

A Schiff-Based Colorimetric Fluorescent Sensor with the Potential for Detection of Fluoride Ions

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Abstract A simple Schiff-based colorimetric fluorescent receptor **1** was prepared. It exhibits a “turn-on-type” mode with high sensitivity in the presence of F^- . The change in color is very easily observed by the naked eye in the presence of F^- , whereas other anions do not induce such a change. Job plot indicated a 1:2 complexation stoichiometry between receptor **1** and F^- . The association constant for **1**- F^- in CH_3CN was determined as $1.32 \times 10^5 M^{-2}$ by a Hill plot.

Keywords Schiff base · Fluorescence · Turn-on

In recent years, the search of colorimetric fluorescent sensors for various chemically or biologically significant ions is emerging as an area of great interest because of their potential applications in clinical biochemistry and in environmental research [1–7]. Among various important analytes, fluoride ions (F^-) are significant due to their role in dental care and treatment of osteoporosis [8]. Generally, receptors for anions based solely on hydrogen bonding interaction cannot serve as efficient sensors in aqueous media, due to strong solvent competition. Thus, sensing F^- in a natural aqueous environment still remains a challenge. Although a considerable number of fluoride sensors have been reported recently

[9–19], however, only a few sensors in which the binding of F^- causes a fluorescence enhancement (turn-on) have been reported [20–28]. In addition, there are very few receptors which can achieve F^- binding in water developed so far [29, 30]. Therefore, for practical applications, it is necessary to develop the F^- sensor that is easily prepared, and possess selective and sensitive signaling mechanisms.

As we know, compound **1** has been reported by Garcia et al. [31]; however, its application has not yet been reported. Herein, we reported its application as a colorimetric and fluorescent sensor for F^- . Schiff-based receptor **1** can be readily prepared by coupling 1,3-diaminobenzene with 2-hydroxybenzaldehyde, as shown in Scheme 1. Receptor **1** has two hydroxyl fragments that can form hydrogen-bonded adducts with anions. It is structurally very simple, stable to heat/light and can be synthesized readily in one step with high yield from commercially cheap starting materials.

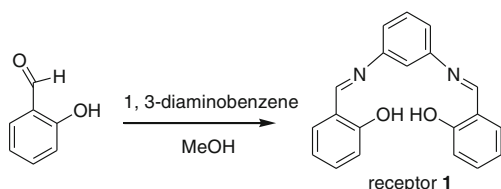
Results and Discussion

The chromogenic behavior of receptor **1** was revealed by UV–vis analysis (Fig. 1). The UV–vis absorptions of receptor **1** were investigated upon addition of various anions (F^- , Cl^- , Br^- , I^- , NO_3^- , HSO_4^- , $H_2PO_4^-$, AcO^-) using tetrabutylammonium as a counterion in CH_3CN . Free receptor **1** exhibited two absorption bands at 270 and 341 nm. In the presence of F^- , a new red-shifted absorption band appeared at 425 nm, while other ions did not cause any significant changes under identical condition. The solution of receptor **1** and F^- showed a color change from colorless to yellow by the naked-eye detection, as showed in Fig. 2. Based on the use of a UV lamp, in the presence of F^- , the solution of receptor **1** showed a dramatic color change from colorless to light green which could easily

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Scheme 1 Synthesis of receptor **1**

be detected by the naked-eye (Figure S1). The result suggests the interaction between F^- and the hydroxyl groups of receptor **1** would go through hydrogen bonds.

To further investigate the chemosensing properties of receptor **1**, free receptor **1** displayed a weak fluorescence emission band at 450 nm when it was excited at 341 nm. Upon addition F^- , receptor **1** exhibited a prominent fluorescence enhancement and accompanied by a red shift of 30 nm from 450 to 480 nm while no meaningful changes in fluorescence intensity were observed upon addition of the other anions (Fig. 3). The results indicated that there is a stable complex presence. The fluorescent enhancement efficiency observed at 480 nm was 57 fold greater than the control in the absence of F^- (Figure S2). The result indicated that there is a strong sensing action taking place between receptor **1** and F^- through hydrogen bonding formation. The possible binding mode was proposed as shown in Scheme 2.

