A Highly Selective Chromogenic and Fluorogenic Chemosensor for Fluoride Ion

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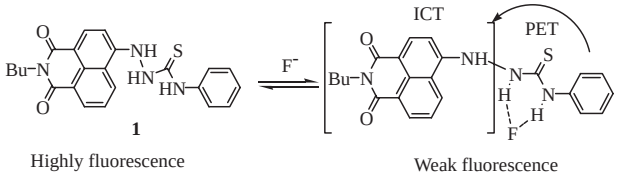
The thiourea binding site anchored to fluorescent 4-amino-1,8-naphthalimide signaling subunit is a highly selective and sensitive chromogenic and fluorogenic reagent for fluoride anion sensing.

The development of selective and sensitive chemosensors for anion is a topic of current attention.[1] The detection and quantification of anions is important in the fields such as biology and environmental chemistry as a consequence of the role played by anions in environmental or chemical processes. Among systems sensing anions, those displaying an optical signal upon anion coordination are of special interest.[2] These systems can be built by combination of anion binding-parts and signaling subunits that transform receptor–anion interactions into optical signals. Signaling units can be fluorescent groups[3] (output signal is a fluorescence change) or dyes[4] (output signal is a colour change). The fluorescence chemosensors for anions are currently interested because they offer the potential for high sensitivity at low analyte concentration.[5] We report here a new selective dual sensing fluoride chemosensor, which consists of a thiourea group binding fluoride and 4-amino-1,8-naphthalimide unit as chromogenic as well as fluorogenic signaling subunit.

The synthesis of chemosensor **1**[6] was carried out by condensation of *N*-butyl-4-hydrazino-1,8-naphthalimide with phenylisothiocyanate in ethylene glycol mono methyl ether heating to 120 °C. The reaction mixture was dropped into water, extracted with dichloromethane and the solid obtained was purified by chromatography on silica gel with hexane:ethyl acetate (1:1) as eluent. As stated above, **1** is a potential chromogenic and fluorescent chemosensor for anion sensing as it contains the hydrogen-bonding site and 4-amino-1,8-naphthalimide signaling subunit.[7]

It was noted in Figure 1 that, while the absorbance of **1** at 390 nm decreased with increasing F^- concentration, two new peaks appeared at 335 and 555 nm. The presence of three isosbestic points at 287, 360, and 445 nm indicates that only two species coexist in the equilibrium. Data can be interpreted on the basis of the equilibrium between **1** and $[\mathbf{1}\cdot F]^-$, in which $[\mathbf{1}\cdot F]^-$ represents the receptor–anion complex that should be responsible for the new absorption band. The curvature in the titration profile reported in Figure 2 confirmed the 1:1 binding stoichiometry. The fact that the purple solution of **1** and F^- mixture in acetontrile was returned to dark yellow when a protic solvent such as methanol or water was added suggests that the interaction between **1** and F^- was hydrogen bonding in nature, likely at the thiourea NH sites.[5b,7] To confirm this assumption, ^{1}H NMR titrations in DMSO-d_6 were carried out (see Supporting Information). It was found that the amide NH proton signal was downfield shifted with increasing F^- concentration. These observations clearly supported the hydrogen bonding interaction between **1** and F^- involving the thiourea NH group. Other anions such as Cl^-, Br^-, and I^- were found to hardly induce similar variations in both the absorption and fluorescence spectra (see Supporting Information). The fact that **1** shows higher binding affinity to F^- and more efficient fluorescence quenching by F^- than other anions is actually not surprising because of the high charge density, small size and strong hydrogen bonding ability of fluoride ion.[8] The origin of the dramatic colour change from dark yellow to purple observed in the presence of fluoride ion and the appearance of a new absorption peak might be ascribed to the enhancement of intramolecular charge transfer (ICT) process within the fluorophore. This enhanced ICT was induced by the photoinduced electron transfer (PET) between thiourea-bound fluoride and the amine at the 4-position of 1,8-naphthalimide (Scheme 1).[9,10]



Scheme 1. Proposed hydrogen bond formation between fluoride and chemosensor **1**.

