Sensors and Actuators B 156 (2011) 126–131

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

A new acridine derivative as a highly selective ‘off–on’ fluorescence chemosensor for Cd^{2+} in aqueous media

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ARTICLE INFO

Article history:
Received 1 November 2010
Received in revised form 20 March 2011
Accepted 31 March 2011
Available online 8 April 2011

Keywords:
Fluoroionophore
PET
Acridine
Cd^{2+}
Sensing

ABSTRACT

A new acridine fluoroionophore containing two diethanolamine ligands, 4,5-bis(N,N-di (2-hydroxyethyl)iminomethyl)acridine (BHIA), was designed and synthesized based on the fluorophore-spacer-receptor format. And its fluorescent sensing behavior towards metal ions was investigated in buffered aqueous media. The presence of Cd^{2+} induces the formation of a 1:1 ligand/metal complex at neutral pH, which exhibits enhanced emission at 454 nm. The fluorescence intensity is linear with the Cd^{2+} concentration in the range of 1.0×10^{-6} to 3.0×10^{-5} M ($R = 0.9967$). Experimental results show a low interference response towards other metal ions. The selective switch-on fluorescence response of BHIA to Cd^{2+} makes it suitable for sensing of Cd^{2+} in aqueous solution. The detection limit is 1.3×10^{-7} M. Moreover, the results indicated that BHIA was a reversible chemosensor for Cd^{2+}, which makes it attractive for sensing applications.

1. Introduction

Owing to their advantages of possessing high sensitivity and selectivity, as well as providing on-line and real-time analysis, the design and synthesis of fluorescent chemosensors for analytical detection of chemical and biological ionic species constitute a very active area of research. Considerable efforts have been devoted to the elaboration of luminescent sensors for various metal ions in the last two decades [1]. However, the development of water-soluble sensors is still a challenging task and the successful examples are still limited [2]. Although more recent reports described receptor molecules that can be used either in mixed aqueous/organic medium or in pure aqueous solution [3], intricate synthetic procedures of such receptors may limit their uses in practice.

Among various metal ions, recognition and sensing of Cd^{2+} ion is one of the major targets for researchers due to the obvious health related hazards of chronic cadmium exposure, including renal dysfunction, calcium metabolism disorders and an increased incidence of certain forms of cancer [4]. However, there are only a handful of reports on Cd^{2+} fluorescent chemosensors [5] and even fewer on Cd^{2+} in aqueous solution [5j–m]. Thus, the development of new cadmium chemosensors that can operate in aqueous medium with good sensitivity and selectivity is currently of great importance. Of particular interest are those fluorescence chemosensors based on “off–on” switching mechanisms.

Acridine and its derivatives are planar tricyclic aromatic molecules which fluoresce at the shorter wavelength end of the visible region with high fluorescence quantum yield [6]. Owing to their interesting features and numerous applications, acridines have been a topic of interest for a long time. However, they are sparsely used as the signaling part in chemosensors for metal ions. Only recently, a few acridine derivatives have been developed as fluorescent chemosensors for metal ions, where macrocyclic receptor molecules have been devised [7]. Utilizing the fluorophore-spacer-receptor motif developed by de Silva and de Silva [8] for photoinduced electron transfer (PET) sensors, we herein design and synthesize a new acridine derivative possessing two diethanolamine groups which behave as N and O-donor ligands. The use of diethanolamine moiety as the ionophore guarantees sufficient water solubility in combination with the binding ability with the selected metal ions. Experimental studies revealed that this fluoroionophore showed a higher affinity for Cd^{2+} ion in aqueous media associated with a fluorescence OFF–ON change (TURN-ON type). The effect of foreign ions on the intensity of BHIA showed a low interference response towards other metal ions.

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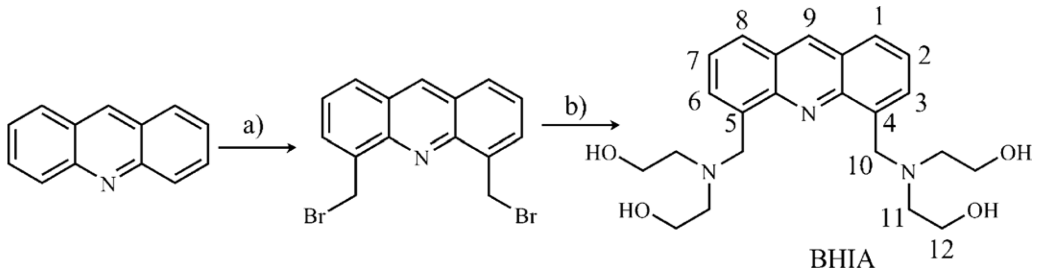
doi:10.1016/j.snb.2011.03.083



Scheme 1. Synthesis of BHIA. Reagents conditions: (a) BMME, H_2SO_4, 50 °C; (b) diethanolamine, K_2CO_3, $CHCl_3$, 50 °C.

2. Experimental

2.1. Reagents

Acridine (98%), bromomethylmethylether (BMME, 90%), diethanolamine (99%) and 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES, 99%) were purchased from Alfa Aesar (Lancaster, UK). All the other chemical reagents were of analytical grade and used as received without further purification. All the metallic ions were supplied from their corresponding nitrates. Stock solution of BHIA was prepared in water at 1.0×10^{-4} mol L^{-1}. All metal ion stock solutions were prepared at 1.0×10^{-2} mol L^{-1} by dissolving appropriate amounts of metal salts in water. Doubly distilled water was used throughout.

