

Dual-function cellulose composites for fluorescence detection and removal of fluoride

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ARTICLE INFO

Keywords:

Fluorescent sensor
Cellulose support
Fluoride sensing
Boronic acid sensor
Functional materials

ABSTRACT

A biodegradable and robust fluorogenic cellulose material for simultaneous fluoride recognition and adsorption at environmentally significant levels is presented. The fluorescent modified cellulose (FMC) containing a boronic acid-based anthracene group as a fluorescent signaling unit displays a selective fluorescence enhancement with F^- . On the other hand, Cl^- , Br^- , SO_4^{2-} , $H_2PO_4^-$ and ClO_4^- did not induce significant changes in fluorescence. Furthermore, FMC shows excellent F^- adsorption over a wide range of pH with a low dosage. Equilibrium studies demonstrate that the adsorption of F^- follows the Langmuir model in an aqueous solution. While, adsorption kinetics were found to follow the pseudo-second-order model. The simplicity of the method and the ability to detect and remove fluoride in waste water is noteworthy given the problems associated with fluoride pollution in drinking water.

1. Introduction

Environmental pollution by fluoride anion is one of the main problems to be addressed in the treatment of drinking water. At low levels fluoride anions have been shown to be effective in the prevention of dental caries [1], however, high levels of fluoride in drinking water can cause both dental and skeletal fluorosis [2,3]. Therefore, it is necessary to develop methods for highly selective and rapid detection and removal of fluoride ions. Various methods have been reported for the detection of fluoride such as fluoride electrodes [4,5], gas chromatography (GC) [6], high pressure liquid chromatograph (HPLC) [7], and flow injection-spectrophotometry [8]. Among various sensors for detecting fluoride ion, fluorescence sensors have been widely investigated due to their high sensitivity, selectivity, and the potential for rapid real-time monitoring [9–14]. Sensors selective for fluoride have been designed *via* hydrogen bonding [15–19], anion- π interactions [20], and Lewis acid-based interactions [21–23]. In particular, those based on the affinity of a boron atom toward fluoride anion represent an attractive approach due to the excellent selectivity and sensitivity for fluoride anion with fluorescence “turn-on” [24–26]. The anthracene moiety is a particularly useful fluorophore used for the construction of fluorogenic chemosensors which have been employed for the detection of a variety of chemical species [27,28]. Therefore, we decided to take advantage of

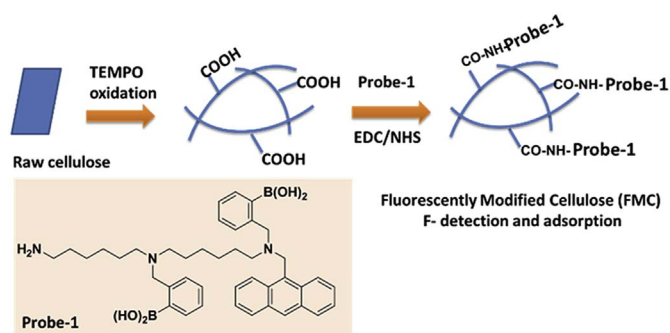
these properties in the design of a fluoride specific sensor, and prepared an anthracene appended boronic acid probe 1 as a robust system for the detection of fluoride (Scheme 1) (see Scheme 2).

Among the techniques used for the removal of fluoride anion from water, adsorption is one of the most effective and efficient methods [29,30]. Biopolymer-based adsorbents have attracted significant attention as promising materials for the removal of fluoride ions, such as chitosan [31,32] and cellulose [33,34]. Cellulose is the most abundant polysaccharide and contains a number of hydroxyl groups which can be used for functional group modification in order to improve the chemical and physical properties [35–37]. Although cellulose based fluorescent sensors have been reported [38], there are few examples in the literature where the dual detection and adsorption properties of functional cellulose materials have been reported for the simultaneous sensing and removal of fluoride ions. Herein, we describe a novel fluorescent probe-modified cellulose material for the simultaneous fluoride ion detection and adsorption (Scheme 1). Such materials have huge potential in sensing and purification technologies, which also contributes to the development of sensing devices.

