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A novel chemosensor based on Fe(III)-complexation for selective recognition and rapid detection of fluoride anions in aqueous media

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ABSTRACT

A novel fluorogenic receptor **1** was prepared by the reaction of thiosemicarbazide with 1-naphthaldehyde. Based on in situ-formed **1**–Fe(III) complexes having the specific binding affinity for F^- anions, this sensory system allows rapid recognition and quantitative detection of fluoride in neutral aqueous media in an 'off–on' fashion. The fluoride measurement method not only exhibits a low detection limit but also has strong anti-interference ability to common coexisting ions, as evidenced by competitive experiments.

1. Introduction

Real-time monitoring and accurate detection of fluoride anions are attracting increasing attention owing to its extremely important role in health and environmental science. Till now, a large quantity of investigations have been conducted to make artificial fluoride receptors, in which great efforts are devoted to neutral chemosensors that contain urea,[1] thiourea,[2] sulfonamide,[3] amide,[4] or phenolic units.[5] Usually, these sensors exhibited an eye-detect color change upon binding fluoride ions due to the deprotonation mechanism.[6] However, this type of receptors is usually difficult to be used in aqueous solution because of the high solvation enthalpy of F^- ($\Delta H^{\Theta}=-504$ kJ mol^{-1}).[7] Considering that fluoride ions are dissolved in aqueous solution in most analytes, the development of F^--sensing systems being applicable to aqueous media is undoubtedly significant, but challenging as well.

Lately, Swager and Kim[8] reported a new fluorescent sensor for fluoride ions based on the chemical affinity between fluoride and silicon, and its applications have been expanded from organic media to aqueous media even to pure water systems.[9,10c,k] This receptor enables discrimination and detection of fluoride anions in the form of inorganic salts in aqueous solution, but often requires several tens of minutes or even hours to complete the determination process because low concentrations of the chemodosimeters severely reduce the reaction rate between the fluoride ions and the silyl moieties. Apparently, this is not favorable for the real-time detection. Moreover, the synthetic work is laborious for these sensory materials. Therefore, it is desirable to explore a simple and efficient approach for selective recognition and rapid detection of fluoride ions, particularly, to allow the fluoride assay in aqueous media with high sensitivity.

An alternative method for anion sensing is based on the specific chemical interaction of Lewis acid with an envisaged basic anion.[10] For example, the strong complexation of Cu^{2+} to cyanide has been applied to quantitative detection of CN^- by using a copper-binding dye as a sensor.[11] Similarly, as a 'hard' base,[12] F^- is inclined to coordinate with 'hard' acids, such as Ca^{2+},[13] Fe^{3+},[14] and Zr^{4+},[15] which allowing the design of metal-binding receptors for selectively recognizing fluoride. Nevertheless, for the metal complex-based F^--sensing systems, tedious sample pretreatment procedures are probably needed to avoid the possible interference of metal ions (e.g., Al^{3+}, Fe^{3+}, etc.), as described by Devine and Partington.[15e]

In the present work, we prepared a simple and efficient fluorogenic receptor **1** containing the thiosemicarbazone fragment (Scheme 1). It was found that the compound selectively complexes with Fe^{3+} ions in neutral aqueous solution, resulting in a significant fluorescence quenching; and upon addition of F^- anions the emission revives immediately as it competes for Fe^{3+} and **1** is liberated. In this way, we designed a rapid 'off–on' fluorescence sensory system based on the selective response of in situ-formed **1**–Fe(III) complexes toward fluoride, as illustrated in Fig. 1. To the best of our knowledge, there are almost no reports on such a method for fluoride detection, although several metal complexes

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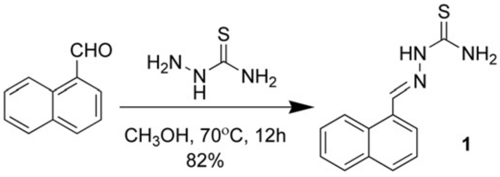


Scheme 1. The synthesis of sensor **1**.

