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A novel colorimetric and fluorescent chemosensor for cyanide ion in aqueous media based on a rhodamine derivative in the presence of Fe^{3+} ion

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ABSTRACT

A rhodamine-based fluorescent and colorimetric chemosensor (RTSB) for Fe^{3+} ion was designed and synthesized, which displayed highly selective and sensitive Fe^{3+}-amplified fluorescence emission and absorbance above 500 nm in aqueous solution with the color change from colorless to pink. Moreover, it also showed highly selective and sensitive recognition toward cyanide ion upon addition of Fe^{3+} with the color change back to colorless in the same solution. The detection limit of the system for CN^- was around 7.2×10^{-8} M (S/N = 3). The chemosensor may be found its potential applications in environmental and biological systems.

1. Introduction

The design and development of sensors for the detection of anions are significant because of the important roles played by anions in biology, medicine, catalysis, and the environment [1–7]. Among those common anions, particular attention has been paid to cyanide ion (CN^-) because of its extreme toxicity in physiological as well as environmental system [8,9]. Cyanide is an important chemical in various industrial processes, including gold mining and electroplating, and its accident release into the environment often causes serious pollution. In view of the above, developments of selective sensors for cyanide ion are desirable toward practical application. Recently, considerable efforts have been undertaken to develop fluorescent probes because of their high selectivity, sensitivity, and simplicity [10,11]. Some fluorescent probes for cyanide ion have been reported [12–22]. These fluorescent probes are based on different mechanisms including hydrogen bonding interactions, nucleophilic addition of cyanide ion, and demetallation of metal coordination complexes. Among these sensing mechanisms, a metal-based receptor is considered to be an ideal approach for CN^- recognition. To date, the reported metal coordination complexes are mainly Cu^{2+}-based complexes, due to the formation of stable complex between CN^- and Cu^{2+} [23–25]. However, few other metal complexes have been reported for sensing CN^- in aqueous media.

The rhodamine framework is an ideal building block to construct fluorescent probes due to its excellent photophysical properties such as long absorption and emission wavelength, large absorption coefficient and high fluorescence quantum yield [26–28]. Many rhodamine-based probes for metal ions have been developed [29]. In contrast, only few rhodamine-based probes for CN^- have been reported [30]. Herein, we report a rodamine B hydrazine and 2-tertbutyldimethyl silyloxy benzaldehyde conjugate derivative (RTSB), which can selectively detect Fe^{3+} in aqueous media. Moreover, in the presence of Fe^{3+}, RTSB shows highly selective and sensitive recognition toward CN^- in H_2O–CH_3CN (1:1, v/v) system over a wide range of tested anions resulting in fluorescence intensity change, blue shift and obvious color change from pink to colorless. Compared with other reported fluorescent chemosensors, this system shows higher selectivity toward CN^- ion (inorganic NaCN) in H_2O–CH_3CN (1:1, v/v). This system can be reused with proper treatment. To the best of our knowledge, this is the first example of colorimetric and fluorescent sensor based on rhodamine-Fe^{3+} complexes that allows the selective detection of CN^- in aqueous media.

2. Experimental

A Techcomp UV-8500 spectrophotometer (Shanghai, China) was used for absorption measurement. The fluorescence spectra were recorded with a Hitachi F-2500 spectrofluorimeter. NMR spectra

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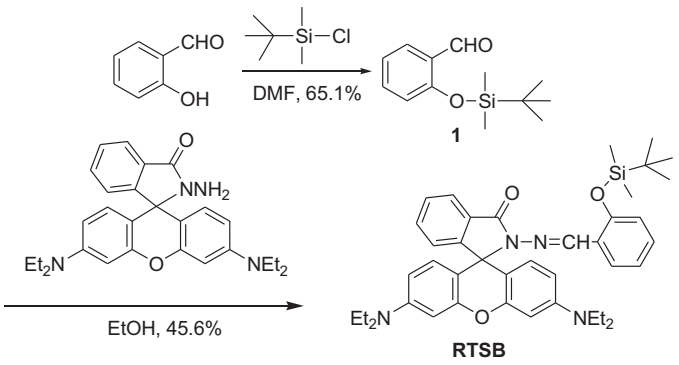

Scheme 1. Synthesis of RTSB.

were measured on a Bruker DMX-500 spectrometer at 500 MHz in CD_3CN. All other chemicals used were local products of analytical grade. Distilled water was used throughout the experiment. The solutions of metal ions were prepared from their perchlorate salts. The solutions of anions were prepared from their sodium salts. All solvent used in spectroscopic analysis are spectroscopic grade.

