

# Development of Fluorescent Sensing of Anions under Excited-State Intermolecular Proton Transfer Signaling Mechanism

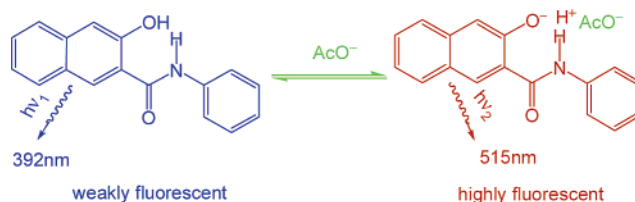
Xuan Zhang,<sup>†</sup> Lin Guo,<sup>†</sup> Fang-Ying Wu,<sup>†,‡</sup> and Yun-Bao Jiang<sup>\*,†</sup>

Department of Chemistry and the MOE Key Laboratory of Analytical Sciences, Xiamen University, Xiamen 361005, China, and Department of Chemistry, Nanchang University, Nanchang 330047, China

ybjjiang@xmu.edu.cn

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## ABSTRACT



A substantially red-shifted fluorescence emission in 3-hydroxy-2-naphthylidene-1-phenylethanone in acetonitrile was developed and drastically enhanced upon addition of anions such as  $F^-$ ,  $AcO^-$ , and  $H_2PO_4^-$ , with the enhancement depending on anion basicity. Excited-state intermolecular proton transfer in the sensor–anion hydrogen-bonding complex was suggested to be the signaling mechanism.

Anion recognition and sensing via artificial receptors are of current interest in supramolecular chemistry because of their importance in biological and environmental assays.<sup>1</sup> Of particular interest in this regard are fluorescent sensors, as they are both highly sensitive and easy to signal.<sup>2</sup> The most

desirable property of an anion sensor based on fluorescence is the ability to respond to applied perturbation in a highly selective and sensitive manner by dramatic change in emission color and/or intensity. For this purpose, many fluorescent sensors for anions have been developed on the basis of a variety of signaling mechanisms such as competitive binding,<sup>3</sup> photoinduced electron transfer (PET),<sup>4</sup> metal-to-ligand charge transfer (MLCT),<sup>5</sup> excimer/exiplex,<sup>6</sup> and intramolecular charge transfer (ICT).<sup>7</sup> It is surprising to note

<sup>†</sup> Xiamen University.

<sup>‡</sup> Nanchang University.

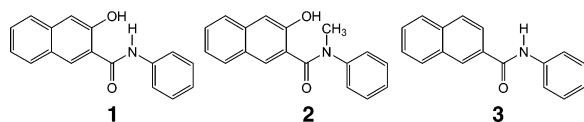
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that, although the phenomenon of excited-state intra-/intermolecular proton transfer (ESPT) has been well documented,<sup>8</sup> it has scarcely been exploited in anion sensing. Recently, Hamilton et al.<sup>9</sup> reported a fluorescent macrocyclic amide anion sensor containing coumarin fluorophore that involves both the excited-state charge transfer and proton transfer dual channels. We report here a simple fluorophore, 3-hydroxyl-2-naphthanilide (**1**, Figure 1), that is com-



**Figure 1.** Structures of sensor **1** and control compounds **2** and **3**.

mercially available and can be used as a highly sensitive fluorescent sensor for anions following an excited-state intermolecular proton transfer signaling mechanism.

The choice of **1** as the fluorescent sensor was mainly based on the fact that (i) **1** contains both OH and amide NH groups that are well-known to be involved in natural anion-binding sites of peptides<sup>10</sup> and have been extensively employed in developing anion receptors and sensors<sup>11</sup> and (ii) the acidities of phenolic OH and aromatic amino NH protons are drastically enhanced upon photoexcitation<sup>8</sup> and therefore an excited-state intermolecular ESPT channel might be opened upon anion binding. Variations of the fluorescence spectra of **1** in acetonitrile in the presence of anions such as F<sup>-</sup>, AcO<sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, and ClO<sub>4</sub><sup>-</sup> (added as tetrabutylammonium salts) were followed. It was found that, whereas **1** emitted only a short-wavelength fluorescence at 392 nm ( $\lambda_{\text{ex}} = 300$  nm) with a very low fluorescence quantum yield ( $\Phi \approx 10^{-4}$ ) in CH<sub>3</sub>CN, a new and substantially red-shifted emission appeared at 515 nm upon addition of F<sup>-</sup> and was dramatically enhanced with increasing F<sup>-</sup> concentration (see Figure 2). Meanwhile, the absorption spectrum of **1** underwent systematic variation when titrated by F<sup>-</sup>, and the solution color turned from colorless to yellow (Figure 3). It

