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A new acridine derivative as a highly selective fluoroionophore for Cu^{2+} in 100% aqueous solution

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ABSTRACT

A new acridine fluoroionophore containing two iminodiacetic acid ligands, Acridinyl Tetra Acid (ATA), was synthesized. The fluorescence sensing behavior of ATA toward metal ions was investigated in buffered aqueous media. The presence of Cu^{2+} resulted in significant quenching of the fluorescence emission from ATA, while other metal ions posed little interferences, if any. The fluorescence response was concentration-dependent and can be well described by the modified Stern–Volmer equation. A good linear relationship ($R^2=0.9952$) was observed up to 3.0×10^{-6} mol L^{-1} Cu^{2+} ions. The detection limit, calculated following the 3σ IUPAC criteria, was 1.24×10^{-7} mol L^{-1}. The presence of Cu^{2+} induces the formation of a 1:1 ligand/metal complex at neutral pH.

1. Introduction

Copper is an essential element for all biological organisms including humans. On the other hand, copper is a toxic pollutant, and human exposure to excess copper in drinking water or other environmental sources can cause serious health problems [1]. Thus, selective recognition and sensing of Cu^{2+} has drawn worldwide attention. Due to its simplicity, high sensitivity, high selectivity, and real-time detection, fluorescence has been a powerful tool for detecting metal ions among various analytical methods. A number of synthetic Cu^{2+} fluorescent probes have been continuously devised [2–15]. In the fluorescent sensors reported for copper, so far, the successful examples of water-soluble Cu^{2+} sensors are still limited due to the strong hydration ability of Cu^{2+} in aqueous solution [10,12]. Also, most chemosensor molecules are structurally complicated and require an elaborate and sophisticated synthetic process. Hence, there is still a need for development of simple and easy-to-make chemosensing molecules for detection of Cu^{2+} ions in aqueous solution.

Acridine and its derivatives are planar tricyclic aromatic molecules which fluorescence at the shorter wavelength end of the visible region with high fluorescence quantum yield [16]. Owing to their interesting features and numerous applications, acridine and its derivatives have been a topic of interest for a long time. However, they are sparsely used as the signaling part in chemosensors for metal ions [17–22]. Following our previous work [23], here we report a new acridine derivative possessing two iminodiacetic acid groups which behave as N-and O-donor ligands. The use of iminodiacetic acid moiety as the ionophore guarantees sufficient water solubility in combination with the binding ability with transition metal ions. Experimental studies revealed that this fluoroionophore showed a higher affinity for Cu^{2+} ion in aqueous media associated with a fluorescence quenching. The effect of foreign ions on the intensity of ATA showed a low interference response toward other metal ions.

2. Experimental

2.1. Reagents

Acridine (98%), Bromomethylmethylether (BMME, 90%) and 4-(2-hydroxyethyl)-1-piperazine-ethanesulfonic acid(HEPES, 99%) were purchased from Alfa Aesar (Lancaster, UK). Diethyl iminodiacetate was obtained from Acros Organics Co. 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 ATA 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

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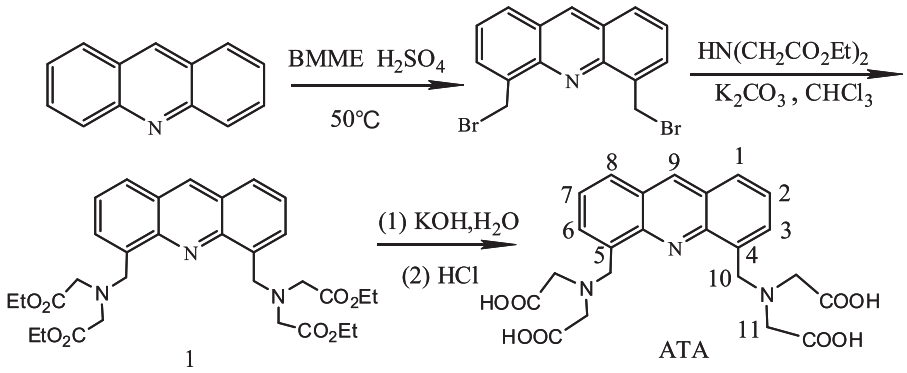

Scheme 1. Synthesis of ATA.

appropriate amounts of metal salts in water. Double 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). 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 LS-55 Luminescence Spectrometer (Perkin-Elmer, USA). 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 ATA

ATA was prepared in three steps from acridine, as shown in Scheme 1. The key intermediate 4,5-Bis(bromomethyl)acridine was synthesized as previously described [23].