2.1. Synthesis

Salicylaldehyde (1 g, 8.2 mmol) and imidazole (0.56 g, 8.2 mmol) were dissolved in 30 mL DMF, followed by addition of *t*-butyl dimethyl chlorosilane and stirred at room temperature for 10 h. The reaction mixture was poured into water, and the residue was extracted three times with ethyl acetate (40 mL). The combined organic layer was dried over anhydrous Na_2SO_4, and concentrated under vacuum to provide a yellow crude product **1** (1.26 g, yield: 65.1%), which was used without further purification.

1 (0.4 g, 1.69 mmol) and rhodamine hydrazide (0.77 g, 1.69 mmol) were dissolved in 40 mL ethanol, and the mixture was refluxed for 4 h. After cooling to room temperature, a pink solid were precipitated. The solid was purified by recrystallization to provide 0.52 g RTSB as a white solid, yield, 45.6% m.p.: 167–169 °C. ^{1}H NMR (CD_3CN, 500 MHz, TMS): δ 9.49 (s, 1H); 7.85 (d, J = 7.5 Hz, 1H); 7.67 (d, J = 7.5 Hz, 1H); 7.56 (t, J = 7.5 Hz, 1H); 7.52 (d, J = 7.5 Hz, 1H); 7.15 (t, J = 7.0 Hz, 1H); 7.06 (d, J = 7.5 Hz, 1H); 6.83 (t, J = 7.0 Hz, 1H); 6.78 (d, J = 8 Hz 1H); 6.46 (d, J = 9.0 Hz, 2H); 6.41 (s, 2H); 6.30 (dd, J = 9.0, 2.0 Hz, 2H); 3.33 (q, J = 7.0 Hz, 8H); 1.08 (t, J = 7.0 Hz, 12H); 0.91 (s, 9H); 0.13 (s, 6H). ^{13}C NMR (CD_3COCD_3, 125 MHz, TMS): δ 164.0, 154.6, 153.4, 151.6, 148.8, 148.7, 145.0, 133.2, 131.4, 130.9, 130.0, 128.7, 128.4, 128.0, 127.4, 126.4, 125.8, 123.7, 122.9, 121.3, 120.0, 107.8, 107.6, 106.9, 98.0, 97.6, 33.1, 44.0, 25.4, 18.0, 12.0, −4.9, −5.0. Anal. Cacld for $C_{41}H_{50}N_4O_3Si$: C, 72.96; H, 7.47; N, 8.30; found: C, 72.64; H, 7.18; N, 8.52.

2.2. General procedure for metal ions and anions detection

A 1.0×10^{-4} M stock solution of RTSB was prepared in CH_3CN. Stock solutions of various other ions and anions were prepared by dissolving their salts in water. To 10-mL volumetric flasks containing different amounts of Fe^{3+} and anions, proper amounts of the solution of RTSB was directly added with micropipette, then diluted with H_2O and CH_3CN to 10 mL and mixed. The absorption and fluorescence sensing were run immediately.

3. Results and analysis

3.1. Synthesis

Synthesis of RTSB is shown in Scheme 1. Reaction of salicylaldehyde with *t*-butyl dimethyl chlorosilane afforded compound **1**, which further reacted with rodamine B hydrazide to give RTSB in 45.6% yield. The structure of RTSB was confirmed by its ^{1}H NMR, ^{13}C NMR, and EA (Fig. S1–2).

