



A Dual Colorimetric and Fluorometric Anion Sensor Based on Polymerizable 1, 8-Naphthalimide Dye

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ABSTRACT

A new polymerizable fluorescent sensor based on the photoinduced electron transfer (PET) has been synthesized for the selective determination of fluoride ions in DMF solutions. The sensing system was prepared by incorporating 4-Amino-1,8-naphthalimide derivatives containing thiourea side chain at the amino moiety (AFTN) as a neutral F⁻ selective fluorophore and was characterized by use of the DSC, FTIR, ¹HNMR, ¹³CNMR and elemental analysis. The ability of AFTN to copolymerize with vinyl monomers of styrene by free radical copolymerization was demonstrated in order to design a potential polymer base fluorophore sensor. The selectivity for F⁻ among the halides is attributed mainly to the hydrogen-bond interaction in the receptor with F⁻. The results showed that this fluoroionophore could serve as a novel fluorescent sensor for further application. Prog. Color Colorants Coat. 6(2013), 87-96. © Institute for Color Science and Technology.

1. Introduction

In recent years, the design and development of synthetic receptors and sensors for the detection of anions have received considerable attention [1]. This is due to the important roles played by anions in biology, medicine, catalysis, and the environment. Among those common anions, particular attention has been paid to fluoride ion because of its important role in dental care and clinical treatment of osteoporosis [2]. However, excess fluoride can cause many serious diseases such as gastric and kidney disorders, skeletal fluorosis, which is a type of fluoride toxicity that generally manifests itself clinically in terms of increase in bone density. The diversity of its

function, both beneficial and hazardous, makes the careful control of fluoride levels in the drinking water. Due to high hydration energy of fluoride ion and its ability to abstract proton to form HF²⁻, the presence of even small amount of water becomes detrimental to estimation of fluoride using chemosensor approach [3]. In this regards, the development chemosensor for fluoride anion is of great importance for environment and human health care. Recently, considerable efforts have been devoted to fluoride ion sensing via UV-Vis, fluorescence, or other methods [4]. Among the reported sensors in this regard, fluorescent chemosensors attract particular

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attention because of their high selectivity, sensitivity, and simplicity [5]. Some fluorescent chemosensors for fluoride ion have been reported. These sensors bind F^- through the hydrogen bonds between F^- and hydrogen bonding donors such as (di) amino, amide, carbamides, as well as pyrroles/calixpyrroles, indoles/indolcarbazoles, (thio) urea [6-11]. Incorporation of fluorescent units into the polymer matrix is expected to improve their performance and efficiency of optical sensors. The most important advantage of the functionalized copolymers as a sensor is firmly bonded to the main chain which eliminates any migration from the matrix. Also copolymers containing a fluorescent structural unit have a proper film forming ability, heat-durability, solvent resistance and high fluorescent quantum yields. They have also good photo stability and reasonable transparency with a strong yellow-green fluorescence [12].

Since the relatively strong fluorescence of **AFTN** was observed to quench by the formation of hydrogen bonds with fluoride ions and to confirm the deprotonation interaction between **AFTN** and F^- , the partial 1H NMR spectra of **AFTN** were measured with different amounts of F^- . In this paper a new polymerizable 4-amino-1,8-naphthalimide dye was designed and synthesized based on the photo-induced electron transfer (PET) principles where a fluorophore is connected to a receptor by a short ethylene spacer for fluoride ions sensing. The ability of dye to copolymerize with vinyl monomers of styrene was examined by free radical copolymerization.

2. Experimental

2.1. Materials and Instrumentation

All solvents used in this work were of analytical grade. Reagent grade acenaphthene, allylamine, ethylenediamine, isothiocyanate, commercial styrene (St), Dibenzoyl peroxide (DBP) and chloroform were purchased from Merck chemical company and used as received. UV-Vis spectrophotometric measurements of the dye and its copolymer in DMF solution were performed on a CECIL CE9200 spectrophotometer. All fluorescence measurements were carried out on a Perkin-Elmer, LS 50B luminescence spectrometer. Fluorescence quantum yield was determined based on the absorption and fluorescence spectra, using fluoresceine as reference ($\Phi_{st} = 0.95$) [13]. FTIR spectra were recorded on a SPECTRUM ONE spectrometer using KBr pellets. NMR spectra were recorded with Bruker DRX AVANCE