The ability of **1** to recognize several anions was also investigated using fluorescence spectroscopy in CH_3CN. Excitation at λ_{max} gave rise to emission between 450 and 650 nm (green colour to naked eye). This emission band is contributed from the 4-amino-1,8-naphthalimide.[10] Upon addition of F^- anions the emission of **1** was substantially reduced in intensity as shown in Figure 3. The mechanism for this quenching could be explained via the PET, which takes place between the thiourea and 4-amino-1,8-naphthalimide fluorophore. The absorption

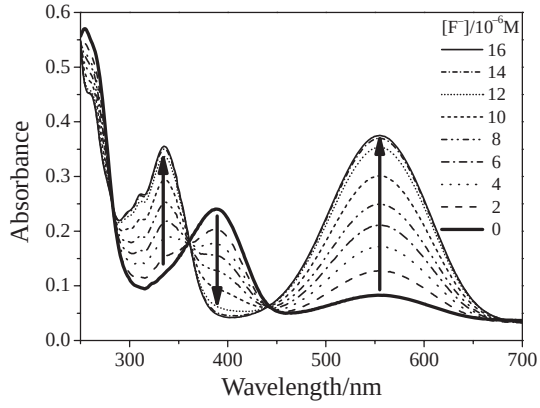


Figure 1. The changes in absorption spectra of **1** (1.4×10^{-5} M) upon addition of TBAF (tetrabutylammonium fluoride salt) in CH_3CN.

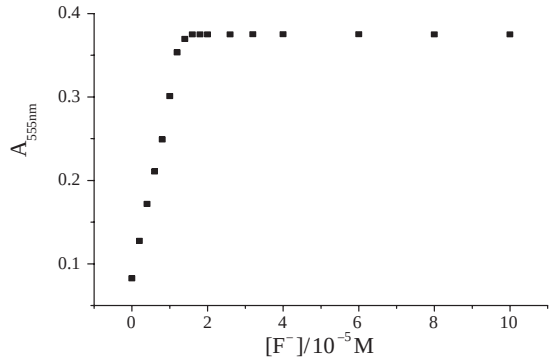


Figure 2. Titration profile for **1** solution (1.4×10^{-5} M in CH_3CN) with TBAF, which indicates the formation of the 1:1 complex [**1**·F^-].

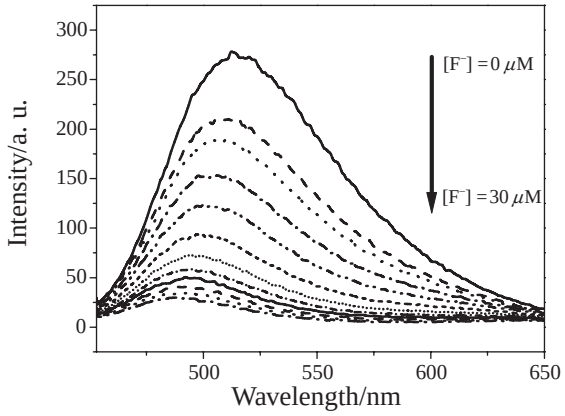


Figure 3. The changes in the fluorescence emission spectra of **1** (2.8×10^{-5} M in CH_3CN) upon titration with TBAF, showing the fluorescence emission 'switched off' upon F^- recognition (excited at 390 nm).

band shift of the system in the presence of fluoride ion is assigned to the enhanced ICT from the 4-position amino group to the imide nitrogen within 4-amino-1,8-naphthalimide fluorophore. The hydrogen-bonding interaction of fluoride ion with thiourea triggers the PET between thiourea and the fluorophore. This causes the fluorescence of **1** 'switched off' rather than 'switched on' upon the anion recognition, unlike many PET sensors for cations.[5a] Fluoride hydrogen bonding changes the photophysical properties of the ICT fluorophore due to its effect on the efficiency of charge transfer.[11,12]

The fluorescence emission of **1** is effectively quenched or completely 'switched off' after the addition of 30 μM of F^-. Addition of H_2O (ca. 10% v/v) to this solution 're-switched on' the emission, demonstrating that the process was near fully reversible, i.e. the hydrogen bonding interaction between F^- and the receptor is broken because the hydrogen bond between F^- and protic solvent is stronger than that of F^- with the receptor.[12]

In summary, it has been shown that thiourea binding site linked to 4-amino-1,8-naphthalimide signaling unit is a selective and sensitive chromogenic and fluorogenic reagent for fluoride anion sensing. A highly specific colorimetric reaction in the presence of fluoride has been found in both CH_3CN and DMSO with naked eyes. This observation is another example where both PET and ICT processes within the same molecule lead to dual optical outputs.[13]

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