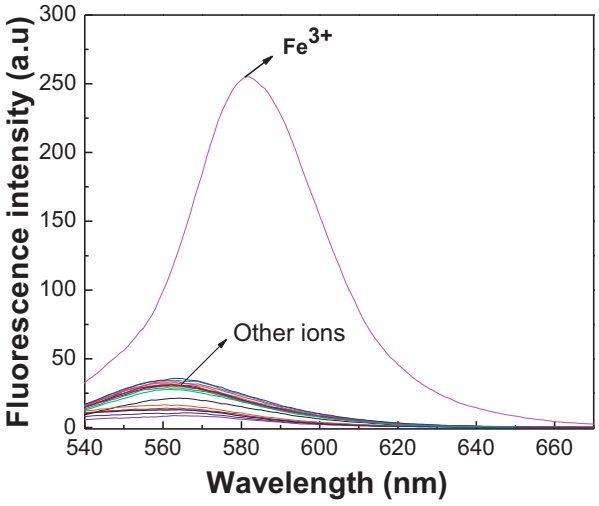

Fig. 1. Fluorescence intensity of RTSB (10 μM) in CH_3CN–H_2O (1/1, v/v) upon the addition of 5 equiv. the different metal ions (Fe3+, Na^+, K^+, Ag^+, Ba^{2+}, Zn^{2+}, Fe^{2+}, Hg^{2+}, Cu^{2+}, Co^{2+}, Pb^{2+}, Mg^{2+}, Ni^{2+}, Cd^{2+}, Al^{3+} and Ce^{3+}). λ_{ex} = 500 nm.

3.2. Spectral responses of RTSB to Fe^{3+}

The absorption spectra of RTSB (10 μM) in H_2O/CH_3CN (1:1 v/v) exhibited weak bands over 500 nm. Upon the addition of Fe^{3+} ion, it appeared a dramatical absorption peak at about 562 nm and the color of the solution changed from colorless to pink. No obvious responses could be observed upon the addition of Na^+, K^+, Ag^+, Hg^{2+}, Cu^{2+}, Co^{2+}, Pb^{2+}, Ba^{2+}, Mg^{2+}, Ni^{2+}, Cd^{2+}, Fe^{2+}, Zn^{2+}, Ce^{3+}, Fe^{3+} and Al^{3+} ions, respectively (Fig. S3 ESI†). UV–vis titrations of RTSB with Fe^{3+} ion in CH_3CN–H_2O (1:1 v/v) were then performed. As shown in Fig. S4, the absorbance was significantly enhanced with increasing Fe^{3+} concentration.

RTSB (1 μM) showed a very weak fluorescence in the absence of metal ions in H_2O/CH_3CN (1:1 v/v). However, the addition of Fe^{3+} (5 equiv.) resulted in a remarkably enhanced fluorescence intensity and obvious red-shift (19 nm) [31]. No obvious responses could be observed upon the addition of Na^+, K^+, Ag^+, Ba^{2+}, Zn^{2+}, Fe^{2+}, Hg^{2+}, Cu^{2+}, Co^{2+}, Pb^{2+}, Mg^{2+}, Ni^{2+}, Cd^{2+}, Al^{3+} and Ce^{3+}, respectively (Fig. 1). These observations indicated that RTSB has a high sensitivity and excellent selectivity for Fe^{3+} in H_2O–CH_3CN (1:1 v/v). Moreover, the competitive experiments also confirmed that background metal ions showed small or no interference with the detection of Fe^{3+} ion in CH_3CN-H_2O (1:1, v/v) (Fig.S5, ESI†). pH fluorescent titration experiments of RTSB in the presence and absence of Fe^{3+} were carried out. The results showed that RTSB exhibited high sensitivity and selectivity for Fe^{3+} within the pH range about 6.5–7.1 (Fig.S6, ESI†). Binding assays using the method of continuous variations (Job's plot, Fig.S7–8, ESI†) were consistent with a 1:1 stoichiometry of the RTSB-Fe^{3+} complex. The binding stiochiometry was also confirmed by the Benesi–Hildebrand method (Fig. S9, ESI†).

3.3. Spectral responses of RTSB to CN^- in presence of Fe^{3+}

The interaction of the RTSB-Fe^{3+} complex with the anions was firstly investigated through UV–vis spectra. When 200 μM aqueous solution of sodium cyanide was added to the solution of RTSB (10 μM) and Fe^{3+} ion (10 μM), a decrease of the intensity of peak and color change from pink to colorless was observed. In the same conditions, no significant changes happened when 200 μM of other