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Ultrasensitive detection of lead (II) based on the disaggregation of a polyether bridged squaraine fluorescent probe

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ABSTRACT

In this work, a novel fluorescent chemosensor, based on a polyether bridged squaraine, has been developed for the detection of Pb^{2+}, and gives excellent sensitivity and selectivity using a cation-induced disaggregation strategy. This probe exhibited a specific "turn on" fluorescent response to Pb^{2+} with a detection limit of 1.70×10^{-8} M, and the identification for Pb^{2+} was not impacted by competing ions such as Na^+, Li^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Ag^+, Cd^{2+}, and Hg^{2+}. Due to the high binding ability of the polyether bridged ionophore toward Pb^{2+}, the disaggregation process could be trigged by the formation of squaraine-Pb^{2+} complex, resulting in a fast fluorescent release. The sensing mechanism has been confirmed by NMR, IR, and dynamic light scattering experiments. Further research shows that this novel fluorescent probe can be applied in the fast detection of Pb^{2+} in urine and shrimp samples.

1. Introduction

Lead is one of the most plentiful and toxic contaminants of the heavy metals [1], and largely derives from anthropogenic sources, such as the combustion of leaded gasoline, unregulated industrial emissions, electronic waste, and leaded paint [2]. Much of this lead circulates in soil and groundwater, and can via the biological enrichment of the food chain enter the human body and not be excreted, thus causing serious and long-term effects to the health of humans [3]. Once introduced into the body, even very low concentration of lead can induce a series of health problems, such as neurological injury, anemia, dysgenesis, muscle paralysis, memory loss, mental confusion, and reduced IQ in children [4,5]. Hence, lead pollution is a constant threat to human health and the environment [6].

Therefore, establishing a rapid and efficient method for the detection of lead has a vital significance in monitoring environmental pollution and lead poisoning auxiliary detection [7]. There are several existing methods to test for lead, such as atomic absorption spectrometry (AAS) [8], inductive coupled plasma-mass spectrometry (ICP-MS) [9], and anodic stripping voltammetry [10]. However, these standard techniques can only measure the total lead content [11], need professional knowledge of the equipment, and often demand extensive sample preparation [4,12]. Particularly worth mentioning is that the optical sensors used in fluoroionophores have gained widespread application because of their high sensitivity, good selectivity, low cost, and ease of operation, and also they can be used to realize real time monitoring [13]. In recent years, many fluorescent chemical sensors were designed for the selective detection of lead based on peptide [14], protein [15], polymer [16], DNAzyme [17,18], and small molecular groups [19–22]. However, most of them show non-specific fluorescence quenching response with lead in organic solvents, and do not respond immediately. Therefore there was a need for the design and synthesis of a new fluoroionophore based "turn-on" probe to realize the detection of lead in a fast and highly efficient manner.

Crown ethers, well-known "host molecules", possess a well-defined cavity, endowing them with demonstrated distinctive ionophoric properties toward many guest molecules [23], so they serve as excellent tools for capturing metal cations [24]. In the current study, a finely adjusted crown ether type ionophore has been designed for specific capture of Pb^{2+}.

Squaraines are a group of fluorescent dyes possessing sharp and intense absorption and fluorescent emission in the visible to near-infrared region (NIR) [25]. One of the characteristics of squaraines is their high tendency to aggregate in aqueous solution, along with an accompanying change of the absorption spectrum and fluorescence

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quenching [26]. The process from aggregation to disaggregation generally reduces recovery or enhancement of fluorescence signals, and thus provides an especial way to design "turn-on" probes [27].

Our group has reported many fluorescence "turn-on" sensors based on disaggregation. For example, we reported the first fluorescence "turn-on" sensor for the detection of Hg^{2+} in 2011, with a structure consisting of a squaraine dye with four dithiocarbamate (DTC) branches [28]. Further work to improve the solubility in water and reduce the interference was also reported [29–32]. In 2015, we reported a fluoroionophore with a monobinding structure for the detection of Hg^{2+} in the presence of EDTA which avoided fluorescence quenching due to the impact of the anilino N [33]. However, all of these fluoroionophores were designed for the detection of Hg^{2+}. None of them were applied for the detection of lead.

Using the special properties of squaraines and crown ethers, we have now designed and synthesized a novel crown ether bridged squaraine fluorescent probe on the basis of previous work, which has been successfully applied to respond with Pb^{2+} immediately, with a detection limit of 1.70×10^{-8} M, which is lower than the concentration limit of lead that is allowed in the drinking water, which is strictly defined by the United States Environmental Protection Agency (EPA) (15 ppb or 15 $\mu g\,L^{-1}$) [34]. The practicality of this novel fluorescent chemosensor was validated for the determination of Pb^{2+} concentration in urine and shrimp samples, demonstrating its advantages of simplicity, selectivity, and sensitivity.

2. Experimental

2.1. Instrumentations

All solvents were purified and redistilled by standard methods prior to use. Unless otherwise mentioned, all chemicals and reagents were obtained from commercial suppliers and used without further purification. ^{1}H NMR (400 Hz) and ^{13}C NMR (100 Hz) spectra were recorded with a Bruker AV-400 spectrometer. The chemical shifts were measured as ppm ($CDCl_3$, TMS as internal standard). FTIR spectra were recorded using a Perkin Elmer Spectrum 2000 Fourier Transform Infrared Spectrophotometer. Electrospray ionization mass spectra (ESI–MS) were measured using an DECAX-3000 LCQ Deca XP ion trap mass spectrometer. Fluorescent emission spectra were recorded using a Cary Eclipse Fluorescence spectrophotometer. Absorption spectra were measured on a Perkin Elmer Lambda 750 UV–vis spectrophotometer. Melting points were determined with a SGW X-4 instrument without correction.

