



# A novel colorimetric and fluorescent probe for detecting fluoride anions: from water and toothpaste samples



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## ABSTRACT

Based on 8-hydroxyquinoline, a 1,8-naphthalimide-derived colorimetric and fluorescent probe was synthesized for naked-eye and fluorescent recognition of F<sup>-</sup> (from both tetrabutylammonium fluoride and NaF) with high sensitivity and excellent selectivity. The probe can be employed to detect F<sup>-</sup> quantitatively within certain concentration range, and the detection limit could be as low as 1.8 μM for tetrabutylammonium fluoride and 9 μM for NaF. With this probe, the tests for fluorine contents in tap water, water sample from Eyebrow Lake and several brands of toothpastes were successfully performed.

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## 1. Introduction

It is important to determine anions in water as they could directly affect the ecosystem and biological components. As the smallest anion, fluoride is an essential element in the human body and plays an important role in human health and environmental issues, and is found to be correlated with quite a few diseases or environmental problems, such as fluorosis, pollution of nuclear plants, and urolithiasis.<sup>1–3</sup> Fluoride is ubiquitous in natural water where groundwater has appreciable level compared with surface water. However, the moderate amount of soluble fluoride is beneficial for body growth but high concentration of fluoride can lead to many diseases such as fluorosis, urolithiasis, acute gastric and kidney problems, and even cancers.<sup>4–6</sup> The U. S. Environmental Protection Agency (EPA) has set 4 mg L<sup>-1</sup> (211 μM) as the maximum contaminant level of fluoride in drinking water.<sup>7</sup> At present, many people still regularly drink water in which the concentration of fluoride is above this level all over the world.<sup>8,9</sup> In order to decrease the possibility of excessive intake, it is of great importance to detect fluoride quantitatively. Currently, standard fluoride-indicating methodologies have been recommended by the World Health Organization for critical information. However, the required well trained staff and professional equipments make it difficult for poor or even middle-income sufferers to promote such techniques. It is

desirable to develop a simple, economical, and selective assay for practical purpose.

For measuring F<sup>-</sup>, fluorescent probes have been the best choice because of their simplicity, high sensitivity and instantaneous response.<sup>10–14</sup> Moreover, to develop an ideal probe for F<sup>-</sup>, many other features should also be considered such as, presenting apparent color changes to realize naked-eye detection,<sup>15</sup> showing optical response with a huge ratiometric value changes to provide more precise built-in correction with minimized environmental effects,<sup>16–18</sup> and practical applications to detect F<sup>-</sup> in real samples.<sup>19</sup> In addition, most of the fluorescent and colorimetric fluoride probes still required fluoride anion from tetrabutylammonium fluoride (TBAF) rather than inorganic fluoride (such as NaF).

As a widely used fluorophore, 1,8-naphthalimide-based derivatives have many excellent optical properties such as good photostability, high fluorescence quantum yields and large Stokes' shift.<sup>20–22</sup> Besides, their photophysical properties can be easily tuned through judicious structural modifications.<sup>23–26</sup> In fact, based on 1,8-naphthalimide, some colorimetric and fluorescent probes toward F<sup>-</sup> have been reported.<sup>27–34</sup> On the other hand, 8-hydroxyquinoline (8-HQ), as prototypical fluorophore, its derivatives have been widely used in fluorescence detection and imaging of metal ions, because metal binding to 8-HQ can block the excited-state intramolecular proton transfer channel and restore the fluorescence.<sup>35–43</sup> In this research, we combined 1,8-naphthalimide with 8-HQ units, and introduced F<sup>-</sup>-sensitive unit to obtain novel 1,8-naphthalimide and 8-HQ derivatives for sensing F<sup>-</sup>.

Herein, a novel 8-HQ derivative of 1,8-naphthalimide (probe **1**, Scheme S1), as a colorimetric and fluorescent probe for F<sup>-</sup> (both

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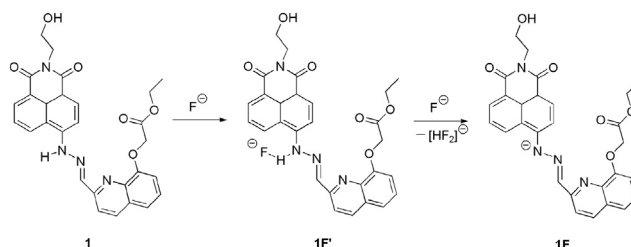
from TBAF and NaF) was easily synthesized. The probe can sense  $F^-$  in colorimetric and fluorescent methods. Moreover, this probe can quantitatively detect  $F^-$  in a wide range with dramatically color and fluorescence change. The detection limit can be as low as 1.8  $\mu\text{M}$ .

