detection (LOD) of 1.8 ppt (9.2 pM), 9.2 ppt (46 pM) and 18.4 ppt (92 pM) for MBO, MBI and MBT respectively). In addition, the binding affinity trend of the mercaptobenzoheterocyclic ligands seems to be in tune with the observed sensitivity trait of Hg^{2+} sensing.

1. Introduction

The emergence of heavy metals into the biota has occurred in tandem with the advent of the tools of contemporary civilization, including automobiles and industrial accomplishments. Over the past 30 years, global mercury emissions have increased significantly mainly due to natural processes [1] and emissions from coal-burning power plants and gold mining [2–4].

This volatile heavy metal has a comparatively long atmospheric residence time, which results in long-range transport and homogenization on a hemispherical scale. In aqueous solution, bacteria can transmute mercury into methyl mercury [5], a potent neurotoxin, which amasses in seafood entering the food chain [6–8]. When ingested by humans, methylmercury causes several serious disorders including neurological damage [9]. For example, when ingested by a pregnant woman, methylmercury readily crosses the placenta and targets the developing fetal brain and central nervous system, which in turn causes developmental delay in the baby [10].

Consequently, the detection of these metals has attained substantial eminence within the scientific community and public consciousness as a result of their diverse lethal biological activities. Thanks to the great efforts of scientists, a number of Hg^{2+} sensors have been developed with good performance, for example, the redox, colorimetric and fluorescent Hg^{2+} sensors by using proteins [11–15], nucleic acids [16–20], DNAs [21–26] and noble metal nanoparticles [27–30]. Research on the synthesis and application of silver nanoparticles (AgNp) has received considerable attention around the world in the recent years [31,32]. The AgNp show excellent chemical stability [33,34] and have been used widely as an antibacterial agent, food storage, textile coatings and toxic chemical sensors [35].

Among the plethora of analytical methods that are accessible for the detection of Hg^{2+} ions, colorimetric methods based on nanomaterials have attracted a great deal of attention because of their distinctive advantages such as simplicity and novelty. Recently, a variety of colorimetric methods for Hg^{2+} detection have been developed by means of nanomaterial sensors, such as gold nanospheres and nanorods combining with DNA oligomers

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[36–38], fluorophores [39] and molecular ligands [40,41]. Although these methods have achieved considerably high sensitivity towards the detection of Hg^{2+}, each of these approaches has its own drawbacks that limit its practical use. Some show cross-sensitivity towards other metal ions and in some cases synthesis technique of probe materials is too complicated. Therefore, the development of practical colorimetric sensors for Hg(II) ion still remains a challenge.

In this article, we report the synthesis of silver nanoparticles (AgNp) capped with compounds having a mercaptobenzoheterocycle framework and their application in Hg(II) sensing in aqueous medium. In addition, our observation on sensitivity versus binding affinity of ligand towards Hg(II) gives insights towards the mechanism of Hg(II) sensing in aqueous medium. Due to unique reactivity of mercaptobenzoheterocyclic ligands with different metals and mineral surface [42–47], they are successfully used in engineering applications like corrosion inhibitors for copper, iron or their alloy [48–52]. We also believe that this is the first report describing the correlation between binding interactions and sensitivity limit in Hg(II) sensing in aqueous medium.

2. Materials & methods

2.1. Materials

Silver nitrate ($AgNO_3$) and sodium borohydride ($NaBH_4$) were obtained from Avra Synthesis Private Limited. 2-Aminophenol, *o*-phenylenediamine, 2-aminothiophenol, carbon disulfide (CS_2) and potassium hydroxide were obtained from Sigma-Aldrich and used without further purification. Milli-Q water was used for all the experiments. Silver nanoparticles (AgNpO, AgNpI, AgNpT) were synthesized according to the procedure in literature [53] with slight modification. MBO, MBI, and MBT were synthesized following the literature procedures [54–56].

2.2. Methods

2.2.1. Synthesis of 2-mercaptobenzoxazole (MBO) [54]

To a well-stirred, ice-cold solution of 2-aminophenol (1.23 g, 0.01 mol) and KOH or K_2CO_3 (0.015 mmol) in an ethanol-water mixture (1:0.5, 6 mL) was added Carbon disulfide (CS_2) (0.015 mol, 1.2 g, 1.0 mL) dropwise. After complete addition of CS_2, the reaction mixture was allowed to attain room temperature followed by heating at 80 °C for 8 h. The reaction mixture was then cooled to room temperature, water was added (10 mL), the mixture was acidified with 2 N HCl, and the solid precipitated was filtered. The crude product was purified on a silica gel (230–400 mesh) column (EtOAc/PET ether, 30:70) to give 2-mercaptobenzoxazole (90%, 1.4 g). FTIR (cm^{-1}): 3323, 1618, 1506, 1448, 1278, 1130. ^1H NMR (DMSO-d^6, 500 MHz): 13.86 (br s, 1H), 7.51(d, J = 7.5 Hz, 1H), 7.31–7.23 (m 3H). ^{13}C NMR (DMSO-d^6, 100 MHz): 180.3, 148.1, 131.1, 125.1, 123.7, 110.4, 109.9.