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Scheme 1. Fluorescently Modified Cellulose (FMC) prepared using probe 1.

2. Experimental

2.1. Materials and equipment

All chemical reagents and solvents were analytical grade and purchased from commercial suppliers. Fluorescent modified cellulose was prepared by the established literature procedure [29]. ^1H NMR and ^{13}C NMR spectra were recorded on either a Bruker AV-300 or AV-250 spectrometer with chemical shifts reported in ppm (in CDCl_3 , TMS as internal standard) at room temperature. Electrospray mass spectra were recorded using a Bruker micro TOF spectrometer using reserpine as calibrant. FTIR spectra were recorded on the Nicolet iS-50 spectrometer at room temperature. SEM spectra were recorded using a JEOL JSM-7500F. Fluorescence measurements were performed on a Lengguang Luminescence spectrophotometer F97PRO (Shanghai), utilising sterna silica (quartz) cuvettes with 10 mm path length and four sides polished. Fluoride ion absorption experiments were employed by a Leici PXSJ-216F fluoride ion meter (Shanghai). Electric conductivity titration was recorded on a Shengci DDS-IIA conductivity meter (Shanghai). Spectral-grade solvents were used for measurements of fluoride absorption and fluorescence detection.

2.2. Synthesis

2.2.1. Synthesis of monoBoc triamine (4)

Bis(hexamethylene)triamine (2.15 g, 10 mmol) was dissolved in MeOH (50 mL) then cooled in an ice bath. $(\text{Boc})_2\text{O}$ (0.436 g, 2 mmol) in

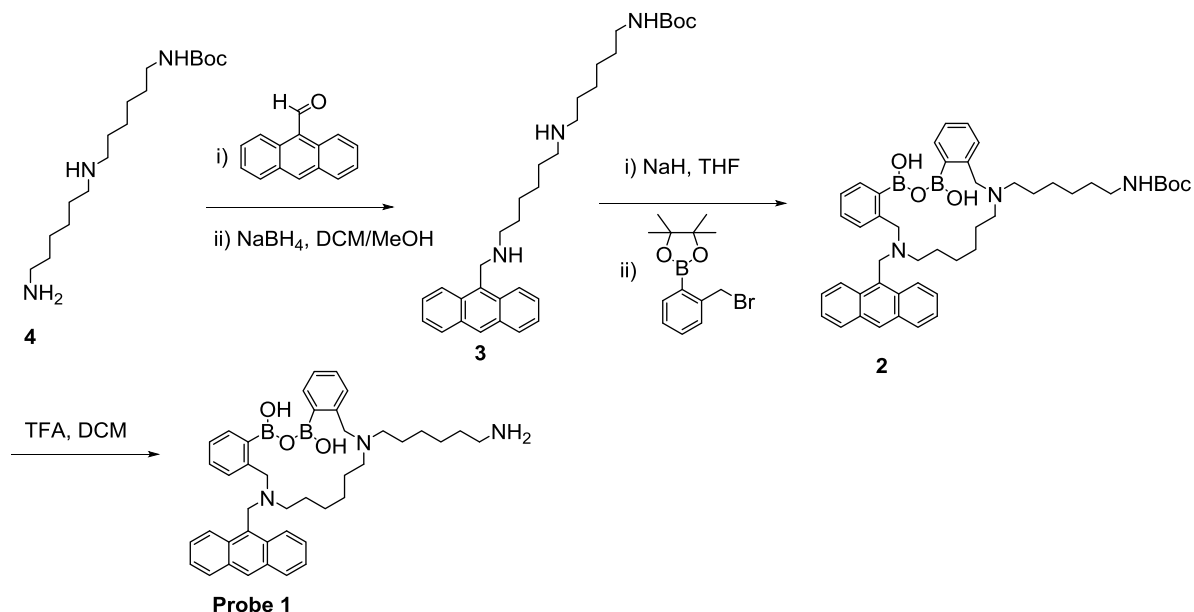
MeOH (10 mL) was added slowly into the solution at 0°C then the mixture was stirred continuously whilst warming from 0°C to room temperature over 2 h (monitoring by TLC). When the reaction finished, methanol was evaporated and water was added into the mixture. The pH of the mixture was adjusted to pH 7 (using 1 N NaOH and 1 N HCl) and extracted with DCM/water to remove the diboc triamine. Then the pH was adjusted to pH 10 with 1 N NaOH and extracted with DCM to give the monoBoc triamine (0.543 g, 86%). ^1H NMR (CD_3OD , 300 MHz, ppm) δ 1.37–1.48 (m, 21H), 1.64–1.65 (m, 4H), 2.85 (t, $J = 6.0$ Hz, 6H, $-\text{CH}_2\text{-N}$), 3.03 (t, $J = 6.0$ Hz, 2H, $-\text{CH}_2\text{-N-Boc}$). ^{13}C NMR (CD_3OD , 75 MHz, ppm) δ 27.6, 27.8, 27.9, 28.0, 28.5, 28.6, 29.3 (Boc-3CH_3), 30.1, 31.2, 41.5, 41.6, 49.9, 80.2, 159.0. ESI mass $[\text{M} + \text{H}]^+$ $\text{C}_{17}\text{H}_{38}\text{N}_3\text{O}_2$ calculated 316.2964 found 316.2958.