## 2. Results and discussion

### 2.1. Sensing properties of probe **1** toward $F^-$ (from both TBAF and NaF)

To study the sensing properties of **1** toward  $F^-$  (from both TBAF and NaF), UV–vis and fluorescence titration experiments were conducted with 0.01 M  $F^-$  water in DMSO solution of **1** ( $1.0 \times 10^{-5}$  M). As for  $F^-$  from TBAF, upon addition of  $F^-$ , the peak at 459 nm in the UV–vis spectrum decreased gradually while two new bands developed at 605 and 640 nm, and then, the band reached maxima at 3 equiv of  $F^-$  (left of Fig. 1). Meanwhile, four clear isosbestic points were observed at 328, 368, 394 and 505 nm, indicating that only one resultant was obtained as the result of the reaction between **1** and  $F^-$ . Moreover, the solution color of **1** changed by degrees from yellow to cyan in the presence of different concentrations of  $F^-$  (up of Fig. 2), implied that compound **1** can serve as a highly sensitive ‘naked-eye’ probe for  $F^-$  in DMSO solution. Fluorescence titration experiment (right of Fig. 1) demonstrated that the fluorescence of the DMSO solution of compound **1** decreased little by little in the presence of different concentrations of  $F^-$ . Such fluorescence change brought from addition of  $F^-$  indicates that compound **1** can be an ‘on-off’ fluorescence probe for  $F^-$  (down of Fig. 2). As for  $F^-$  from NaF, similar UV–vis and fluorescence spectra changes as those upon addition of TBAF were obtained (Figs. S1 and S2), demonstrating that compound **1** can be a dual-model probe toward  $F^-$  from both TBAF and NaF. The

observed spectral changes are attributed to the interaction between  $F^-$  ion with the amino proton of the probe **1** through hydrogen bonding interactions (Scheme 1).<sup>44</sup> Since the N–H proton becomes strongly acidic as the amino nitrogen is bonded to the strongly electron withdrawing 1,8-naphthalimide and quinoline moiety, the addition of excess  $F^-$  would lead to the deprotonation of the N–H proton (Scheme 1).



Scheme 1. Proposed sensing mechanism toward  $F^-$ .

As demonstrated in Fig. 3a and b, in the concentration range of 3.3 and 23.3  $\mu\text{M}$ , the absorption peaks of **1** are in good linear relationship with  $F^-$  (from TBAF) concentration, while in the range between 0 and 23.3  $\mu\text{M}$ , a good linear relationship between the fluorescence peak with  $F^-$  (from TBAF) concentration was obtained. As for the detection of  $F^-$  (from NaF),  $F^-$  can be quantitatively detected in concentration range between 167 and 833  $\mu\text{M}$  (UV–vis titration experiment) and 167–1000  $\mu\text{M}$  (fluorescence titration experiment) (Fig. 3c and d). Such results imply that  $F^-$  can be quantitatively detected in a wide concentration range both with UV–vis and fluorescence spectroscopy. In terms of the IUPAC definition, the LOD was calculated using the relationship  $\text{LOD} = (3.3 \times \text{standard deviation}) / \text{slope}$ . According to the UV–vis and fluorescence titration experiments, the LOD values were calculated as 16 and 18  $\mu\text{M}$  for  $F^-$  from TBAF respectively, and the LOD values were 9 and 53  $\mu\text{M}$  for  $F^-$  from NaF, which were sufficiently low for the detection of  $F^-$  in drinking water (The U. S. EPA has set 211  $\mu\text{M}$  as the maximum contaminant level).<sup>45,46</sup> In general, the LOD value is usually lower by emission method than that by absorption method. The higher LOD obtained by emission method may be ascribed to the influence of water on the emission spectra of compound **1** in DMSO and no influence of water was observed on the