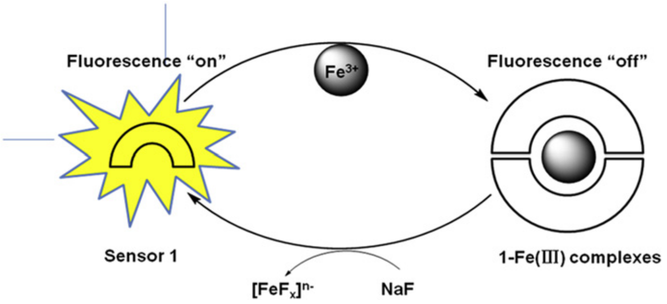


Fig. 1. Design of the 'off–on' fluorescence sensory system for detection of F^- in aqueous media. The formation of **1**–Fe^{3+} complex results in fluorescence quenching of **1**. In the presence of fluoride ions, Fe^{3+} is pulled away from the in situ-formed complex, which recovers the receptor's fluorescence.

were known to be capable of recognizing azide, acetate ions or other anions in aqueous solution.[16]

2. Results and discussion

Receptor **1** was obtained by the condensation reaction of thiosemicarbazide with 1-naphthaldehyde in high yield (Scheme 1), and its structure has been proved by various spectroscopic characterizations (see Supplementary data). As shown in the UV–vis spectra (Fig. S2), the receptor compound exhibited a characteristic absorption band centered at 348 nm in a DMSO/H_2O (3:7, v/v) solution, which is attributed to the π–π^* transition.

The examination of the receptor's complexation with metal cations was carried out by both UV–vis and fluorescence spectroscopy. In a typical experiment, nitrate salts of various cations were slowly added to the aqueous solution of **1** (30 mM HEPES, 30% DMSO, pH 7.2). Upon addition of $Fe(NO_3)_3$, the intensity of the absorption maximum of **1** increased dramatically. However, no obvious spectral changes could be observed when other ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cr^{3+}, Cd^{2+}, Ag^+, Al^{3+}, Mn^{2+}, and Zn^{2+}) were added, respectively. These results clearly suggested that the metal complexation of **1** show a great preference for ferric ion over other cations (Fig. S2).

The corresponding fluorescence spectra have been measured for the receptor's solution (10.0 μM) in the absence and presence of various metal ions. From Fig. 2 (inset) it can be seen that its intense emission peak at 400 nm is nearly totally quenched upon addition of 100 equiv of Fe^{3+}, concomitant with a new weak band at around 440 nm (see Fig. S3), which may be ascribed to the ICT (internal charge transfer) effect.[17] In contrast, the addition of Cu^{2+}, Ni^{2+}, and Ag^+ ions (100 equiv, respectively) only caused a slight drop in the fluorescence intensity, whereas a minor fluorescence increment was observed upon addition of Zn^{2+} (Fig. S3). The other metal ions, including Na^+, K^+, Mg^{2+}, Ca^{2+}, Co^{2+}, Cr^{3+}, Cd^{2+}, Al^{3+}, and Mn^{2+}, produced no obvious spectral responses when they were added respectively.

As shown in Fig. 2, receptor **1** is selective for Fe^{3+} with fluorescence switching 'off' upon complexing the ion. Also, the competitive experiments confirmed that most background metal ions exhibited negligible effect on the specific host–guest interaction between the receptor and Fe^{3+} (Fig. S4). The Job's plot of **1** with Fe^{3+} reveals the formation of a ratio of 2:1 complex (Fig. S5). The response parameter α, defined as the ratio of free ligand concentration to initial ligand concentration, was plotted as a function of the Fe^{3+} concentration, giving a calibration curve for the quantitative analysis of Fe^{3+} ions (Fig. S6). From these data, the association constant (log K_a) of **1** for Fe^{3+} was calculated to be 3.44 according to Li's equations.[18]