UV-vis and fluorescence titration of receptor **1** with F^- were performed. While the addition of increasing amounts of F^- to a solution of receptor **1** in CH_3CN , the two absorption bands at 270 and 341 nm decreased gradually and concomitantly a rising new absorbance that peaked at 425 nm appeared, shown

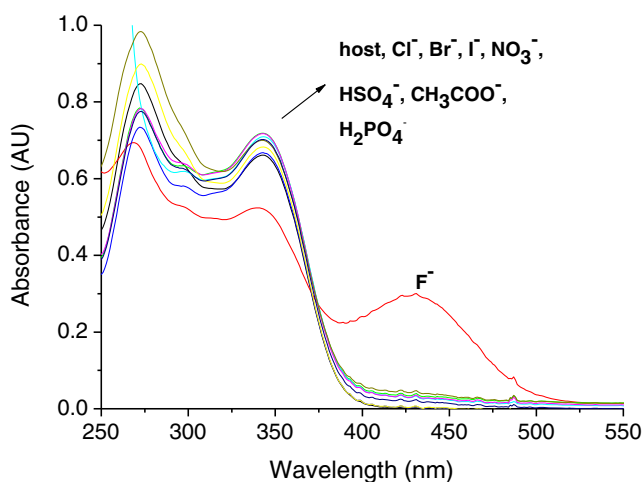


Fig. 1 UV-vis spectra of **1** (30 μ M) recorded in CH_3CN after addition of 20.0 equiv of various anions

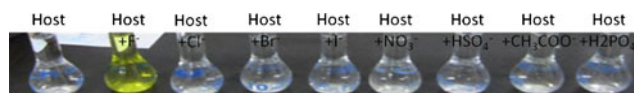


Fig. 2 Color change of receptor **1** in the presence of different anions

in Fig. 4. An isosbestic point is clearly observed at 375 nm, indicating the formation of a new complex between **1** and F^- occurred. Moreover, from the fluorescence titration profile (Fig. 5), the association constant for **1**- F^- in CH_3CN was determined as $1.32 \times 10^5 M^{-2}$ by a Hill plot (Figure S3). The result showed that F^- interacts with the receptor **1** more strongly due to their higher electronegativity and smaller size compared to the other halides. Job plot indicated a 1:2 complexation stoichiometry between receptor **1** and F^- (Figure S4). By using above-mentioned fluorescence titration results, the detection limit for F^- was determined as $5.08 \times 10^{-7} M$. The detection limit was sufficiently low to detect micromolar concentration of the F^- , which belongs to the range found in many chemical and biological systems.

The selectivity towards F^- was ascertained by the competition experiment. As shown in Figure S5, receptor **1** was treated with 20.0 equiv. of F^- in the presence of other anions of the same concentration. Relatively low interference was observed for the detection of F^- in the presence of other anions except HSO_4^- . The receptor **1** responses for F^- in the presence of HSO_4^- are relatively low but clearly detectable. Thus, receptor **1** can be used as a selective fluorescent sensor for F^- in the presence of most competing anions.

Reversibility is a prerequisite in developing novel chemosensors for practical application. The reversibility of

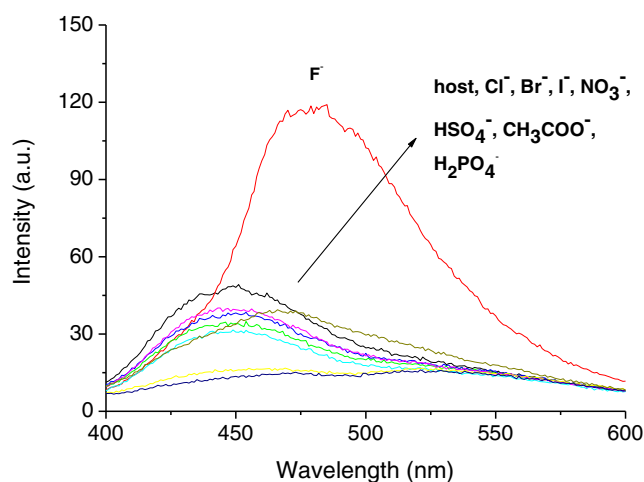
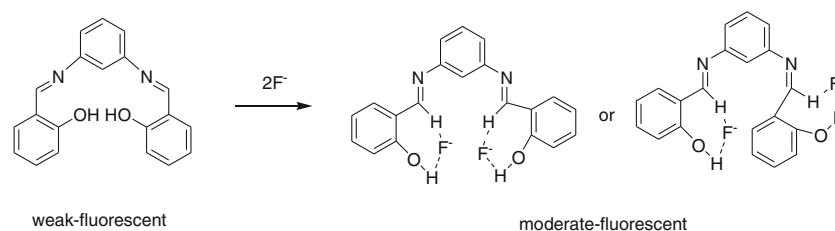


