



# A coumarin-based fluorescent and colorimetric chemosensor for rapid detection of fluoride ion



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## ABSTRACT

A novel coumarin-based compound **1** featuring thiosemicarbazone as binding unit, was reported as a colorimetric and fluorescent probe for the detection of fluoride anion. The addition of F<sup>-</sup> to a solution of probe **1** in tetrahydrofuran resulted in evident naked-eye color change from green-yellow to orange-red under daylight and obvious fluorescence quenching within 3 s. And the detection limit toward F<sup>-</sup> was calculated to be as low as  $2.16 \times 10^{-7}$  mol/L. <sup>1</sup>H NMR titrations proved that the interaction between **1** and fluoride ion: hydrogen bond at low fluoride ion concentration, deprotonation at high fluoride ion concentration. Besides, it exhibited highly sensitivity and selectivity for F<sup>-</sup> over other examined ions (Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, AcO<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, HSO<sub>4</sub><sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>) in tetrahydrofuran solution.

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## 1. Introduction

The recognition and sensing of anions has been a key research theme because of the fundamental and crucial roles of anions in biological and environmental fields.<sup>1–5</sup> Among the entire range of biologically anions, fluoride anion possesses significant potential in the prevention of dental caries and treatment for osteoporosis.<sup>6,7</sup> However, excess intake fluoride can cause many serious diseases such as fluorosis, acute stomach and kidney problems.<sup>8,9</sup> Besides, fluoride ion is one of the most attractive targets owing to its smallest ionic radius, highest charge density and hard Lewis basic nature.<sup>10–12</sup> Thus, simple and efficient detection of F<sup>-</sup> with high selectivity and sensitivity is in great need.

So far fluoride-detecting and-sensing techniques can be classified into several kinds, such as (a) the electrode method<sup>13</sup>; (b) <sup>19</sup>F NMR analysis<sup>14</sup>; (c) fluorescent or colorimetric sensing. Compared with other detecting methods, colorimetric and fluorescent chemosensors have been recognized as a promising and powerful tool

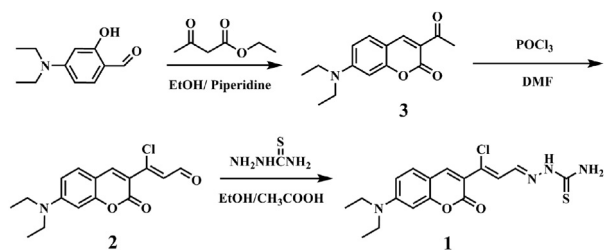
for sensing fluoride ion owing to its advantages of high selectivity, sensitivity and practical operation.<sup>15–18</sup> Recently, Molecules containing thiosemicarbazone were used to detect fluoride anion. Su et al.<sup>19</sup> reported two thioxanthone-based F<sup>-</sup> sensors, in which thiosemicarbazone acted as responding unit, their work offer the possibility and convenience for the multiple detection of Hg<sup>2+</sup> and F<sup>-</sup>. Jiang<sup>20</sup> et al. reported a simple and efficient chemosensor, 2-(naphthylmethylene) hydrazinecarbothioamide, which showed high selectivity and sensitivity toward fluoride anion in both absorption and fluorescence modes. For this kind of sensors, N-H deprotonation, or hydrogen-bond-induced  $\pi$ -electron delocalization, are believed to be responsible for signaling the binding event.<sup>21–23</sup>

With this in mind, compound **1**, 3-chloro-3-(7-(diethylamino)-2-oxo-2H-chromen-3-yl)allylidene-hydrazine-carbothioamide, in which substituted coumarin acted as signaling unit and thiosemicarbazone acted as responding unit, was rationally designed and synthesized. Compared with conventional coumarin dyes, both 7-diethylamino and imine units in **1** extended the conjugate structure of the fluorophore. As expected, probe **1** showed strong emission at 499 nm in THF with a fluorescent quantum yield of 0.34. Furthermore, the fluorescence turn-off sensor showed high selectivity for fluoride ion through the deprotonation action and

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Scheme 1. Synthetic route of compound 1.

the photo-induced electron transfer (PET) mechanism. More importantly, probe **1** could detect fluoride anion by a fast method which was observable with naked eyes. And it showed a faster response (within 3s) to fluoride ion than that of some related literature.<sup>24–26</sup>

## 2. Results and discussion

### 2.1. Synthesis

Compound **1** was synthesized according to the route in Scheme 1. The intermediate **2** and final product **1** were confirmed by <sup>1</sup>H NMR, <sup>13</sup>C NMR, and HRMS spectra (Electronic Supporting Information (ESI), Figs. S1–S6).

### 2.2. Spectral properties of compound 1

The interactions between compound **1** and various anions (F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, AcO<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, HSO<sub>4</sub><sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>) were investigated in THF solution through colorimetric and fluorescent analysis. When probe **1** was treated with F<sup>-</sup>, the system changed from green-yellow to orange-red within 3s, while other anions did not show prominent visible color changes (Fig. 1a). Besides, under 365 nm UV lamp, the color of the system changed from light green to dark, only responding to F<sup>-</sup> among eight anions (Fig. 1b).