2.2. Materials and general procedure for analysis

Acetic acid salts and the nitrates of metal ions (Na^+, Li^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Al^{3+}, Pb^{2+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^+, Cd^{2+}, Hg^{2+}) were used as metal cation sources for fluorescence spectroscopy. The solutions of metal ions were prepared in deionized water. The stock solution of squaraine dye was prepared by dissolving **SQ-1** in MeCN. In the ion titration experiments, 2.0 mL solution of **SQ-1** was taken in a quartz cuvette of 1 cm path length, and small volumes (0.1–1.0 μL) of the metal solutions were added to the cuvette.

2.3. Procedure for Pb^{2+} determination in real samples

Urine samples were collected from a healthy male without pretreatment and diluted 10 times with acetonitrile, and then spiked with known amounts of Pb^{2+} ion for fluorescent measurement.

The commercial dried shrimp were splintered into pieces. To 500 mg of the dried shrimp samples in a Teflon reactor, 10 mL of 12 M nitric acid was added. Then the samples were placed in a BHW-09C heating block and heated under 90 °C for predigestion for 30 min. The basic microwave digestion procedure consisted of a temperature–time ramp for 30 min with a final temperature of 150 °C, held for 15 min. The power applied was 800 W. For each digestion run, one blank sample was included. After the digestion, the samples were cooled to room temperature. Then the Teflon reactors were placed in a BHW-09C heating block and excess acid expelled at 120 °C, with concentration of the digestion fluid to 1–2 mL. The pH of the solution was adjusted to 7.0 by adding saturated NaOH solution, and the clear digested samples were transferred to a 50 mL volumetric flask, and deionized water was then added to make a final volume of 50 mL. The prepared dried shrimp sample was diluted 10 times with acetonitrile and then spiked with known amounts of Pb^{2+} ion for fluorescent measurement.

2.4. Synthesis

2.4.1. Synthesis of *SQ-1*

Polyether tethered bisaniline **2** (200 mg, 0.29 mmol) and squaric acid (33 mg, 0.29 mmol) were dissolved in 30 mL *n*-heptanol in a 100 mL round bottom flask equipped with a Dean-Stark trap. The resulting solution was stirred under reduced pressure (76 mmHg, 133 °C) for 12 h. After cooling to room temperature, most of the solvent was removed under vacuum, and then the crude product was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc, v/v = 10:1–6:1) and (CH_2Cl_2/MeOH, v/v = 30:1) to obtain the desired shiny red squaraine dye (69 mg), yield: 31%. FTIR (KBr): ν_{max} 2924, 1590, 1514, 1456, 1403, 1346, 1220, 1173, 807, 764 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, J = 9.1 Hz, 2H), 6.90–6.87 (m, 4H), 6.34 (d, J = 9.2 Hz, 2H), 6.03 (s, 2H), 4.34 (t, J = 4.9 Hz, 4H), 4.23 (t, J = 5.0 Hz, 4H), 4.16 (s, 8H), 3.38 (t, J = 7.6 Hz, 8H), 1.67–1.59 (m, 8H), 1.43–1.34 (m, 8H), 0.98 (t, J = 7.3 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.02, 181.57, 162.26, 155.04, 149.11, 133.83, 121.56, 114.65, 112.29, 106.36, 94.66, 70.30, 69.79, 69.71, 69.00, 51.23, 29.69, 20.25, 13.91; ESI–MS: m/z 793.5 ($[M+Na]^+$); Anal. Calcd for $C_{46}H_{62}N_2O_8$: C 71.66, H 8.11, N 3.63; found: C 71.48, H 8.02, N 3.75.

2.4.2. Synthesis of *2*

A mixture of polyether tethered bisaniline **3** (1.00 g, 2.13 mmol), *n*-butyl bromide (1.73 g, 12.6 mmol), and anhydrous sodium carbonate (0.67 g, 6.32 mmol) was dissolved in 30 mL isopropanol–H_2O (1:1, v/v) in a 50 mL round bottom flask. The reaction solution was stirred for 24 h at 70 °C. After cooling down, the mixture was extracted three times with CH_2Cl_2, and then the combined organic phase was washed twice with saturated salt water, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The resulting oily crude product was purified by column chromatography on silica gel (PE/EtOAc, v/v = 10:1) to give **2** as yellow oil (0.51 g), yield: 35%. FTIR (KBr): ν_{max} 2956, 2871, 1611, 1570, 1506, 1456, 1368, 1328, 1290, 1199, 1136, 1059, 953, 823, 745, 688 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (t, J = 8.1 Hz, 2H), 6.91–6.87 (m, 4H), 6.26 (d, J = 8.6 Hz, 2H), 6.22 (s, 2H), 6.18 (d, J = 8.2 Hz, 2H), 4.17 (t, J = 4.8 Hz, 4H), 4.10 (t, J = 4.7 Hz, 4H), 3.90 (t, J = 4.8 Hz, 8H), 3.21 (t, J = 7.5 Hz, 8H), 1.58–1.51(m, 8H), 1.37–1.28 (m, 8H), 0.93 (t, J = 7.3 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.13, 149.62, 149.08, 129.77, 121.77, 115.10, 105.25, 100.49, 99.12, 70.13, 69.96, 69.03, 67.19, 50.85, 29.52, 20.41, 14.10; ESI–MS: m/z 693.5 ($[M+H]^+$).

2.4.3. Synthesis of *3*

A catalytic amount of $FeCl_3$ and activated carbon were suspended in 10 mL MeOH in a 100 mL three-necked round-bottom flask. To the mixture, polyether tethered bis(*m*-nitrophenyl) **4** (2.40 g, 4.54 mmol) was added, and then 20 mL hydrazine hydrate was slowly added under a nitrogen atmosphere. The solution was