2.2.2. tert-Butyl(6-((6-((anthracen-9-ylmethyl)amino)hexyl)amino)hexyl) carbamate (3)

MonoBoc triamine (3.065 g, 9.7 mmol) and 9-anthracenecarboxaldehyde (1.8 g, 8.74 mmol) were dissolved in DCM/Methanol (1:1) (50 mL) and stirred overnight. After crude NMR confirmed that the imine had been generated, the reaction was cooled to room temperature. NaBH_4 (3.67 g, 9.7 mmol) was added and stirred for another 2 h. After the reaction was completed, more water (50 mL) was added to quench the unreacted NaBH_4 . After evaporating methanol, the aqueous layer was extracted with DCM, dried with Na_2SO_4 and purified by flash column chromatography using DCM/MeOH as eluent to afford the product (3.67 g, 83%). ^1H NMR (CDCl_3 , 250 MHz, ppm) δ 1.16–1.46 (m, 25H), 2.39–2.45 (m, 4H), 2.75 (t, $J = 7.5$ Hz, 2H), 2.93 (m, 2H), 4.56 (s, 2H), 7.30–7.45 (m, 4H), 7.85 (d, $J = 7.5$ Hz, 2H), 8.22–8.25 (m, 3H). ^{13}C NMR (CDCl_3 , 62 MHz, ppm) δ 26.5, 26.7, 27.0, 27.3, 27.7, 28.2, 28.4, 28.6, 30.0, 40.4, 45.7, 49.9, 50.0, 50.5, 78.5, 123.4, 124.9, 125.7, 126.2, 128.0, 130.2, 131.5, 131.8, 156.1. ESI mass $[\text{M} + \text{H}]^+$ $\text{C}_{32}\text{H}_{48}\text{N}_3\text{O}_2$ calculated 506.3747 found 506.3708.

2.2.3. Synthesis of BOC protected anthracene based boronic acid sensor (2)

Tert-butyl(6-((6-((anthracen-9-ylmethyl)amino)hexyl)amino)hexyl) carbamate (3.543 g, 7.01 mmol) was dissolved in dry THF (50 mL). NaH (0.616 g, 15 mmol, 60% in mineral oil) was slowly added into the solution and stirred for 20 min, then 2-(bromomethyl)phenylboronic acid pinacol ester (4.45 g, 15 mmol) was added. The reaction was continuously stirred for 2 h. After the reaction finished, the reaction mixture was quenched with water and poured into saturated NaHCO_3



Scheme 2. Synthetic route for probe 1. Note: The Boronic acids of Probe 1 and compound 2 were isolated as the anhydrides.

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