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A near-infrared fluoride sensor based on a substituted naphthalenediimide–anthraquinone conjugate

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ABSTRACT

The synthesis and characterization of a highly selective fluoride receptor based on a naphthalene diimide substituted with an anthraquinone (**NDI-AQ**) moiety is described. In $CHCl_3$, the receptor was shown to be highly selective for fluoride ($K_a \sim 10^3\ M^{-1}$) over other anions (AcO^-, HSO_4^-, Br^-, Cl^-, I^-, ClO_4^-, $H_2PO_4^-$, and NO_3^-) with pronounced changes in absorption characteristics, that is, red-shift of the absorption band to 790 nm (NIR). The visual color change, NIR shift in absorption, emission spectroscopy, and electrochemistry thus support an intramolecular charge transfer (ICT) effect upon fluoride binding to the **NDI-AQ** receptor.

The ability to sense fluoride ions is of importance to many areas of chemistry due to its essential roles in medical, biological and environmental processes.[1] Consequently the development of fluoride specific receptors is an area of continued focus and in recent years the design of colorimetric and fluorescent receptors for the sensing of fluoride anions has advanced steadily.[2] The method of covalently binding a receptor to a signaling subunit is the most widely used approach, where pyrroles, urea, thiourea, amides, phenols, imidazole, or calixarene have been used as coordination sites.[3] In such receptors, color or fluorescence emission changes are observed due to interaction of the anion with the coordination site of the sensor via hydrogen bonding and electrostatic interactions, which induces changes in the electronic properties of the signaling unit.[4] These approaches are widely used by researchers due to the low cost involved in the fabrication of the receptor and the convenient detection of anions. The design and development of anion sensors still remains a challenging task, as anions tend to have a low stability constant, and some receptors also display a complex pH-dependence.[1d] Chemosensors with a near-infrared (NIR) optical response should be more useful, as they are more likely to not show interference from other chromophores, and can be run with an inexpensive compact laser, light emitting diodes or NIR diodes.[5,6]

Among aromatic molecules that have found utility in the design of chromophoric supramolecular materials, naphthalene diimide (NDI) derivatives have attracted particular attention due to their n-type properties.[7,8] NDIs are compact, highly colored, and have rich spectroscopic and electrochemical properties. Substituted NDI derivatives, in particular, are ideally suited to sensor design.[8] Recently, we and other researchers have shown that naphthalenediimide (NDI) derivatives are very effective colorimetric sensors for a range of anions.[7] In other reports, anthraquinone (AQ) derivatives have also been employed as colorimetric sensors for anions and cations.[9] To the best of our knowledge, a donor–acceptor system of this class of compound, exhibiting a solution dependent intramolecular charge transfer (ICT) has not been explored in either a receptor or sensor capacity.

Considering the above facts, and our interest in expanding the development of chemosensors based on NDI probes. We herein report the synthesis and characterization of a substituted NDI derivative functionalized with an AQ subunit. The colorimetric and spectroscopic behavior of the synthesized receptor toward ion detection was studied via ICT effects.

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The synthesis of **NDI-AQ** (**1**) was achieved by reacting 1,4,5,8-naphthalenetetracarboxylic dianhydride (**NDA**) with 5.3 equiv of Br_2 in a mixture of sulfuric acid and oleum (*v:v*, 4:1) at 140 °C for 4 weeks. 2,3,6,7-Tetrabromonaphthalene diimide (**3**) was prepared over two steps by the reaction of **2** and 4 equiv of *n*-octylamine in refluxing acetic acid for 30 min to give 2,3,6,7-tetrabromo-4,8-bis(octylcarbamoyl) naphthalene-1,5-dicarboxylic acid, which was further treated with excess PBr_3 in refluxing toluene for 12 h to afford **3** in 31% overall yield.[10] The **NDI-AQ** conjugate was synthesized via nucleophilic substitution of the substituted tetrabromonaphthalene diimide **3** with 1,2-diamino anthraquinone (**4**) in dry DMF at 120 °C (Scheme 1). The receptor **1** was obtained as a dark blue solid in 80% yield after purification by column chromatography (for details see ESI). It is important to note that the addition of a second equivalent of anthraquinone **4** to compound **3**, substituting the two remaining bromine atoms, may have increased the sensitivity of the sensor toward fluoride. However, this was not possible despite many attempts. The fact that monoannulation resulted in high yield could be attributed to two main factors. Firstly, aniline amines such as **4** are less nucleophilic than the aliphatic amines where tetra-substitution takes place,[11] and secondly, once the first addition is complete, the deactivating feature of the two donating amino groups prevents further addition.[12] This result is also important as it may allow variation to the structure through the two remaining aryl bromide groups.

The colorimetric behavior of the **NDIA-AQ** (**1**) receptor toward ion detection was studied by employing various anions such as AcO^-, HSO_4^-, Br^-, Cl^-, I^-, ClO_4^-, $H_2PO_4^-$, NO_3^-, and F^- (added as their *tert*-butyl-ammonium salts). The result of adding 5 equiv of various anions to **1** in $CHCl_3$ is shown in Figure 1. It was observed that the **NDI-AQ 1** receptor was selective for fluoride at μM concentrations. Complete loss of the blue color was observed when F^- was introduced to a solution of receptor **1** in chloroform due to the ICT effect.

