Tetrahedron Letters 56 (2015) 4762–4766

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

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

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ARTICLE INFO

*Article history:*
Received 9 March 2015
Revised 19 May 2015
Accepted 17 June 2015
Available online 24 June 2015

*Keywords:*
Naphthalenediimide
Intramolecular charge transfer
Colorimetric and optical
Near-IR
Fluoride sensing

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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http://dx.doi.org/10.1016/j.tetlet.2015.06.050
0040-4039/

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** ($1 \times 10^{-5}$ 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.

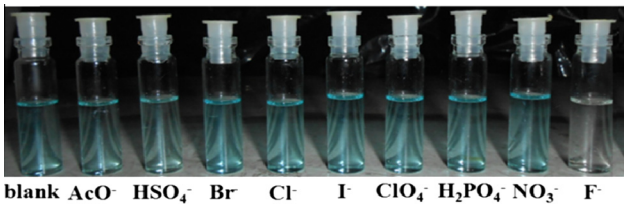



**Figure 1.** Color changes upon addition of 5 equiv of anions (as their *tert*-butyl-ammonium salts) to receptor **1** ($1 \times 10^{-5}$ M in chloroform).

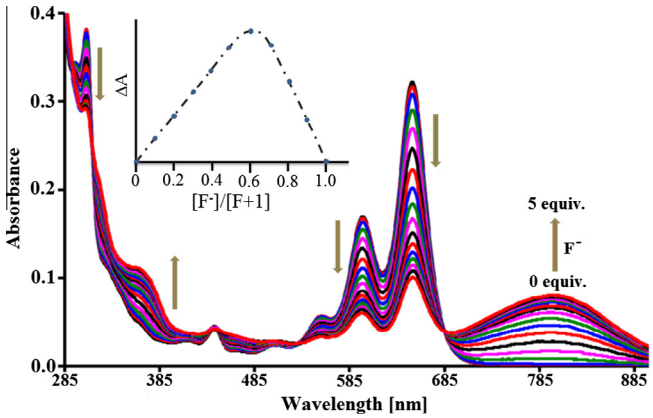
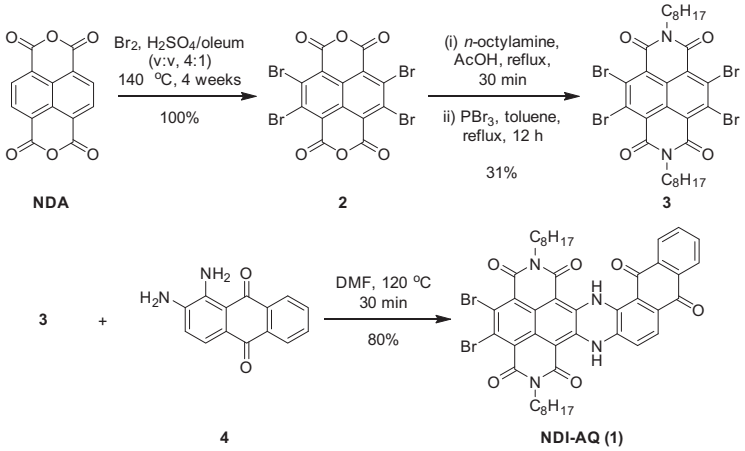



**Figure 2.** UV–vis absorption titration of **NDI-AQ** ([**1**] = $1 \times 10^{-5}$ M in $CHCl_3$) upon addition of fluoride ions (0–5 equiv of the solution $5 \times 10^{-4}$ M). Inset shows the Job plot of fluoride to receptor **1** with 2:1 stoichiometry of the complex.

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.