NMR spectrophotometer on a 500 MHz for proton and 125 MHz for carbon in DMSO, respectively. Molecular weights and polydispersity of synthesized polymer was determined by gel permeation chromatography (GPC) analysis with a Atilent 1100 RI (reflectometer index) PLGell 10 μ m, 300 mm (500 $^\circ$ A, 10 $^\circ$ A, 10 $^\circ$ A in a series) relative to polystyrene standards in chloroform solution. Differential scanning calorimetric (DSC) and Glass transition temperatures (T_g) of the copolymer was performed using Perkin- Elmer- pyris 6 DSC under the nitrogen atmosphere at a heating rate of 10 $^\circ$ C min $^{-1}$.

2.2. Synthesis of AFTN

2.2.1. N-Allyl-4-bromo-1,8-naphthalimide (2).

A mixture of 4-Bromo-1,8-naphthalic anhydride (2.8 g, 0.01 mol) and ethanol (50 mL) were prepared and heated to 55 $^\circ$ C. Then allylamine (0.75 ml, 0.01 mol) was added. The resulting solution was refluxed for 4 hours, after which the solution was collected by suction filtration and washed with distilled water and dried [14]. This gave **2** in 92% (2.91 g) as an off-white powder; mp = 141.46 $^\circ$ C. **FTIR (KBr), ν (cm $^{-1}$):** 3067 (C-H str. aromatic); 2931 (C-H str. aliphatic); 1698, 1662 (C=O str. Carbonyl); 1670 (C=C str. allyl); 1588, 1458 (C=C str. aromatic); 556 (C-Br str). **1H NMR (500 MHz, DMSO-d $_6$):** 8.95 (1H, d, naphthalimide-H5), 8.78 (1H, d, naphthalimide-H7), 8.35 (1H, d, naphthalimide-H2), 7.82 (1H, b s, naphthalimide-NH), 7.87 (1H, t, naphthalimide-H6), 7.84 (1H, d, naphthalimide-H3), 5.91 (1H, m, CH=), 5.07 (2H, =CH $_2$), 4.62 (2H, d, N-CH $_2$). **^{13}C NMR (100 MHz, DMSO-d $_6$):** 164.3, 163.4, 136.3, 135.0, 134.8, 131.6, 130.3, 129.1, 128.0, 126.5, 125.8, 125.0, 122.6, 116.8, and 43.4.