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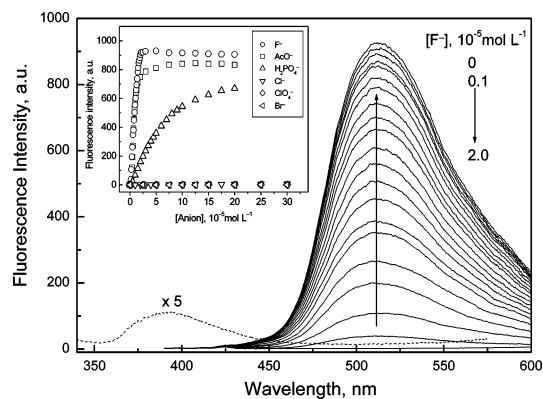
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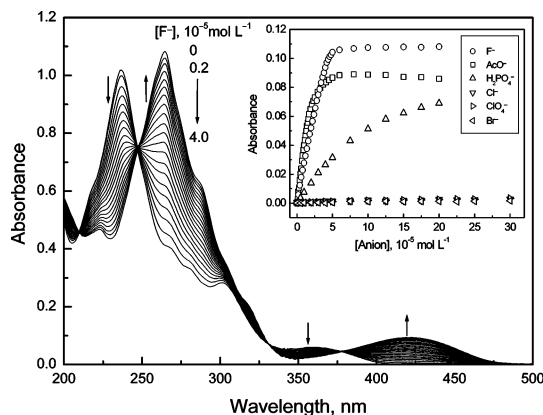
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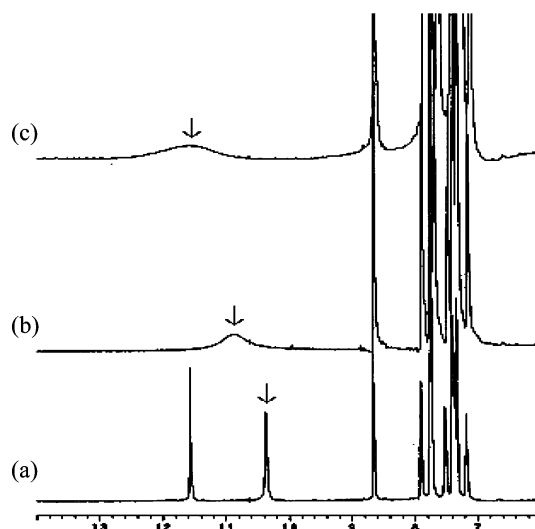


**Figure 2.** Fluorescence spectra of **1** (10  $\mu\text{M}$ ) in CH<sub>3</sub>CN upon addition of F<sup>-</sup> with an excitation wavelength of 377 nm (300 nm for the dashed line). From bottom to top, [F<sup>-</sup>] ( $\mu\text{M}$ ) increases from 0.0 to 20 at regular intervals of 1.0. Inset shows plots of fluorescence intensity at 515 nm as a function of anion concentration.

was noted in Figure 3 that, while the absorbance of **1** at 360 and 236 nm decreased with increasing F<sup>-</sup> concentration, two new peaks appeared at 422 and 264 nm and four distinctive isosbestic points were observed at 210, 248, 330, and 377 nm, respectively. The fact that the yellow solution of **1** and F<sup>-</sup> mixture in acetonitrile was returned to colorless when a protic solvent such as methanol or water was introduced suggested that the interaction between **1** and F<sup>-</sup> was hydrogen bonding in nature, likely at the amide NH<sup>11</sup> and phenol OH<sup>12</sup> sites. To confirm this assumption, NMR titrations<sup>13</sup> were carried out. It was found that the amide NH proton signal was broadened and underwent a continuous downfield shift from 10.377 to 10.882 to 11.584 ppm with increasing F<sup>-</sup> concentration from 0 to 0.5 to 1.0 equiv, whereas the OH proton signal (11.572 ppm) could not be similarly followed as it completely disappeared upon addition of 0.5 equivalents of fluoride ion (Figure 4). These observa-



**Figure 3.** Variation traces of the absorption spectrum of **1** (20  $\mu\text{M}$ ) upon titration by tetrabutylammonium fluoride in CH<sub>3</sub>CN (step: 2.0  $\mu\text{M}$ ). Inset shows plots of absorbance at 422 nm as a function of anion concentration.