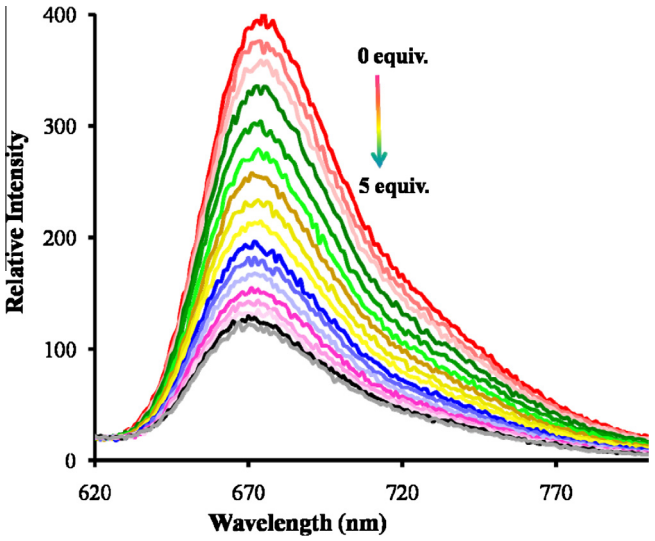



**Figure 3.** Fluorescence spectra ($\lambda_{ex}$ = 600 nm) of **NDI-AQ** ($1 \times 10^{-5}$ M in $CHCl_3$) in the presence of 0–5 equiv of $F^-$ ($5 \times 10^{-4}$ M).

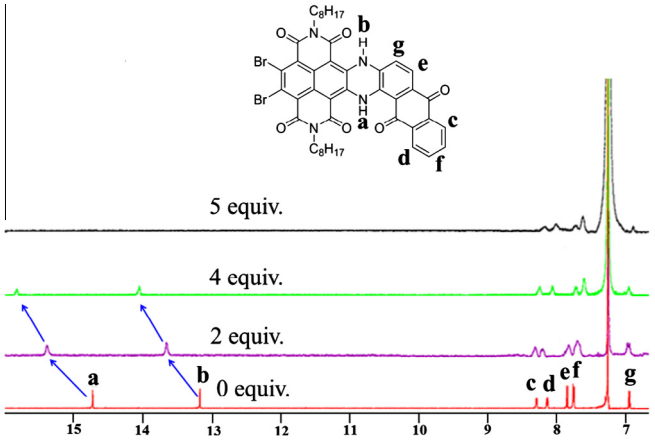



**Figure 4.** $^1$H NMR (300 MHz) spectra of chemosensor **NDI-AQ** in $CDCl_3$ in the presence of 0–5 equiv of fluoride ions.

of the $F^-$ anion were estimated to be approximately $3.87 \times 10^{-5}$ M and $1.16 \times 10^{-5}$ M, respectively (Fig. S3).

$^1$H NMR titration experiments confirmed that $F^-$ complexation with the receptor **1** occurred via hydrogen bonding (Fig. 4). Peaks of the **NDI-AQ** receptor in $CDCl_3$ that were observed at $\delta$ 13.20 and 14.75, were shifted downfield ($\delta$ 13.82 and 15.49) upon the addition of 2 equiv of $F^-$. When four equivalents of $F^-$ were used, the peaks shifted further downfield ($\delta$ 14.10 and 15.85) with a decrease in intensity. Finally, upon the addition of 5 equivalents of $F^-$, complete disappearance of these peaks was observed. At the same time, signals for protons on the aryl rings were shifted upfield.

The voltammogram of **NDI-AQ** in the absence of fluoride showed three prominent cathodic processes in the region of −1.09 to −1.43 V (vs $Fc/Fc^+$), two of which were chemically reversible under the conditions examined, and an overlapping chemically irreversible peak. The anodic scan also showed a series of overlapping peaks in the range +0.44 to +0.88 V.[13] The voltammograms were a series of overlapping peaks with no contributions from both the NDI core and AQ group.[14] In compound **NDI-AQ**, the redox processes at the NDI and anthraquinone center overlap, to give the complicated voltammogram seen in curve (a1), which was shown by the DPV trace (a2) to be a series of overlapping peaks on both the anodic and cathodic scan (Fig. 5).

Upon the addition of 2 equiv of $F^-$, the change in the voltammogram and DPV was profound. The cathodic processes shifted to a more negative potential, in one large overlapping peak in the voltammogram (b1), which was revealed by DPV (b2) to be a series of redox processes. The greatest change was seen in the oxidation processes on the anodic scan. A large peak, revealed by DPV (b2) to be at least two overlapping redox processes, was observed, which was shifted to a far more cathodic potential (−0.2 to 0 V vs $Fc/Fc^+$) than the experiment conducted in the absence of $F^-$. This indicated that the binding of fluoride led to a change in the electronic structure of **NDI-AQ** resulting in a compound that was far more easily oxidized than when the **NDI-AQ** was not bound to fluoride.