2.2.2. Synthesis of 2-mercaptobenzimidazole (MBI) [55]

o-Phenylenediamine (1.4 g, 0.013 mol) was dissolved in absolute ethanol (8 mL) in a 50 mL flask. Carbon disulfide (2 mL) was then added to the solution followed by the addition of a solution of potassium hydroxide (0.87 g, 0.015 mol) in water (5 mL). The reaction mixture was thoroughly stirred and refluxed for 5 h. It was initially yellow, and then turned to brown as the reaction progressed. Evolution of hydrogen sulfide gas was observed. After completion of the reaction, the mixture was poured into a beaker with ice-water and acidified with 4N hydrochloric acid to pH 4–5 to obtain a white precipitate. The precipitate was then filtered and recrystallized from ethanol to yield 2-mercaptobenzimidazole (1.63 g, 84%). FTIR (cm^{-1}): 3153, 1512, 1465, 1355, 1178. ^1H NMR (DMSO-d^6, 500 MHz): 12.51(br s, 2H), 7.14–7.09 (m, 4H). ^{13}C NMR (DMSO-d^6, 100 MHz): 168.1, 132.2, 122.2, 109.4.

2.2.3. Synthesis of 2-mercaptobenzothiazole (MBT) [56]

Carbon disulfide (400 mg, 0.4 mL, 5.5 mmol) was added to a mixture of KOH (5 mmol) in 80% aqueous ethanol (7.0 mL), and the reaction mixture was stirred at room temperature for 15 min. 2-Aminothiophenol (630 mg, 5 mmol) was added, and the reaction mixture was heated at 100 °C for 10 h and then cooled to room temperature. The reaction mixture was then diluted with water (10 mL), adjusted to pH ~5 with dilute hydrochloric acid. The shiny precipitate was filtered, recrystallized and dried overnight under vacuum to yield 2-mercaptobenzothiazole in 87% yield. FTIR (cm^{-1}): 3110, 1595, 1496, 1456, 1425, 1319, 1076, 1033. ^1H NMR (DMSO-d^6, 500 MHz): 13.72 (br s, 1H), 7.67 (d, J = 7.5 Hz, 1H), 7.39–7.35 (m, 1H), 7.30–7.17 (m, 2H). ^{13}C NMR (DMSO-d^6, 100 MHz): 189.7, 141.2, 129.2, 127.0, 124.1, 121.6, 112.3.

2.2.4. Synthesis of MBO capped silver nanoparticle (AgNpO)

Sodium borohydride ($NaBH_4$) (11.0 mg, 0.3 mmol) and MBO (15.1 mg, 0.1 mmol) were taken in a 100 mL conical flask and 30 mL water was added to it. The borohydrate-MBT mixture was allowed to stir for 30 min in an ice bath. The resulting mixture was added dropwise to a cold aqueous solution of silver nitrate (16.9 mg, 0.1 mmol) until the color of the solution became vivid yellow and allowed to stir for another 2 min. The synthesized AgNpO solution was then centrifuged and washed 2 times and re-dispersed in MQ-water.

2.2.5. Synthesis of MBI capped silver nanoparticle (AgNpI)

Sodium borohydride ($NaBH_4$) (11.0 mg, 0.3 mmol) and MBI (15.0 mg, 0.1 mmol) were taken in a 100 mL conical flask and 30 mL water was added to it. The borohydrate-MBT mixture was allowed to stir for 30 min in an ice bath. The resulting mixture was added dropwise to a cold aqueous solution of silver nitrate (16.9 mg, 0.1 mmol) until the color of the solution became vivid yellow and allowed to stir for another 2 min. The synthesized AgNpI solution was then centrifuged and washed 2 times and re-dispersed in MQ-water.

2.2.6. Synthesis of MBT capped silver nanoparticle (AgNpT)

Sodium borohydride ($NaBH_4$) (11.0 mg, 0.3 mmol) and MBT (16.7 mg, 0.1 mmol) were taken in a 100 mL conical flask and 30 mL water was added to it. The borohydrate-MBT mixture was allowed to stir for 30 min in an ice bath. The resulting mixture was added dropwise to a cold aqueous solution of silver nitrate (16.9 mg, 0.1 mmol) until the color of the solution became vivid yellow and allowed to stir for another 2 min. The synthesized AgNpT solution was then centrifuged and washed 2 times and re-dispersed in MQ-water.

2.3. Characterization

All the UV–vis measurements were carried in Cary100-Bio spectrophotometer. For the calibration plot, optical density (OD) was measured at 431, 407, 414 nm (λ_{max} value of yellow coloured AgNp). Transmission Electron Microscopy (TEM) analysis was carried in Technai 200 kV STwin microscope. The structures of the synthesized mercaptobenzoheterocyclic compounds were confirmed by ^1H and ^{13}C NMR spectra (ppm, δ) on a Bruker NMR spectrometer (400 MHz and 500 MHz), in DMSO-d^6.