**Figure 4.**  $^1\text{H}$  NMR (500 MHz) spectra of **1** in  $\text{CD}_3\text{CN} + 10\%$   $\text{DMSO-}d_6$  in the presence of (a) 0, (b) 0.5, and (c) 1.0 equiv of tetrabutylammonium fluoride. Arrows point to the NH proton signal. Complete  $^1\text{H}$  NMR spectra can be found in Figure 1SH in Supporting Information.

tions clearly supported the hydrogen bonding interaction between **1** and  $\text{F}^-$  involving the amide NH and phenol OH groups. Other anions such as  $\text{AcO}^-$ ,  $\text{H}_2\text{PO}_4^-$ , and  $\text{Cl}^-$  were found to induce similar variations in both the absorption and fluorescence spectra to extents that depended on the anion's basicity, whereas  $\text{Br}^-$  and  $\text{ClO}_4^-$  hardly induced any spectral changes.<sup>14</sup> The Job plots for complexation of **1** with anions obtained from both absorption and fluorescence titrations pointed to the 1:1 stoichiometry between **1** and  $\text{AcO}^-$ ,

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(13)  $^1\text{H}$  NMR titrations were carried out in  $\text{CD}_3\text{CN} + 10\%$   $\text{DMSO-}d_6$ . Titrations were also performed in  $\text{DMSO-}d_6$ , and the chemical shifts of NH and OH protons were found at 10.612 and 11.350 ppm in the absence of fluoride ion, respectively. The peaks were broadened and shifted to 10.670 and 11.377 ppm in the presence of 0.1 equiv of fluoride ion, and while the NH proton signal further shifted to 10.961 ppm, the OH proton signal disappeared upon addition of 0.3 equiv of fluoride ion. Complete  $^1\text{H}$  NMR spectra in  $\text{DMSO-}d_6$  can be found in Figure 2SH in Supporting Information.

(14) Absorption and fluorescence spectra of **1** in the presence of  $\text{AcO}^-$  (Figures 3SA and 3SF) and  $\text{H}_2\text{PO}_4^-$  (Figures 4SA and 4SF) are provided in Supporting Information.

**Table 1.** Association Constants ( $K_{\text{ass}}$ ,  $\text{M}^{-1}$ ) for Anions with **1** in Acetonitrile from Absorption (422 nm) and Fluorescence ( $\lambda_{\text{em}} = 515$  nm,  $\lambda_{\text{ex}} = 377$  nm) Titrations<sup>a</sup>

anion	$K_{\text{ass}}$ (abs.)	$K_{\text{ass}}$ (flu.)
$\text{Br}^-$ , $\text{ClO}_4^-$	na <sup>b</sup>	na <sup>b</sup>
$\text{Cl}^-$	$(2.73 \pm 1.14) \times 10^3$	$(1.00 \pm 0.16) \times 10^3$
$\text{H}_2\text{PO}_4^-$	$(1.13 \pm 0.06) \times 10^4$	$(1.20 \pm 0.08) \times 10^4$
$\text{AcO}^-$	$(5.94 \pm 0.39) \times 10^5$	$(4.43 \pm 1.08) \times 10^5$
$\text{F}^-$	$>10^6$ <sup>c</sup>	$>10^6$ <sup>c</sup>

<sup>a</sup> Anions exist as their tetrabutylammonium salts. <sup>b</sup> Not available because of the minor spectral change. <sup>c</sup> Too high to be accurately determined.

whereas a 1:2 ratio was found between **1** and  $\text{F}^-$ . A Hill plot suggested that two  $\text{F}^-$  ions bind sequentially to **1**. The association constants ( $K_{\text{ass}}$ ) between **1** and anions were fitted from nonlinear regressions,<sup>15</sup> and the data are listed in Table 1. The fact that **1** shows higher binding affinity to and more efficient fluorescence enhancement by  $\text{F}^-$  than other anions is actually not surprising because of its high charge density and small size, which enables it to be a strong hydrogen bonding acceptor that shows interaction with phenol or amide derivatives containing only a single hydrogen bonding donor group.<sup>11g,12</sup>