The visual observation of color change, NIR shift in absorption, emission spectroscopy, and electrochemistry thus supported an ICT effect upon fluoride binding to receptor **1**.[7] DFT studies were carried out to gain additional understanding of the ICT mechanism. DFT computational studies were performed using the Gaussian 09

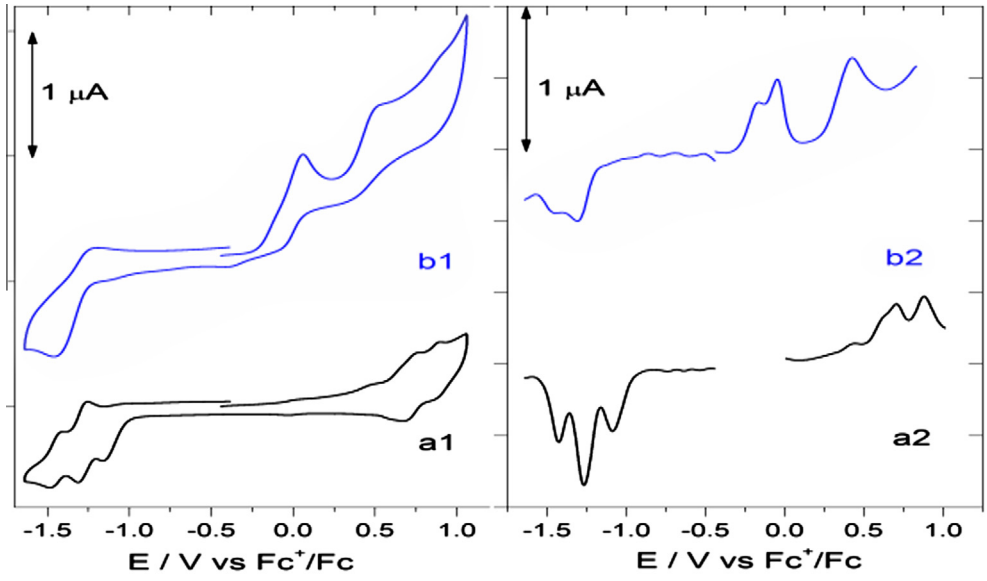



**Figure 5.** Voltammogram (a1) and differential pulse voltammogram (DPV) (a2) of 0.3 mM **NDI-AQ**. Voltammogram (b1) and DPV (b2) of 3 mM **NDI-AQ** in the presence of 0.6 mM $TBA^+F^-_4$. Conditions: supporting electrolyte 0.1 M $TBAPF_6$/DCM, glassy carbon working electrode, voltammogram scan rate 50 mV/s. See ESI for all conditions.