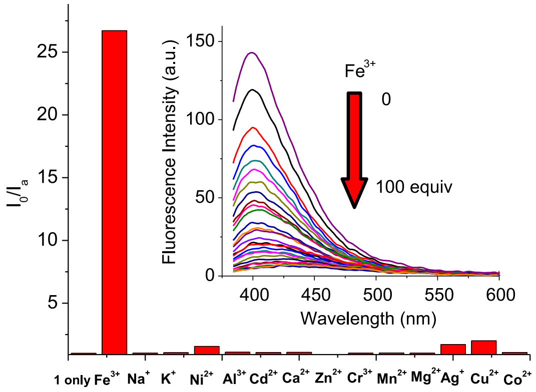
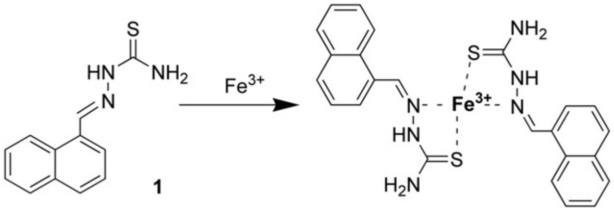


Fig. 2. Fluorescence emission response profiles of sensor **1** with various metal ions in aqueous media (30 mM HEPES, 30% DMSO, pH 7.2). I_0/I represents the ratio of the original intensity of sensor **1** at 400 nm to its intensity upon cation binding. Inset: fluorescence emission spectra (λ_{ex}=348 nm) of sensor **1** (10.0 μM) upon successive addition of Fe^{3+} (0–100 equiv) in above-mentioned aqueous media.

On the basis of above observations, we assume that in the **1**–Fe(III) complexes the metal ion may be coordinated by two thiosemicarbazone N, S-donor ligands (Scheme 2). The binding fashion is somewhat similar to that seen in the case of salicylalthiosemicarbazonatoferrate(III) complex.[19]



Scheme 2. The proposed binding mode in **1**–Fe^{3+} complex.

The binding and recognition ability of in situ-generated **1**–Fe(III) complexes toward various anions were then studied through UV–vis and fluorescence spectra. In these experiments, different sodium salts, instead of tetrabutylammonium salts required for the case of organic systems, as the anion sources were added to the aqueous DMSO solution of **1** (10.0 μM) in the presence of 100 equiv of Fe^{3+}. The results indicated that the addition of sodium fluoride (500 equiv) decreases dramatically the sensor's absorption, whereas none of any other anions (Cl^-, Br^-, I^-, N_3^-, SCN^-, AcO^-, NO_2^-, etc.) cause any noticeable change in the spectra (Fig. S7).

The fluorescence response of **1**–Fe(III) complexes with different anions is depicted in Fig. 3. From the inset it can be seen that only F^- anions produce a significant luminescence enhancement. The 'on/off' emission intensity ratio has reached as high as 25, thus it is visually dramatic in the dark. Also notable is the fluoride-induced emission features are almost identical with that of **1** in the absence of any guest species, indicating the observed fluorescence response should arise from the regeneration of receptor **1**. This can be rationalized since the harder F^- replaces the neutral ligands and capture Fe^{3+} to form more stable species $[FeF_x]^{n-}$.

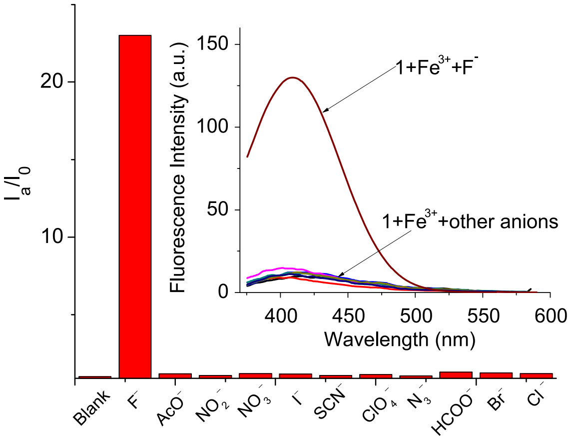


Fig. 3. Fluorescence emission response profiles (λ_{ex}=348 nm) of sensor **1** (10.0 μM) at 400 nm for solutions containing various anions (5.0 mM) in the presence of Fe^{3+} (100 equiv). Inset: fluorescence spectra of **1** (10.0 μM)+Fe^{3+} (100 equiv) in aqueous media (30 mM HEPES, 30% DMSO, pH 7.2) upon addition of various anions (500 equiv).