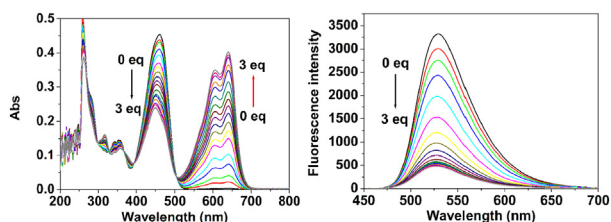


Fig. 1. Absorption (left) and emission (right) spectra change of compound **1** ( $1.0 \times 10^{-5}$  M, DMSO) upon addition of TBAF ( $1.0 \times 10^{-2}$  M, water) at various volumes (0, 0.5  $\mu\text{L}$ , 1  $\mu\text{L}$ , 1.5  $\mu\text{L}$ , 2  $\mu\text{L}$ , 2.5  $\mu\text{L}$ , 3  $\mu\text{L}$ , 3.5  $\mu\text{L}$ , 4  $\mu\text{L}$ , 4.5  $\mu\text{L}$ , 5  $\mu\text{L}$ , 5.5  $\mu\text{L}$ , 6  $\mu\text{L}$ , 6.5  $\mu\text{L}$ , 7  $\mu\text{L}$ , 8  $\mu\text{L}$ , 9  $\mu\text{L}$ , 10  $\mu\text{L}$ , 11  $\mu\text{L}$ , 12  $\mu\text{L}$ ) in water. The excitation wavelength was 460 nm.

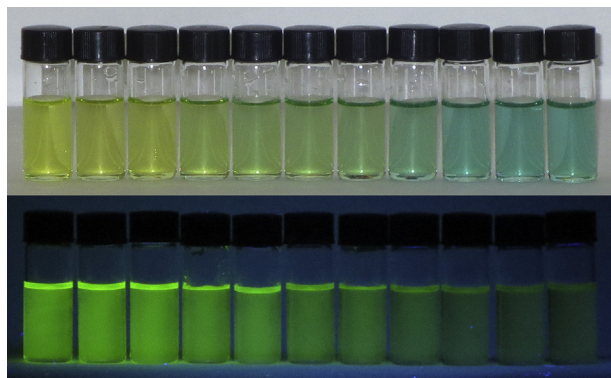


Fig. 2. Photographs of compound **1** ( $1.0 \times 10^{-5}$  M, DMSO) upon addition of TBAF at various concentrations (0,  $0.33 \times 10^{-5}$  M,  $0.67 \times 10^{-5}$  M,  $1.0 \times 10^{-5}$  M,  $1.3 \times 10^{-5}$  M,  $1.7 \times 10^{-5}$  M,  $2.0 \times 10^{-5}$  M,  $2.3 \times 10^{-5}$  M,  $2.7 \times 10^{-5}$  M,  $3.0 \times 10^{-5}$  M,  $3.3 \times 10^{-5}$  M, from left to right) in water in daylight (up) and under a UV lamp (365 nm, down).

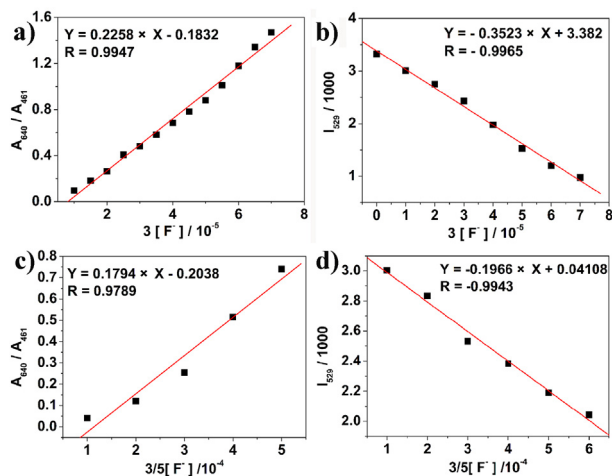


Fig. 3. The linearity of absorbance (a) and emission intensity (b) of compound **1** ( $1.0 \times 10^{-5}$  M, DMSO) with respect to TBAF concentrations. The linearity of absorbance (c) and emission intensity (d) of compound **1** ( $1.0 \times 10^{-5}$  M, DMSO) with respect to NaF concentrations. The excitation wavelength was 460 nm.  $A_{640}$  and  $A_{461}$  represent the absorbance at 640 nm and 461 nm.

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