Compound 1: 4,5-Bis(bromomethyl)acridine (0.8 g, 2.19 mmol) was added to a stirred solution of diethyl iminodiacetate (1.6 mL, 8.76 mmol) and potassium carbonate (0.7 g) in $CHCl_3$ (20 mL). The reaction mixture was stirred at 50 °C for 7 h. After cooling to room temperature, the reaction mixture was filtered. The filtrate was washed thrice with water and the organic layer was dried over anhydrous magnesium sulfate. The solvent was evaporated and the crude product was purified by silica gel chromatography (petroleum:ethyl acetate=4:1) to get the product as a red–brown oil (0.87 g, 68% yield). ^{1}H NMR ($CDCl_3$) δ 8.71 (s, 1H), 7.97 (d, 2H), 7.90 (d, 2H), 7.54 (t, 2H), 4.78 (s, 4H), 4.08 (q, 8H), 3.73 (s, 8H), 1.18 (t, 12H).

ATA: compound 1 (1.0 g, 1.72 mmol) was added to a stirred solution of KOH (0.14 g, 2.58 mmol) in distilled water (15 mL). The reaction mixture was then refluxed for 8 h. The reaction mixture was cooled to room temperature and then 1 M HCl solution was added to make the pH 2.0. The resulting precipitate was filtered and washed with distilled water. The product was dried under vacuum to give ATA as yellow solid (0.64 g, 80% yield). Melting point 227–228 °C; ^{1}H NMR (DMSO-d6) 9.12 (s, 1H), 8.13(d, 2H), 8.03(d, 2H), 7.34 (t, 2H), 4.81(s, 4H), 3.73(s, 8H) and 12.34 (w, 4H); ^{13}CNMR (DMSO-d6) 172.87, 137.24, 134.06, 131.94, 128.74, 128.42, 128.41, 128.12, 127.02, 126.97, 123.17, 57.96, and 54.39; IR_{max} 3446, 3419, 3122, 2929, 2856, 1728, 1631, 1384, 1261, 1149, 1083, 914, 883, and 767 cm^{-1}; Calculated for $C_{23}H_{23}N_3O_8$: C—58.84, H—4.94, N—8.95. Found: C—58.90, H—4.91, N—8.98.

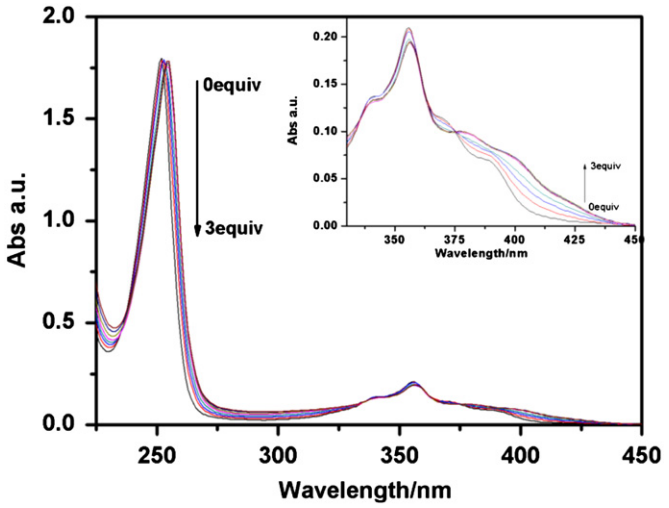

Fig. 1. Absorption spectra of ATA in the presence of different concentrations of Cu^{2+} in water at pH 7.4. $C_{ATA}=2.0\times10^{-5}$ mol L^{-1}.

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 ATA stock solution, different volumes of cation stock solution and 0.5 mL of 1 M stock solution of NaCl 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 taking measurements. Samples for the IR measurement, namely the ATA–Cu^{2+} complex, were prepared by using the following procedure: ATA (0.01 g, 0.02 mmol), dissolved in 10 mL of CH_3CN, was mixed with $Cu(NO_3)_2\cdot3H_2O$ (0.0049 g, 0.02 mmol), in 5 mL of ethanol, and the mixture was stirred for 2 h at room temperature. Then the solvents were evaporated under reduced pressure. The residue was dissolved in 5 mL CH_3CN and mixed with 20 mL diethyl ether. An yellow precipitate was obtained for the IR measurement.

3. Results and discussion

3.1. Spectral characteristics of ATA and Cu–ATA

As shown in Fig. 1, the UV/vis spectrum of ATA is characterized by two bands centered at 253 nm and 356 nm, which are attributed to π–π* transitions of acridine ring [24]. Upon addition of Cu^{2+} ion, the band at 253 nm exhibits a small red-shift of ca. 3 nm, while the band at 356 nm remains unchanged. In addition,