This sensory system demonstrates good selectivity toward F^- over many common anions (Fig. 3). The sensor's fluorescence cannot be switched 'on' when presented with heavier halides (Cl^-, Br^-, I^-) or pseudohalides (SCN^-, N_3^-) as well as other anions. It should be emphasized at this point that one distinguishing feature of the present method is the discrimination between F^- and carboxylate anions (such as CH_3COO^-), which is scarcely seen in the early reported receptors for fluoride and acetate anions in aqueous media[20] due to the fact that the related species have similar basicity (acetate ion is actually slightly more basic than fluoride ion).[21] Of course, orthophosphate (PO_4^{3-}) and carbonate (CO_3^{2-}) anions can induce the precipitation of ferric ion, resulting in an intense fluorescence emission (data not shown). Moreover, this detection method suffers from the interference of cyanide causing undesirable changes in fluorescence. Fortunately, these interferences could be reduced to some extent through an easy sample pretreatment suggested by Bellack.[22]

To further examine the F^--selective sensor, we also assessed the possible interference from coexisting related cations. The competitive experiments showed that most of positively charged species, including ammonium ions (NH_4^+, n-Bu_4N^+), alkali metal ions (Na^+, K^+), alkaline earth metal ions (Mg^{2+}, Ca^{2+}) as well as others, such as Cu^{2+}, Al^{3+}, Cr^{3+}, Cd^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, do not produce substantial disturbance to the fluoride sensing (Fig. 4).

Fluorescence titrations were carried out by stepwise addition of NaF to an aqueous solution of receptor **1** (10.0 μM) in the presence of Fe^{3+} (100 equiv). As shown in Fig. 5, a gradual enhancement of emission intensity is observed with increasing amount of F^- added. The inset displays a good linear relationship between the relative emission intensity (I/I_0) and the fluoride ion concentration (R^2=0.99). According to the universal method for calculating the detection limit,[23] the F^- concentration at I_a/I_0 (the signal-to-background ratio)=3 is 140 μM, which is lower than the enforceable drinking water standard for fluoride of 4 mg/L (221 μM) given by the EPA (United States Environmental Protection Agency).

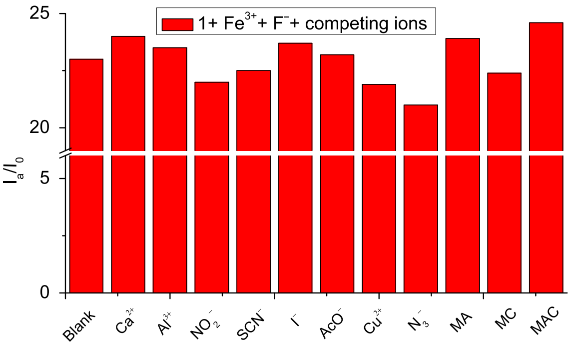


Fig. 4. Fluorescence emission response profiles (λ_{ex}=348 nm) of sensor **1** (10.0 μM) at 400 nm in aqueous media (30 mM HEPES, 30% DMSO, pH 7.2) upon addition of various ions in the presence of Fe^{3+} (100 equiv) and F^- (500 equiv). The added amount was 100 equiv and 500 equiv for each cation and anion, respectively. Blank: **1**+Fe^{3+}+F^-; MA: the mixed anions containing Cl^-, Br^-, CH_3COO^-, $HCOO^-$, ClO_4^-, and NO_3^-; MC: the mixed cations including Na^+, K^+, Mg^{2+}, Ca^{2+}, Cu^{2+}, Al^{3+}, Cr^{3+}, Cd^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, NH_4^+, and n-Bu_4N^+; MAC: the mixed anions and cations.

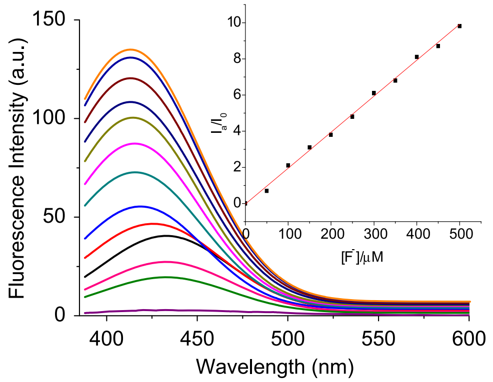


Fig. 5. Fluorescence titration spectra of sensor **1** (10.0 μM) with F^- (0–5.0 mM) in aqueous media (30 mM HEPES, 30% DMSO, pH 7.2) in the presence of Fe^{3+} ions (100 equiv), λ_{ex}=348 nm. Inset: relative emission intensity (I/I_0) versus the F^- concentration (0–500 μM).