2.2.2. N-Allyl-4-(2-aminoethylene amino)-1,8-naphthalimide (3).

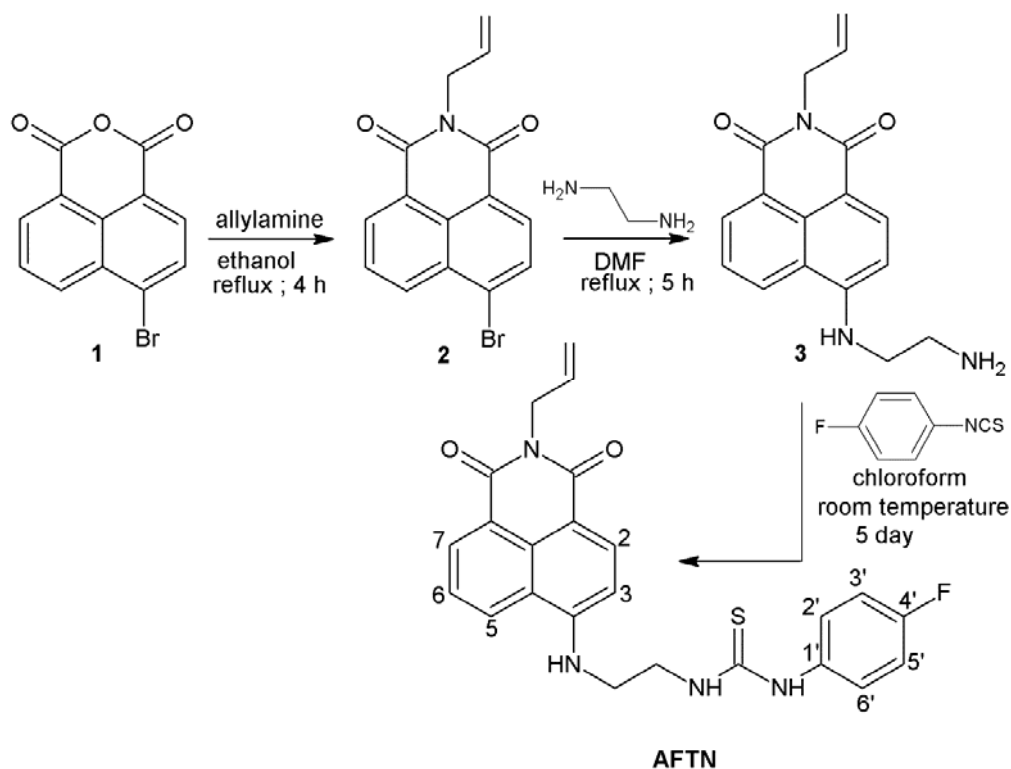
0.1 g $CuSO_4 \cdot 5H_2O$ was added to a solution of ethylenediamine (6.0 ml, 90 mmol) and compound **2** (1.0 g, 3.0 mmol) in 15 ml of DMF. The resulting mixture was then refluxed for 5 h with stirring. After cooling to room temperature, the solution was poured into 100 ml water, and the precipitate was collected by filtration, washed with water and dried [15]. Recrystallized in ethanol to give **3** as yellow-orange crystals in 59% yield (0.55 g), mp = 107.3 $^\circ$ C. **FTIR (KBr), ν (cm $^{-1}$):** 3430 and 3375 (N-H str. first amine); 3057 (C-H str. aromatic); 2931 (C-H str. aliphatic); 1674, 1645 (C=O str. Carbonyl); 1680 (C=C str. allyl); 1585, 1458 (C=C str.

aromatic); 1244 (C-N str.). ¹HNMR (500 MHz, DMSO-d₆): 8.65 (1H, d, naphthalimide-H7), 8.43 (1H, d, naphthalimide-H5), 8.27 (1H, d, naphthalimide-H2), 7.82 (1H, b s, naphthalimide-NH), 7.67 (1H, t, naphthalimide-H6), 6.85 (1H, d, naphthalimide-H3), 5.91 (1H, m, CH=), 5.07 (2H, =CH₂), 4.62 (2H, d, N-CH₂), 3.45 (4H, m, CH₂CH₂NH₂). ¹³CNMR (100 MHz, DMSO-d₆): 164.3, 163.4, 151.4, 135.1, 134.1, 131.6, 130.3, 128.4, 125.2, 122.6, 121.0, 116.8, 108.6, 104.6, 43.4, 42.2, and 36.8.

2.2.3. N-Allyl-4-[2'-(p-fluorobenzylthioureido)-ethylamino]- 1,8-naphthalimide (AFTN).

p-fluorophenyl isothiocyanate 97% (0.05 g, 0.27 mmol) was added to a solution of **3** (0.099 g, 0.27 mmol) in dry DMF (50 mL). The resulting solution was stirred at room temperature for 5 days under nitrogen [11, 16]. The resulting precipitate was collected by vacuum filtration and washed with chloroform to yield the desired product as a yellow-orange solid (0.1 g, 65%) after purification from ethanol. mp 209.93 °C; FTIR (KBr), ν (cm⁻¹):

