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Novel 4-amino-2-methyl-8-(trifluoromethyl)quinoline-based magnetic nanostructures for highly sensitive detection of zinc ions in aqueous solutions

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ABSTRACT

Novel 4-amino-2-methyl-8-(trifluoromethyl)quinoline based magnetic nanosensors, Fe_3O_4@SiO_2-PEG-4AQ and Fe_3O_4@SiO_2-4AQ, were successfully fabricated and characterised. Enhanced fluorescent intensity was demonstrated by both nanosensors. Upon complexation with zinc ions, a further enhancement of 13.5-fold was revealed by Fe_3O_4@SiO_2-PEG-4AQ. A red shift of 42 nm was also observed. The presence of other metal cations including Ni^{2+}, Co^{2+}, Ca^{2+}, Cd^{2+}, Hg^{2+}, Mg^{2+}, Mn^{2+} and Ag^{+}, showed no interference towards Zn^{2+}. A sensitive detection limit of 0.0065 μM and 0.0125 μM was indicated by Fe_3O_4@SiO_2-PEG-4AQ and Fe_3O_4@SiO_2-4AQ respectively. The high sensitivity and selectivity remained constant within a wide range of pH values and were reversible upon treatment with EDTA. The PEG spacer between the magnetic core and the fluorophore offered further improvement of fluorescence intensity and detection sensitivity. To the best of our knowledge, this is the first study on 4-aminoquinoline based reusable nanochemosensor for zinc ion detection.

1. Introduction

Zinc is an essential trace element and plays a significant role in biological and environmental applications. Among the transition metals, zinc ion (Zn^{2+}) is one of the most difficult to detect by regular metal detection instruments due to its specific electron configuration (full d-shell of electrons) [1]. Fluorescent chemosensors have attracted enormous attention in the recent decades due to their low cost, high sensitivity and technical simplicity. Among many of the reported chemosensors for Zn^{2+}, some suffer from poor water solubility and low selectivity especially when the ions of zinc, cadmium and mercury coexist [2–4], some show reduced fluorescence as a consequence of quenching, limiting the sensors' applicability [5,6]. The development and discovery of highly selective and sensitive fluorophores and fluorescent chemosensors for Zn^{2+} has been an ongoing topic of research. Quinoline-based chemosensors have been extensively used as a fluoroscopic agent for detection of zinc ions in aqueous solutions [7–9]. These sensors rely largely on photo-induced electron transfer (PET), intermolecular charge transfer (ICT) and fluorescence resonance energy transfer (FRET) for the fluorescence signal transduction in their designs [10,11]. Among the reported studies, 8-aminoquinoline and its derivatives are the most commonly used due to their ability to chelate Zn^{2+} ions via the chelated complex that is formed by the heterocyclic nitrogen atom and the exocyclic amino group [12–14]. The 4-isomer of aminoquinoline, 4-amino-2-methyl-8-(trifluoromethyl)quinolone, however, has attracted little attention, despite many studies of its luminescent properties, which is reportedly due to the controversy over the chemical properties of the 4-isomer compared to the 8-isomer. Several researchers [15–17] have shown that the chemistry of 4AQ is atypical to normal arylamine while other aminoquinoline isomers are well behave in this respect. In fact 4-isomer is more similar to a cyclic amidine than to an aminoquinoline. The chemical structures of the two isomers are displayed in Scheme 1.

An early report indicated that the 4-isomer is a pH-sensitive and non-emissive probe that shows enhanced fluorescence intensity upon protonation due to enhanced ICT [18]. Recent years have seen increasing research activities in the development of 4-isomer derivatives for luminescent sensing of transition metals. However understanding of the sensing mechanism is limited. For instance, Kaur and co-workers [19] synthesised a metal cation sensor based on a 4-aminoquinoline derivative. They reported its sensing application through quenching of fluorescence in the presence of Hg^{2+}, Fe^{3+} and Cu^{2+}. In a similar study, Singh et al. [20] fabricated pH-sensitive benzo-xanthene-4-aminoquinoline conjugates for sensing thorium (Th^{4+}). The fluorescence intensity was quenched due to chelation-enhanced fluorescence quenching caused by specific interaction of Th^{4+} with two nitrogen