In order to deduce the anion sensing ability of compound **1**, titrations were carried out in THF solution and were monitored by UV–visible spectroscopy. The experiment was performed by preparing a solution ( $1 \times 10^{-5}$  mol/L) of the sensor in THF and followed by the addition of tetrabutylammonium fluoride (TBAF) solution (0.02 mol/L). Fig. 2a displayed the UV–vis absorption titrations of the compound **1** with various amount of fluoride ion in THF at 20 °C. The molar extinction coefficient of **1** (445 nm) was  $7.08 \times 10^4$  L/(mol cm) by calculation. Upon treatment with F<sup>-</sup>, the main absorption band at 445 nm of **1** gradually decreased with concomitant formation of a long wavelength absorption band centered at 510 nm (4–10 equiv), and with an isosbestic point at

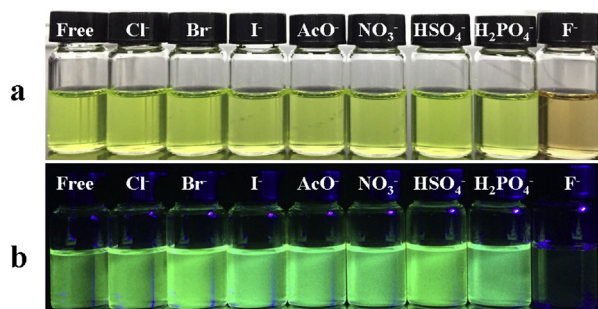


Fig. 1. Color changes of **1** ( $1.0 \times 10^{-5}$  M) towards 10 equiv of various anions in THF under daylight (a) and 365 nm UV lamp (b).

around 480 nm. Correspondingly, the absorption red-shift of 65 nm resulted in the solution distinct color change, which can be directly observed by naked eyes. Besides, the absorption peak at 445 nm and 510 nm reached equilibrium upon adding 10 equiv of fluoride ion (Fig. S7).

The fluorescence responses of **1** toward various amount of fluoride ion were also performed in THF at 20 °C. As shown in Fig. 2b and Fig. S8, upon the addition of F<sup>-</sup>, the fluorescence intensity of **1** at 499 nm was almost linearly decreased and 91% of the fluorescence intensity was quenched by calculation upon addition of 10 equiv of fluoride ion.

The interference of other anions to the detection of F<sup>-</sup> were also investigated to test the sensing selectivity, and the experimental results suggested that sensor **1** showed high selectivity for the fluoride anion in colorimetric and fluorometric modes. As depicted in Fig. 3a and b, neither prominent absorption nor fluorescence changes were found with excess addition of other halide ions (Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>) as well as AcO<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, HSO<sub>4</sub><sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>. It means probe **1** showed specific sensitivity and selectivity for F<sup>-</sup> over other examined ions in tetrahydrofuran solution (see Fig. 4).

### 2.3. Calculation of detection limit

The detection limit was calculated on the basis of fluorescence titrations (see Fig. 4). A plot of fluorescence intensity change of **1**

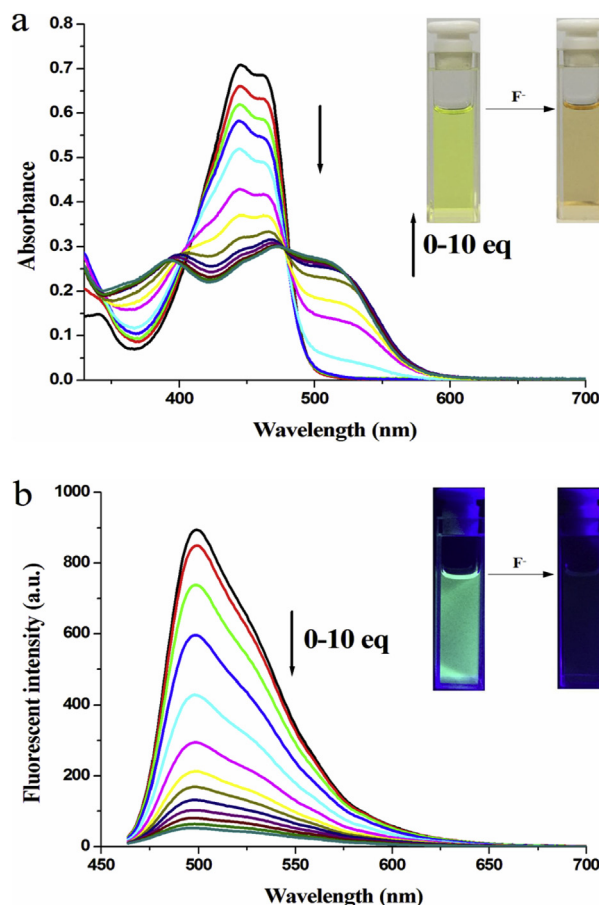


Fig. 2. UV–vis absorption spectra of **1** ( $1 \times 10^{-5}$  M) in the presence of TBAF in THF. Inset: color change of **1** upon addition of F<sup>-</sup> (100 μM) under daylight. b The fluorescent spectra of **1** ( $1 \times 10^{-5}$  M) in the presence of TBAF in THF. Inset: color change of **1** upon addition of F<sup>-</sup> (100 μM) under 365 nm light. ( $\lambda_{ex} = 445$  nm).

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