An Axial Subphthalocyanine as Ratiometric Fluoride Ion Sensor

Yang Li, Sheng Xu, Xin Li, Kongchang Chen, and He Tian*
Labs for Advanced Materials and Institute of Fine Chemicals,
East China University of Science and Technology, Shanghai 200237, P. R. China

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A subphthalocyanine derivative (SubPc **1**) with a naphthalimide fluorophore at the axial position was designed and synthesized for fluoride ion selective and sensitive sensing. The obvious changes in UV–vis and fluorescence spectra could be observed by naked eyes.

Subphthalocyanine derivatives (SubPc) are attractive compounds owing to their special chemical and physical properties for the potential application in optoelectronic devices.[1] For the purpose of exploring their application in the material science, SubPc as dosimetric system was found effective in sensing anion.[2] Anion recognition and sensing via artificial receptors are of current interest in supramolecular chemistry because of their importance in biological and environmental assays.[3] Fluoride ion, the smallest anion, has unique chemical properties, and its recognition and detection are of growing interest because it is associated with nerve gases, the analysis of drinking water, and the refinement of uranium used in nuclear weapon manufacture.[4,5] In this domain, the study of fluoride sensors based on boron-containing π-electron systems is especially noteworthy.[6]

To increase the selectivity and sensitivity, ratiometric measurements are utilized, which involve the observation of changes in the ratio of the intensities of the absorption or the emission at two wavelengths. Up to now, some ratiometric fluorescent sensors for fluoride ion have been found in the literature.[4h,4i,6d]

To extend the ratiometric response approach, we here report the design, synthesis, and binding study of receptor **1**, a 1,8-naphthalimide (NAP) fluorophore connected to the center boron atom via a piperazinyl–ethoxy–phenoxy linker in SubPc (see Figure 1). An excitation energy transfer (EET) occurs from the naphthalimide chromophore (NAP as an energy donor: D) to the SubPc chromophore (an energy acceptor: A). In the absence of fluoride ions, naphthalimide chromophore shows relatively poor fluorescence ("off" state) as a consequence of EET. At the same time, SubPc shows inherent fluorescence ("on" state). In the presence of fluoride ions, the complex was disturbed by the fluoride ions accompanied with the quenching of fluorescence of SubPc unit (switching "off") and fluorescent enhancement of 1,8-naphthalimide (turning "on"). The possible function is revealed in the Figure 2.

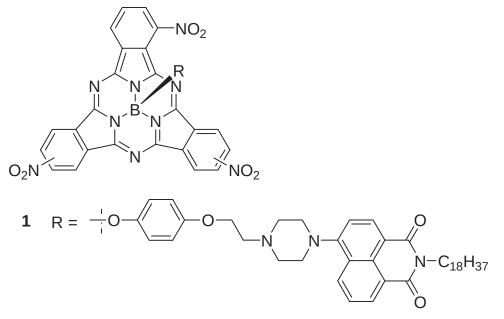

Figure 1. The chemical structure of compound **1**.

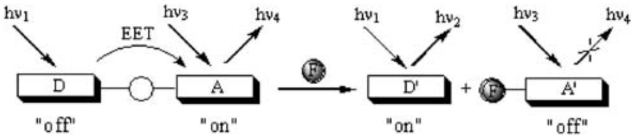

Figure 2. Schematic representation of the different emission processes occurring in **1** on coordination of fluoride ion.

SubPc **2** was similarly prepared by substitution of the axial chlorine group of SubPc[2] by 4-(2-iodoethoxy)phenol.[7] Initially, we decided to compare the ability of SubPc **1** to bind different anions (as their tetrabutylammonium salts) in THF solution using UV–vis spectrometric titration methods. The chromogenic sensing ability of **1** was studied in THF in the presence of 50 equivalents of F^-, Cl^-, Br^-, I^-, and $ClO_4{}^-$ anions. The significant color bleaching was observed in the presence of fluoride ions. Other anions, however, can hardly change the color of **1**. The discriminative color changes of **1** upon the different anions are shown in Figure S13 and the abstract color graph;[7] it easy to detect fluoride anion by naked eyes.