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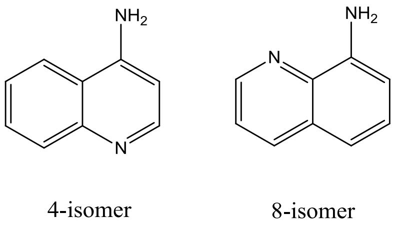

Scheme 1. The structure of the 4-iosmer and 8-isomer of aminoquinoline.

atoms of the linker of the xanthene-aminoquinoline conjugate. More recently, Wang et al. [21] synthesised an Hg^{2+}-selective fluorescent sensor by grafting 4-aminoquinoline onto glycosyl pyridyl-triazole and reported that the significantly enhanced flurocent behaviour of the probe towards Hg^{2+} could be attributed to a binding mode of triazolyl quinoline with Hg^{2+}.

This study aims to create a novel 4AQ-based nano-magnetic structure and further to investigate its selectivity and sensitivity towards zinc ions in aqueous solutions. Magnetic core-shell structures are widely considered in the design of recyclable and reusable nanochemosensors [22–25] in which the magnetite (Fe_3O_4) nanoparticles are used as a core and various silicon precursors are used to 'shell' the core and to conjugate a selected fluorophore to the surface of the magnetic nanoparticles. The silica shell is capable not only to prevent the aggregation of magnetic nanoparticles [13,25], but also to protect the sensor from the interference of other spieces [13,26]. A recent study reported that the presence of polyethylene glycol (PEG) as a spacer between the core nanostructure and the fluorophore moiety has a strong positive impact on the fluorescent properties of the magnetic nanochemosensor [22]. In this study, 4-amino-2-methyl-8-(trifluoromethyl)quinoline (4-AQ), was introduced onto the surface of a nanomagnetic core using a facile method, and was systematically investigated in regard to its selectivity and sensitivity towards a series of metal ions, and its pH dependence, stability and reusability.

The nanomagnetic core-shell structure containing 3-glycidyloxypropyl siloxane was first synthesised using a previously reported method [22]. Polyethylene glycol (NH_2-PEG-COOH, $M_w = 3000$) was then conjugated to the surface of the nanoparticles. The free carboxylic acid groups of the PEG spacer were further grafted with 4AQ to form a novel nanostructure of Fe_3O_4@SiO_2-PEG-4AQ. This chemical synthesis route is illustrated in Scheme 2. Using a similar chemistry, the non-PEG magnetic nanostructure, Fe_3O_4@SiO_2-4AQ, was also prepared. Both nanosensors were fully characterised and investigated as potential sensors for Zn^{2+} detection in aqueous solutions. High sensitivity and stability were observed.

2. Experimental

2.1. Materials

Tetraethoxysilane (TEOS) (99.99%), (3-glycidyloxypropyl) trimethoxylsilane (GPS) (98%), 4-amino-2-methyl-8-(trifluoromethyl) quinoline (4-AQ), N-(3-dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (EDC) (98%), N-hydroxysuccinimide (NHS) (98%) were obtained from Sigma–Aldrich. Amino-PEG-carboxylic acid NH_2-PEG-COOH (90%, $M_w = 3000$) was purchased from Nanocs (USA).

2.1.1. Synthesis of the 3-glycidyloxypropyl siloxane-shelled magnetic nanostructure Fe_3O_4@SiO_2-GPS (Scheme 2a)

Fe_3O_4 nanoparticles were first prepared and further functionalised using TEOS and GPS according to our previously reported method [22]. The produced Fe_3O_4@SiO_2-GPS contains 2.22×10^{-3} mmol 3-glycidyloxypropyl per mg nanoparticles, which was determined using UV–vis spectroscopy and thermogravimetric analysis. The details of the experimental procedure and the characterisation methods can be found in Pourfallah and Lou [22].