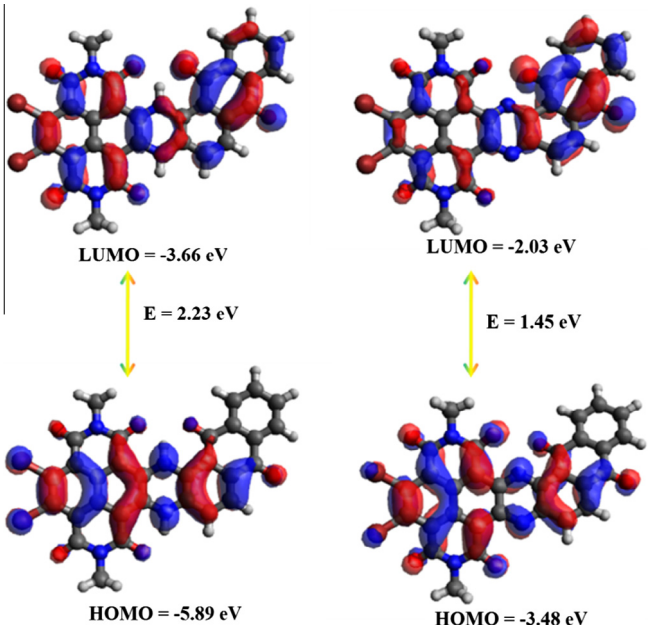



**Figure 6.** HOMO and LUMO orbitals for **NDI-AQ** (left) and deprotonated species (right).

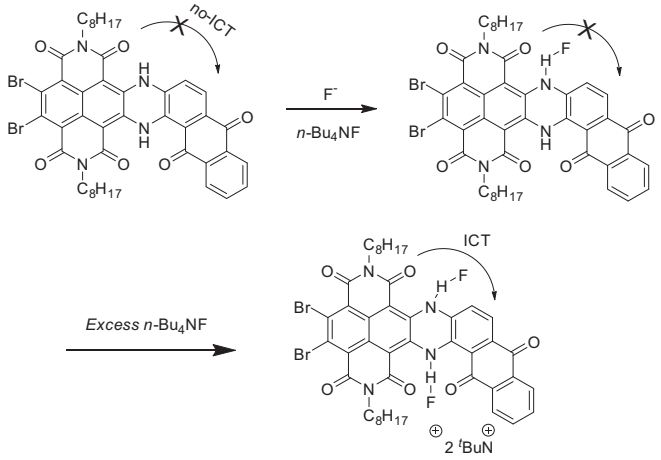



**Figure 7.** Anion sensor structure illustrating the recognition of fluoride via an ICT effect.

ab initio/DFT quantum chemical simulation package to determine the HOMO and LUMO energy differences of the receptor **NDI-AQ** and the corresponding deprotonated species (Fig. 6).[15] The geometry optimization of **NDI-AQ**, **NDI-AQ+F**, **NDI-AQ+2F**, the **NDI-AQ** anion and of **NDI-AQ** dianion molecules with truncated alkyl chains were carried out at the B3LYP/6-311++G** level of theory. The polarizable continuum model (PCM) was employed to investigate the effect of the solvent ($CHCl_3$) on geometries. In order to confirm that the optimization for **NDI-AQ** and its deprotonated species were real structures on the potential energy surface, frequency calculations were also carried out at the same level of theory, and frequencies for all species were found to be positive. Based upon the molecular geometries obtained, the frontier molecular orbitals of all five species were calculated at the same level of theory and pictures generated using Avogadro.[16] For the receptor **NDI-AQ**, the HOMO orbitals were found to be mainly distributed at the NDI along with substituted six membered ring systems and half of the anthraquinone subunit, whereas the LUMO was mostly located on the complete **NDI-AQ** molecular system (Fig. 6). It was observed that the AQ subunit contributed little to the HOMO, but its contribution to the LUMO was greatly increased. This indicated that the electron flow takes place from NDI to AQ in both states, that is, HOMO and LUMO. The HOMO and LUMO pictures of **NDI-AQ** bonded to $F^-$ and deprotonated **NDI-AQ** species are shown in Figure 6 and Figures S5–S8. It was also found that the energy gap between the HOMO and LUMO of the $F^-$ bonded and deprotonated probes of **NDI-AQ** decreases, and became smaller than that of the **NDI-AQ** receptor, which was clearly observed in the voltammograms in Figure 5, where the first cathodic, and first anodic processes was clearly compressed when $F^-$ was added to the solution.

These results clearly support hydrogen bonding interaction between the N–H of the receptor **1**, and the $F^-$ anions, followed by deprotonation of N–H. With excess $F^-$, fluoride ions interact with both the core N–Hs and the induced negative charge is delocalized over the molecule (Fig. 7).

In conclusion, we have reported a near-infrared (NIR) donor–acceptor based sensor, that is, a fluorescent, neutral and selective colorimetric sensor for the fluoride ion. Among the anions tested, **NDI-AQ** showed excellent selectivity for fluoride anion over other anions ($AcO^-$, $HSO_4^-$, $Br^-$, $Cl^-$, $I^-$, $ClO_4^-$, $H_2PO_4^-$ and $NO_3^-$). Sensing of ions via an ICT effect was confirmed via UV–vis, fluorescence, electrochemistry, and DFT calculations. Due to the visible color changes, as well as the appearance of a NIR signal at 790 nm, it is possible to conceive the use of this receptor in various sensing applications, including situations such as anion transport and purification, where the availability of cheap and easy-to-make anion receptors would be advantageous.

## Acknowledgments

S.V.B. (IICT) is grateful for the financial support from the DAE-BRNS (Project Code: 37(2)/14/08/2014-BRNS), Mumbai, and Intelcoat project CSC0114, Council of Scientific and Industrial Research (CSIR), New Delhi, India. S.R.B. acknowledges CSIR, New Delhi, for SRF support. S.V.B. (RMIT) acknowledges the financial support from the Australian Research Council under a Future Fellowship Scheme (FT110100152). A.L.P. acknowledges DST (Project. No. FS/FST/PSI-018/2009) for financial assistance. L.A.J. acknowledges RMIT University for receipt of a Vice Chancellors (Industry) Fellowship.

## Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2015.06.050.

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