Fig. 3 Fluorescence emission spectra ($\lambda_{ex.} = 341$ nm) of **1** (30 μ M) in the presence of 20 equiv of various anions in CH_3CN



Scheme 2 Proposed binding structure between the receptor **1** and F^-

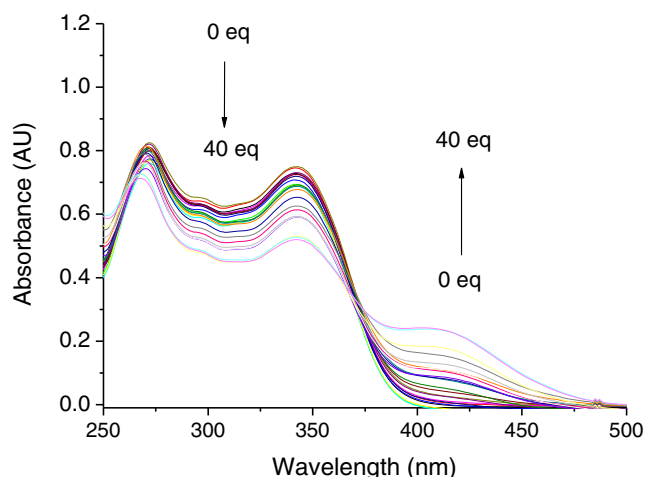


Fig. 4 UV-vis spectra of **1** (30 μ M) in CH_3CN upon addition of increasing concentrations F^-

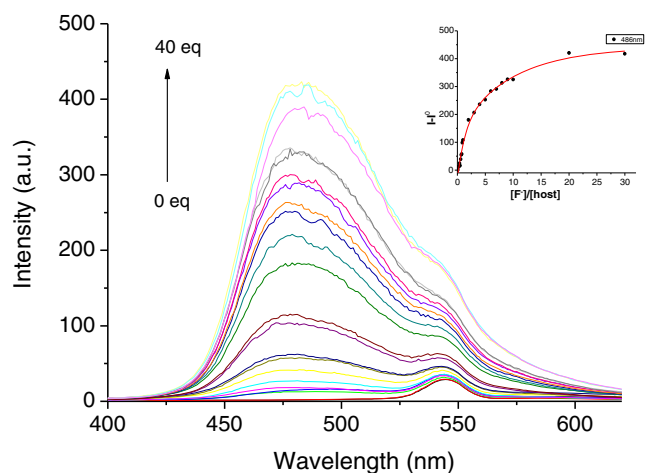


Fig. 5 Fluorescence spectra of **1** (30 μ M) in CH_3CN upon addition of increasing concentrations F^- ; Inset is a plot of intensity change vs equiv. of F^- added

the recognition process of receptor **1** was performed by adding an F^- binding agent, $Ca(NO_3)_2$ (Fig. 6). The addition of $Ca(NO_3)_2$ to a mixture of receptor **1** and F^- resulted in diminution of the fluorescence intensity at 480 nm, which indicated the regeneration of the free receptor **1**. Such reversibility is important for the fabrication of devices to sense the F^- .