2.1.2. Synthesis of Fe_3O_4@SiO_2-4AQ (Scheme 2a)

Fe_3O_4@SiO_2-4AQ was synthesised by mixing 100 mg of Fe_3O_4@SiO_2-GPS (0.222 mmol GPS) with 50.2 mg (0.222 mmol) of 4-amino-2-methyl-8-(trifluoromethyl)quinoline in 20 ml DI water. The mixture was stirred at 65 °C for 6 h in the dark. After the completion of the reaction, the Fe_3O_4@SiO_2-4AQ product was collected by an external magnet and washed sequentially by ethanol (4 × 20 ml) and DI water (4 × 20 ml).

2.1.3. Synthesis of Fe_3O_4@SiO_2-PEG-4AQ (Scheme 2b)

The synthesis of Fe_3O_4@SiO_2-PEG-4AQ was carried out in two stages. The first stage was the amination of the epoxy ring of the GPS by mixing Fe_3O_4@SiO_2-GPS (10 mg, 0.022 mmol) with amino PEG acid (NH_2-PEG-COOH, 66 mg, 0.022 mmol) using a similar procedure described in the authors' previous study [24]. This led to the formation of Fe_3O_4@SiO_2-PEG. The second stage involved the activation of the carboxylic acid group by the carbodiimide reagent (EDC-NHS) prior to the reaction with 4-amino-2-methyl-8-(trifluoromethyl)quinoline. For this purpose, EDC (0.162 mg, 1.04×10^{-3} mmol) and NHS (0.06 mg, 5.2×10^{-4} mmol), with EDC: NHS in a 2:1 mol ratio, were dissolved in ice-cold water (20 ml). Fe_3O_4@SiO_2-PEG nanoparticles (10 mg containing 2.1×10^{-4} mmol COOH) were then added to the mixture and stirred for 15 min. The 4AQ fluorophore (0.047 mg, 2.1×10^{-4} mmol) was also added to the mixture of nanoparticles and the slurry was constantly stirred for 4 h in an ice bath in the dark. After 4 h, the ice bath was removed and the reaction was carried out while being stirred at room temperature overnight. Upon completion of the reaction, the produced nanosensors were separated from the mixture by an external magnet and washed sequentially by ethanol (4 × 20 ml) and DI water (4 × 20 ml).

2.2. Characterisation

The morphology examination was carried out using a Transmission Electron Microscope (JEOL JEM-2100 TEM). The sample preparation was accomplished by distributing an ethanol suspension of nanoparticles onto a carbon-coated copper grid. A Thermo Scientific Nicolet iS50, fitted with a diamond ATR sampling accessory, was used to obtain the Fourier transform infrared (FTIR) spectra of the synthesised nanostructures. The spectra were recorded in the range of 400–4000 cm^{-1}. UV absorption spectra were recorded on a Lambda 25 Perkin Elmer UV–Vis Spectrometer. Scans were recorded in the wavelength range from 200 to 800 nm with a band width of 1 nm. Thermogravimetric analysis (TGA) was performed using a TGA/DSC (Mettler-Toledo Star®) thermal analysis system. All TGA experiments were carried out under air atmosphere at a heating rate of 5 °C/min from 35 to 800 °C. X-ray diffraction (XRD) analysis was performed using a Bruker AXS diffractometer with Co Kα radiation ($\lambda = 1.79$ Å). A scan rate of 0.015°/s was used to record the patterns in a 2θ range of 20–80°, and the accelerating voltage and current were 35 kV and 40 mA, respectively.

The fluorescence emission spectra were obtained from a Perkin Elmer L55 fluorescence spectrometer with an excitation source set at 330 nm and a scanning rate of 5 nm/min. The stock solutions were prepared separately in DI water, each at a concentration of 1 μM. Various metal ion solutions, including Cu^{2+}, Ni^{2+}, Co^{2+}, Ca^{2+}, Cd^{2+}, Hg^{2+}, Mg^{2+}, Fe^{3+}, Mn^{2+} and Ag^{+} were also prepared (10 μM, chloride). The quantum yields and the Job plots were obtained by using the methods stated elsewhere [22].