2.2. Instrumentation

IR spectra were taken as KBr pellets on a SHIMADZU 8400S infrared spectrometer (Nicolet, Waltham, Japan). ^{1}H NMR spectra were recorded on a DRX-300 spectrometer (Fällenden, Switzerland). Mass spectra were recorded with a Waters ACQUITY(TM) UPLC combined with a TQ Detector mass spectrometer. Elemental analyses were performed on an Elementar Analysensteme Gmbh VarioE1 analyzer. The UV absorption experiments were carried out on a UV-2450 spectrophotometer (Shimadzu, Japan). Fluorescence measurements were performed on a RF-5301 PC spectrofluorometer (Shimadzu, Japan). The samples were excited at 356 nm with an excitation and emission slit width of 5 nm. The pH measurements were carried out on a pHS-3C acidometer (Shanghai Precision & Scientific Instrument Co., Ltd, China).

2.3. Synthesis of BHIA

BHIA was prepared in two steps from acridine, as shown in Scheme 1. The key intermediate 4,5-bis-bromomethylacridine was synthesized as previously described [9] with slight modification. Briefly, BMME (6.08 g, 44.64 mmol) was added to a solution of acridine (2.0 g, 11.16 mmol) in concentrated (98%) H_2SO_4 (20 mL) at 50 °C. The mixture was stirred at 50 °C under nitrogen for 12 h. The reaction mixture was poured into ice and then filtered. The filter cake was dissolved in $CHCl_3$ and the solution was washed thrice with water. The $CHCl_3$ layer was dried over $MgSO_4$ and evaporated under vacuum. The residue was purified by silica gel chromatography (chloroform:cyclohexane = 7:3), affording the product as a pale yellow solid (2.43 g, 60% yield). ^{1}H NMR ($CDCl_3$) δ: 8.81 (1H, s), 8.00 (2H, d), 7.94 (2H, d), 7.51 (2H, t), 5.45 (4H, s).

BHIA: the mixture of 4,5-bis-bromomethylacridine (0.20 g, 0.55 mmol), diethanolamine (0.23 g, 2.2 mmol) and potassium carbonate (0.7 g) was stirred at 50 °C for 7 h in $CHCl_3$ (20 mL). The reaction mixture was filtered and the filtrate was washed thrice with water. The organic layer was dried over $MgSO_4$ and evaporated under vacuum. The crude product was purified by silica gel chromatography (chloroform:ethanol:diethylamine = 18:4:1), affording the product as a yellow solid (0.16 g, 70% yield). IR ν_{max} (KBr) 3411, 3309, 3274, 2945, 2846, 2819, 1066, 1033 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 8.77 (1H, s), 7.94 (2H, d), 7.86 (2H, d), 7.53 (2H, t), 4.63 (4H, s), 3.67 (8H, t), 2.92 (8H, t). ^{13}C NMR ($CDCl_3$) δ: 148.263, 137.996, 131.578, 128.725, 127.615, 126.492, 60.754, 57.222, 55.675, 30.7. MS(ESI) m/z 414.6 $(M+H)^+$. Anal. Calcd. for $C_{23}H_{31}N_3O_4$: C, 66.80; H, 7.56; N, 10.16. Found: C, 66.69; H, 7.53; N, 10.12.

2.4. General procedure

The titration experiments were carried out in water by adding aliquots of different metal ions. In brief, 0.1 mL of BHIA stock solution and different volumes of cation stock solution were added into a comparison tube. The mixed solution was diluted to 5 mL with 0.01 M HEPES buffer, pH 7.4. The working solution was shaken thoroughly for 10 min before making measurements. Samples for the IR measurement, namely the BHIA–Cd^{2+} complex, were prepared by the following procedure: BHIA (0.02 g, 0.48 mmol), dissolved in 10 mL of CH_3CN, was mixed with $CdCl_2 \cdot 2.5H_2O$ (0.011 g, 0.48 mmol), in 5 mL of ethanol, and the mixture was stirred for 2 h. Then the solvents were evaporated under reduced pressure. The residue was dissolved in 5 mL CH_3CN and mixed with 20 mL diethyl ether. A yellow precipitate was obtained for the IR measurements.

3. Results and discussion

3.1. Effect of pH on the fluorescence of BHIA

Britton–Robinson (B–R) buffer solutions were used to adjust the acidity of solution. Fig. 1 shows the pH-dependent fluorescence spectra of BHIA in water. It is seen that the fluorescence intensity increases with decreasing pH and reaches its maximum at pH around 6. The result is in accordance with the PET quenching mechanism that has been described previously [8]. A

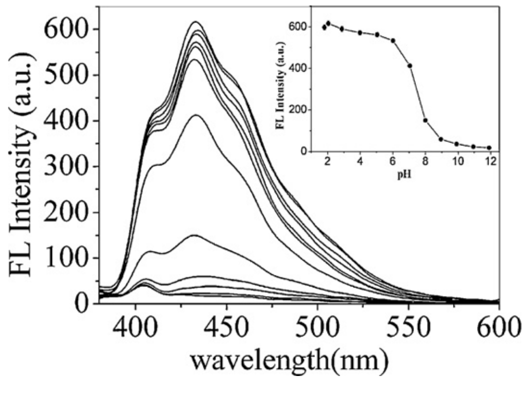


Fig. 1. Effect of pH on the fluorescence spectra of BHIA. $C_{BHIA} = 8.0 \times 10^{-6}$ mol L^{-1}. Inset: fluorescence intensities of BHIA at different pH values.