In order to demonstrate the practical utility of receptor **1**, we examined the detection of F^- in the media containing water. Therefore, the solution of receptor **1** in acetonitrile was added a few drops (0.3 mL) of drinking water (concentration of F^- lower than 5 ppm) and doubly distilled water, respectively. The color of the solution containing drinking water changed from colorless to deep yellow by the naked-eye detection (Fig. 7). In contrast, the color of the solution containing doubly distilled water remained the original color. On the other hand, doubly distilled water containing F^- was

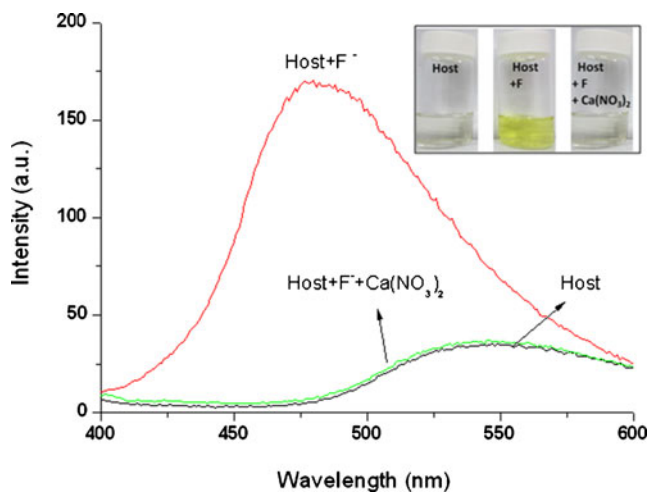


Fig. 6 Fluorescence emission spectra of receptor **1** in the presence of F^- (10.0 equiv) or $Ca(NO_3)_2$ (20.0 equiv) in CH_3CN solution. λ_{ex} =341 nm

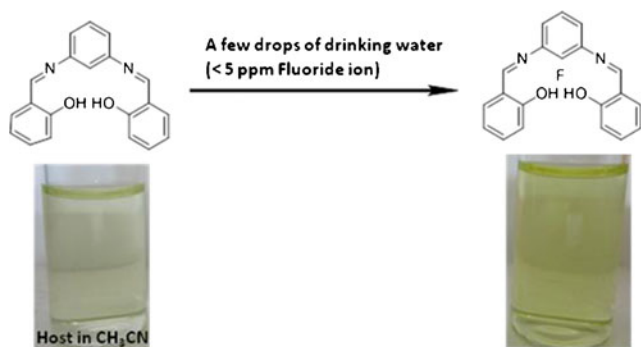


Fig. 7 Color change of receptor **1** after addition of drinking water

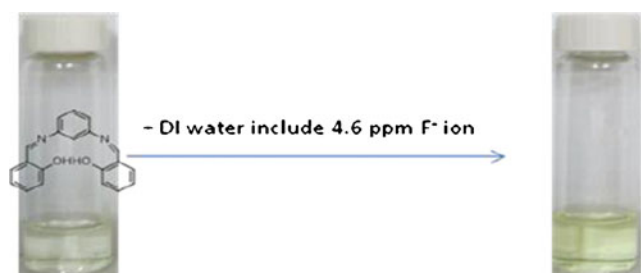


Fig. 8 Color change of receptor **1** after addition of doubly distilled water containing F^-

also tested in the above condition. After addition of doubly distilled water containing F^- (4.6 ppm) into the solution of receptor **1** in acetonitrile, the color of solution obviously changed from colorless to yellow by the naked-eye detection (Fig. 8). The result showed that receptor **1** can be used for F^- detection in aqueous media.

The binding ability of receptor **1** for F^- was also proved from 1H NMR titration experiments in CD_3CN . A partial 1H NMR spectrum of receptor **1** was shown in Fig. 9. Before the addition of F^- , the 1H NMR chemical shifts of the hydroxyl protons of receptor **1** were 13.1 ppm, it indicated the intramolecular hydrogen bonding formation between two hydroxyl groups. After the addition of 1.0 equiv. of F^- , the resonances were shifted upfield to 10.2 ppm. This might be due to the formation of hydrogen bonds among F^- , the hydroxyl groups and imino groups of receptor **1**. In addition, in the presence of 0.5 equiv. of F^- , the proton of imino (H_3) was split into two peaks. The protons of benzene (H_{4-9}) became more complex. The results indicated that there are two conformation imine complex presences.