The effect on the absorption spectra of **1** upon the titration of fluoride ions was also carried out.[7] One can easily observe an elimination of both the Soret (291 nm) and Q (565 nm) bands in the presence of the fluoride ions, accompanied with an increase of a new band (696 nm). Two clear isosbestic points at 585 and 485 nm are observed during the titration, indicating the formation of a well-defined $\mathbf{1}\cdot F^-$ complex. This result was consistent with the known sensing system.[2a]

The sensitivity of SubPc **1** was shown by the variation of the UV–vis absorption spectra of **1** with increasing amounts of fluoride ions (see Figure S3).[7] We treat the data in Table S1[7] based on the linearization of the binding isotherm according to Benesi–Hildebrand equation,[8] from which binding constants could be calculated ($K_a = 1.30 \times 10^5\,M^{-1}$). Otherwise, Cl^-, Br^-, I^-, or $ClO_4{}^-$ was hardly found to induce similar variations in absorption spectra.[7] It is known that the nucleophilic character of anionic species is solvent dependent and that protic solvents decrease the anion's nucleophilicity by hydrogen bonding to the nucleophile's lone pair (solvent effects). Upon addition of small amounts of water (3–5%) in SubPc system[2c] the apparent constants for fluoride, acetate and dihydrogen phosphate are drastically reduced except for cyanide.

Of all detected signals, fluorescence of the chemosensor is particularly attractive on account of its simplicity and high sensitivity. We then went on to investigate the anion-sensing capability of **1** in THF solution using fluorescence titration methods.

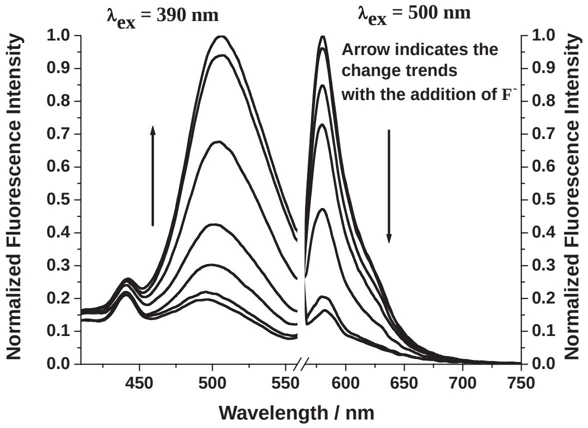

Figure 3. Normalized fluorescence response for the titration of THF solution with concentration of 0, 5, 10, 15, 25, 40, and 50 μM TBAF.

The fluorescent ratiometric responses to fluoride ions are shown in Figure 3. In the absence of F^-, sensor **1** shows a weak emission at 495 nm (excited at 390 nm, which is the absorption maximum wavelength of the naphthalimide) and a SubPc characteristic fluorescence at 578 nm (excited at 500 nm), respectively. There is overlap between the absorption spectrum of SubPc and the fluorescence spectrum of the piperazine-substituded naphthalimide.[7] Consequently, excitation energy transfer (EET) can occur from the excited naphthalimide to the SubPc unit, which may account for the weak fluorescence at 495 nm. Addition of fluoride ions causes an obvious decrease of the intensity at 578 nm (I578) (excited at 500 nm). Otherwise an increase of the naphthalimide fluorescence intensity at 495 nm (I495) is observed. Fluoride ion complexation to the center boron atom leads to the closing of the EET channel. The EET channel closing is a possible reason for the enhancement of fluorescence at 495 nm. The intermolecular energy transfer is negligible at such a low concentration. Accordingly, the naphthalimide fluorophore shows strong fluorescence at 495 nm.

Upon addition of other anions such as Cl^-, Br^-, I^-, and $ClO_4{}^-$, no significant change in the fluorescence spectra was observed, except for quenching by the heavy atom effect.[7] We subsequently chose two wavelengths, 495 and 578 nm, where the intensity was notable and illustrated the dual emission response. It is evident that these anions did not have a significant impact on the fluorescence of **1**. These studies indicate that compound **1** is highly selective for fluoride sensing.

In summary, we have presented a subphthalocyanine derivative with a naphthalimide fluorophore at the axial position which has the ability to selectively recognize and detect fluoride ion. SubPc **1** interacts irreversibly with the analyte by higher affinity of a boron atom toward the fluoride anion than other anions. The large absorption variation can be observed by naked-eye upon the addition of fluoride ion. The binding of fluoride ion leads to a ratiometric dual fluorescence response. It provides a feasible way to construct ratiometric fluorescence chemosensor and extend the application of subphthalocyanine derivative in material science.

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