UV–vis absorption spectroscopy was employed to determine the selectivity of receptor **1** and quantify the spectral changes upon F^- binding. Typically, receptor **1** (1×10^{-5} M in $CHCl_3$) exhibited three absorption bands; strong bands at 600 and 651 nm, and a weak band at 290 nm. Upon addition of up to 5 equiv of the F^- ion, the absorption intensity bands at 600 and 651 nm steadily decreased along with the appearance of a new band at 790 nm (near-infrared). In the presence of 5 equiv of F^-, the band at 790 nm predominated with an isosbestic point at 685 nm (Fig. 2). In contrast, the addition of other anions (AcO^-, HSO_4^-, Br^-, Cl^-, I^-, ClO_4^-, $H_2PO_4^-$ or NO_3^-) to a $CHCl_3$ solution of the receptor **1** did not induce any spectral changes (Fig. S1, ESI), indicating that anion–π interactions were not significant with these anions.

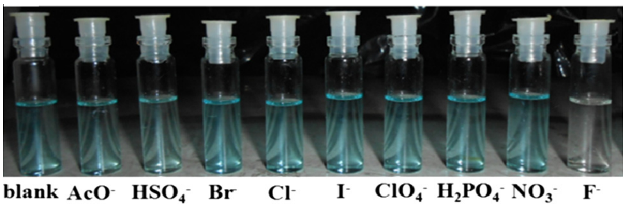


Figure 1. Color changes upon addition of 5 equiv of anions (as their *tert*-butyl-ammonium salts) to receptor **1** (1×10^{-5} M in chloroform).

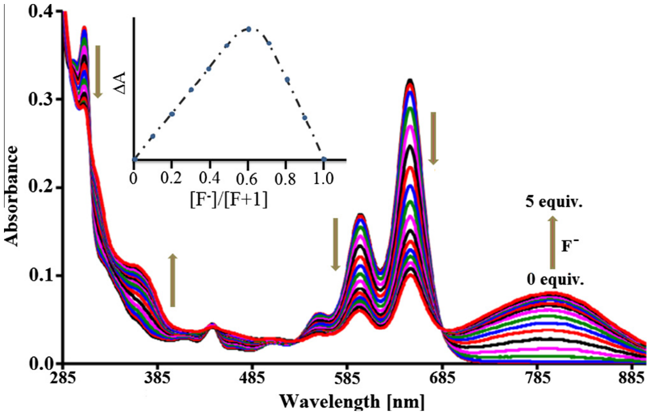
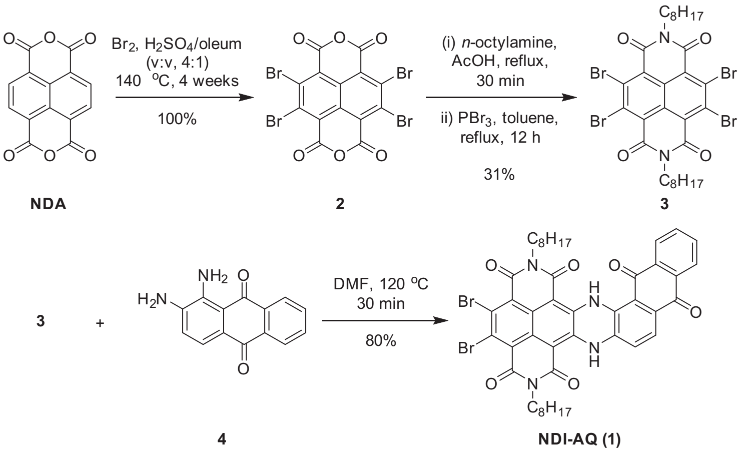


Figure 2. UV–vis absorption titration of **NDI-AQ** ([**1**] = 1×10^{-5} M in $CHCl_3$) upon addition of fluoride ions (0–5 equiv of the solution 5×10^{-4} M). Inset shows the Job plot of fluoride to receptor **1** with 2:1 stoichiometry of the complex.

The fluorescence emission spectra of **NDI-AQ** (Figure 3) consists of a strong bands at 677 (excitation at 600 nm). As shown in Figure 3, ~70% quenching was observed for **NDI-AQ** upon addition of 0-5 equiv. of F^- (added as their tert-butyl-ammonium salts), due to the fluorides high charge density.[8b] Smaller effects (<5% quenching) were observed for all other anions requiring 20 equiv to achieve this response (Fig. S4). These results clearly shows that **NDI-AQ** has a selective colorimetric and emission response to the presence of fluoride.

These results indicated that **1** had a selective colorimetric response to the presence of fluoride ions and a 2:1 stoichiometry of the complex was determined by a Job plot (inset Fig. 2). The binding constant of **NDI-AQ** to F^- was determined to be $4 \times 10^3\ M^{-1}$ (Fig. S2). The quantification limit and detection limit



Scheme 1. Synthesis of the **NDI-AQ** (**1**) receptor.