3. Conclusion

In conclusion, we have established a simple and efficient method for selective recognition and rapid detection of fluoride anions in neutral aqueous media. The sensor is also applicable to other protonic media, such as methanol, ethanol or THF/water mixture. The realization of this 'off–on' type sensory system is based on the receptor's specific affinity for ferric ions and the selective response of in situ-formed **1**–Fe(III) complexes toward F^-. The fluoride detecting method not only has briefness in the receptor synthesis and assay manipulation but also has other distinct advantages over previously reported systems, such as a quite low detection limit, high selectivity of F^- over AcO^-, as well as good tolerance to common coexisting species including Al^{3+}, Cr^{3+}, and Ca^{2+}.

4. Experimental section

4.1. General

1-Naphthaldehyde and thiosemicarbazide were purchased from Aladdin Shanghai Reagent Company. DMSO was distilled in the presence of CaH_2 under reduced pressure before use. The nitrate salts of Fe^{3+}, Na^+, K^+, Cu^{2+}, Co^{2+}, Mg^{2+}, Ni^{2+}, Cr^{3+}, Mn^{2+}, Zn^{2+}, Ag^+, Cd^{2+}, Ca^{2+} and the sodium salts of F^-, Cl^-, Br^-, I^-, CH_3COO^-, $HCOO^-$, ClO_4^-, CN^-, SCN^-, NO_2^-, N_3^-, CO_3^{2-}, PO_4^{3-}, NO_3^- were purchased from Aladdin Shanghai Reagent Company and recrystallized before use. Other reagents were used without further purification.

^1H NMR spectra were recorded on a Bruker Avance AMX-400 NMR instrument. ^{13}C NMR spectra were recorded on a Bruker Avance AMX-500 NMR instrument. Elemental analysis was performed on a ThermoFinnigan Flash EA 1112 analyzer. UV–vis spectra were obtained in DMSO at 25 °C using a quartz cell of 1 cm on MOS-450 (Biologic Company, France). Steady-state fluorescence spectra were recorded on a Perkin–Elmer LS-55 fluorescence spectrometer in the right-angle geometry (90° collecting optics, λ_{ex}=348 nm).

4.2. Synthesis and characterization of receptor 1

The receptor **1**, (2*E*)-2-(naphthylmethylene)hydrazinecarbothioamide, was synthesized according to the literature procedure.[24] To a solution of 1-naphthaldehyde (6.00 g, 38.5 mmol) in CH_3OH (500 mL) was added thiosemicarbazide (3.55 g, 39 mmol). After refluxing at 70 °C for 12 h, the solvent was removed under reduced pressure giving the crude product. The product was recrystallized from ethyl acetate to give a pale yellow solid (7.83 g) in 82% yield. [Found: C, 62.02; H, 4.73; N, 17.90. $C_{12}H_{11}N_3S$ requires C, 62.36; H, 4.84; N, 18.33%]; ^1H NMR (400 MHz, DMSO-d_6, δ): 11.46 (1H, s), 8.89 (1H, s), 8.32 (1H, d, J 8.47 Hz), 8.30 (1H, s), 8.21(1H, d, J 7.28 Hz), 7.98 (3H, m, J 8.16 Hz), 7.62 (1H, t, J 15.26 Hz), 7.54 (2H, q, J 20.01 Hz). ^{13}C NMR (125 MHz, DMSO-d_6, δ): 178.3, 141.6, 133.9, 131.0, 130.8, 129.8, 129.3, 127.8, 126.7, 126.3, 126.1, 123.4.

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Supplementary data

The ^1H NMR and ^{13}C NMR of receptor **1** and some selected graphs. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2011.08.035.

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