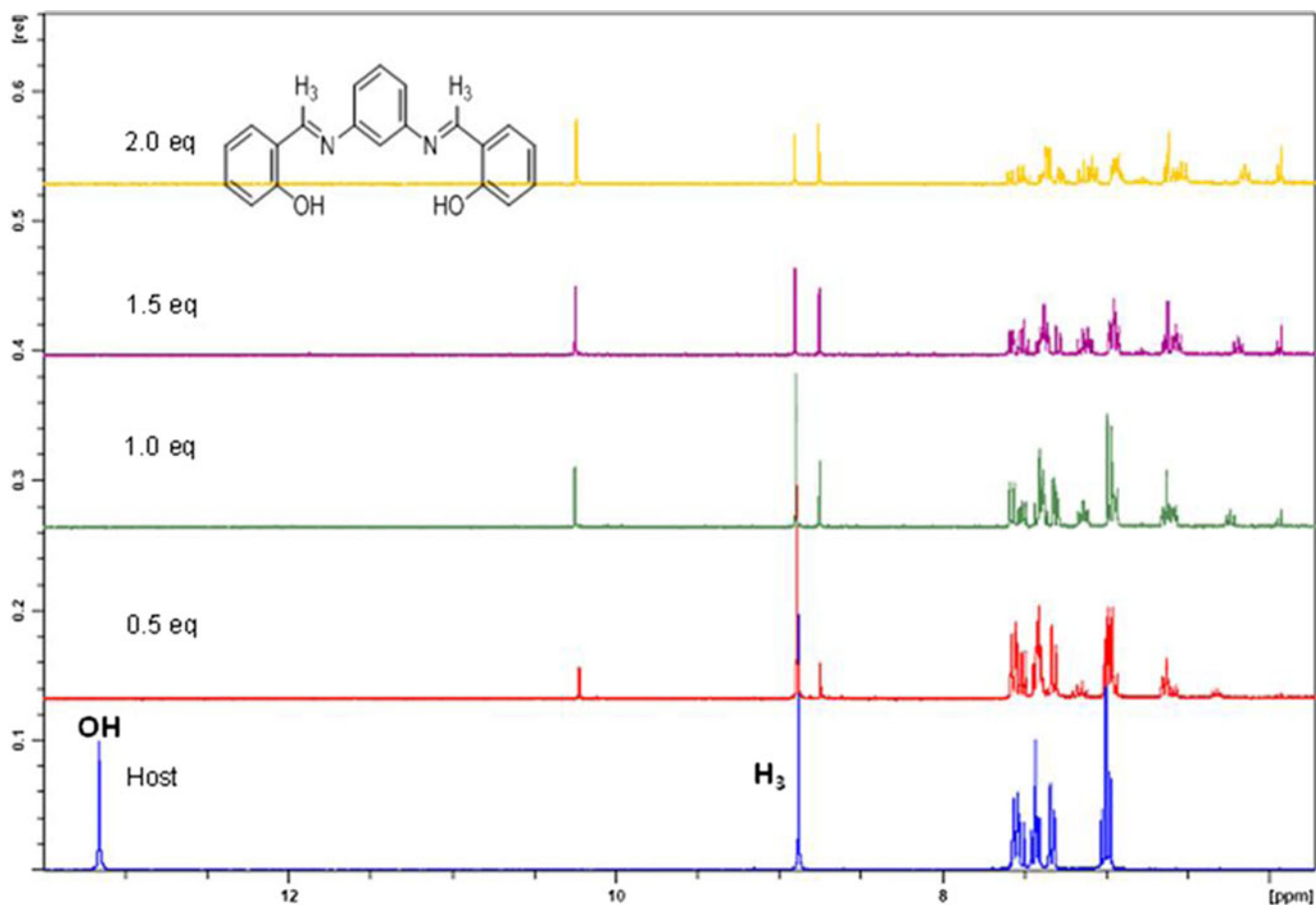


Fig. 9 1H NMR titration plots of **1** with F^- in CD_3CN

Conclusion

In summary, we designed and synthesized a highly sensitive Schiff-based receptor **1** for selective detection of F^- . Upon complexation with F^- , the solution of receptor **1** exhibited an obvious color change from colorless to yellow by naked-eye detection. In addition, the addition of $Ca(NO_3)_2$ quenches the fluorescence of receptor **1**· F^- complex, indicating that receptor **1** was a reversible chemosensor. Hence, receptor **1** can be used as a selective turn-on type colorimetric fluorescent sensor for detecting F^- in drinking water without any spectroscopic instrumentation.

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