To further identify the proton transfer site and possible anion binding mode, two control compounds **2** and **3**<sup>16</sup> (Figure 1) were synthesized, in which the amide proton and hydroxyl group were removed, respectively. It was found that with the *N*-methyl derivative **2**, variations of absorption and fluorescence spectra upon addition of  $\text{F}^-$ , though similar to those found with **1**, were much less minor, giving association constants of  $10^3$   $\text{M}^{-1}$  in order of magnitude.<sup>17</sup> With **3**, however, addition of  $\text{F}^-$  did not induce any discernible spectral change. It is therefore obvious that proton transfer occurs between the hydroxyl group of the sensor and anions in the excited state, while both OH and amide NH in **1** play an important role in its binding to anions. As observed from Figures 3 and 4, **1** binds anion in the ground state through hydrogen bonding interaction via amide NH and phenolic OH.<sup>11,12</sup> This leads to an increased local concentration of the anion, and as a consequence, intermolecular proton transfer in the excited state of **1** to weakly basic anions occurs,<sup>9</sup> with the formation of contact and/or solvent-separated ion pairs in polar solvents such as  $\text{CH}_3\text{-CN}$  due to the enhanced acidity of the aromatic hydroxyl

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(16) Compounds **2** and **3** were synthesized by reaction of 3-hydroxyl-2-naphthoyl chloride and 2-naphthoyl chloride with *N*-methylaniline and aniline, respectively. **Compound 2**:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  3.562 (s, 3H), 7.103–7.373 (m, 10H), 7.581 (d, 1H,  $J = 8.0$  Hz), 10.263 (s, 1H). **Compound 3**:  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ , ppm)  $\delta$  7.122 (t, 1H,  $J = 8.0$  Hz), 7.380 (t, 2H,  $J = 7.5$  Hz), 7.614–7.666 (m, 2H), 7.830 (d, 2H,  $J = 8.0$  Hz), 8.012–8.068 (m, 3H), 8.095 (d, 1H,  $J = 7.5$  Hz), 8.582 (s, 1H), 10.427 (s, 1H).

(17) Absorption and fluorescence spectra of **2**–anion complex exhibit maxima at 400 and ca. 580 nm, respectively.

proton.<sup>8,18</sup> Actually, similar spectral variations were observed with **1** in CH<sub>3</sub>CN in the presence of an organic base triethylamine. It should be noted that both the absorption and fluorescence spectra of 2-naphthol, a model molecule of **1**, showed weak responses to F<sup>-</sup> ( $K_{\text{ass}} \approx 10^3 \text{ M}^{-1}$ ) in CH<sub>3</sub>CN, and a weak fluorescence emission at ca. 420 nm was observed upon introduction of F<sup>-</sup>, which is similar to the observation made in water on the deprotonation of 2-naphthol by anions where the new emission was assigned to the naphtholate anion.<sup>19</sup> These facts support the occurrence of proton transfer between the hydroxyl group of sensor **1** and anions in the excited state. In a recent report,<sup>20</sup> it was shown that the deprotonation of pyrrole NH group in the ground state by F<sup>-</sup> induced substantial color change. It would therefore be assumed that the intermolecular proton transfer could serve as a new signaling mechanism in constructing chemosensors for anions.

In the presence of anion, the excitation spectrum of **1** ( $\lambda_{\text{em}} = 515 \text{ nm}$ ) exhibits variations similar to those observed with the absorption spectrum. This means that two pathways exist

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to form the red-shifted fluorescence emissive state, i.e., direct excitation from the ground-state **1**–anion binding complex with  $\lambda_{\text{ex}}$  of 422 nm, and the initial excitation of the sensor moiety in the binding complex ( $\lambda_{\text{ex}} = 300 \text{ nm}$ ) that leads to proton transfer from the excited-state sensor to anion.<sup>9</sup> The difference of the ground- and excited-state  $\text{p}K_{\text{a}}$  values of **1** was calculated as 11 on the basis of the Förster cycle,<sup>8a,c,21</sup> which indeed pointed to a dramatically enhanced acidity in the excited state.

In conclusion, we presented a simple fluorescent sensor for anions following the excited-state intermolecular proton transfer signaling mechanism. Although detailed photophysical studies are required, this signaling mechanism would open up a new horizon for developing fluorescent chemosensors for anions.

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**Supporting Information Available:** Complete <sup>1</sup>H NMR spectra of **1** in CD<sub>3</sub>CN + 10% DMSO-*d*<sub>6</sub> and in DMSO-*d*<sub>6</sub> (Figures 1SH and 2SH) in the presence of F<sup>-</sup> and absorption and fluorescence spectra of **1** in acetonitrile in the presence of AcO<sup>-</sup> (Figures 3SA and 3SF) and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> (Figures 4SA and 4SF).

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