3337 (N-H str. secondary amine), 2927 (C-H str. aliphatic), 1688 (C=C str. allyl), 1670, 1650 (C=O str. carbonyl), 1586, 1456 (C=C str. aromatic), 1390 (C-F str.), 1368 (C=S str.), 1239 (C-N str.). ¹HNMR(500 MHz, DMSO-d₆): 9.11 (1H, s, CSNH), 8.65 (1H, d, J=8.3 Hz, naphthalimide-H7), 8.43 (1H, d, J=6.7 Hz, naphthalimide-H5), 8.27 (2H, naphthalimide-NH,NHCS), 8.15 (1H, d, J=8.5 Hz, naphthalimide-H2), 7.95 (2H, C6H4), 7.86 (1H, t, J=5.3 Hz, naphthalimide-H6), 7.70 (2H, C6H4), 6.85 (1H, d, J=8.6 Hz, naphthalimide-H3), 5.91 (1H, m, CH=), 5.07 (2H, =CH₂), 4.61 (2H, d, J=5.2 Hz, N-CH₂), 3.45 (4H, m, NCH₂CH₂). ¹³CNMR (125 MHz, DMSO-d₆): 181.0(C=S), 164.3 (C-F), 163.4 (C=O), 162.7 (C=O), 151.4 (naphthalimide, C-4), 135.1 (benzene, C-1), 134.1 (naphthalimide, C-2,7), 131.6 (CH=), 130.3 (benzene, C-3',5'), 129.5 (naphthalimide, C-6), 125.2 (benzene, C-2',6'), 122.6 (naphthalimide, C-8), 121.0 (naphthalimide, C-10), 116.9 (=CH₂), 108.6, 104.6 (naphthalimide, C-3), 43.4, 42.2, 36.9 (CH₂ aliphatic).



Scheme 1: Synthesis of AFTN.

2.3. Synthesis of copolymer St-AFTN

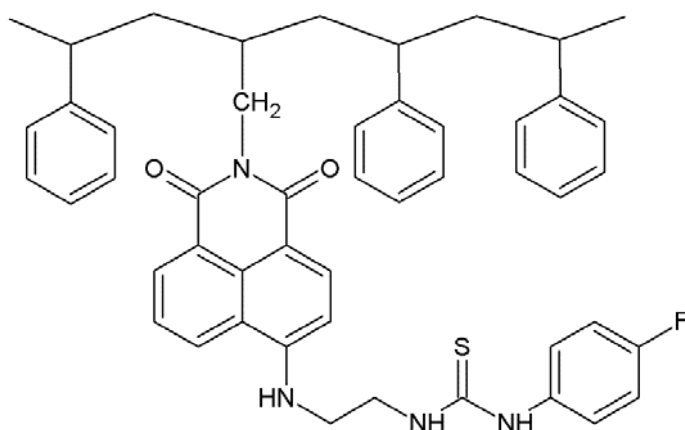
Free radical copolymerization of styrene with AFTN was carried out in bulk (Scheme 2). Styrene (1 g), AFTN (0.01 g) and DBP (0.05 g) were mixed in an ampoule flushed with pure dry nitrogen. The ampoule was sealed and heated at 80 °C in a thermostat for 24 h. The transparent colored polymers obtained were dissolved in chloroform and precipitated with ethanol four times until the filtrate became colorless. The purified polymer was dried under vacuum at 40 °C and analyzed [17,18]. Copolymer (St - AFTN); **T_g**: 78.93 °C, **M_w** = 328570, **M_n** = 143900 and **M_w/M_n** = 2.28, **FTIR (KBr): ν(cm⁻¹)**: 3446 (N-H str. secondary amine), 3060 (C-H str. aromatic), 2921 (C-H str. aliphatic), 1634 (C=O str. carbonyl), 1604, 1489 (C=C str. aromatic), 1446 (C-F str.), 1374 (C=S str.), 1024 (C-N str. amine).

3. Results and discussion

3.1. Design and synthesis of AFTN and its copolymer

The design of AFTN is based on the classical PET principle developed by de Silva [19]. The synthesis of AFTN is shown in scheme 1. For this sensor, the starting point was the N-allyl-4-bromo-1,8-naphthalimide, **2**, which was synthesized by refluxing 6-bromo-1,8-

naphthalic anhydride and allylamine in ethanol, and obtained as an off-white solid in 92% yield after washed with water. The next step was the introduction of ethylene spacer moiety in AFTN. The synthesis of the ethylene moiety **3** was first attempted from ethylenediamine, which would incorporate the spacer as well as the ethylene part of the receptor moiety in one step. This resulted in the formation of the desired product **3** in 59% yields, after precipitation from water and a recrystallization from ethanol. Finally the PET sensor was formed, in a quantitative yield, by a similar nucleophilic displacement of **3** using p-fluorophenyl isothiocyanate at room temperature in dry CHCl₃ followed by precipitation and recrystallization from ethanol, giving the desired product in 65% yield. All the compounds were fully characterized using conventional spectroscopic techniques. Polystyrene is a widely used polymer that it was interesting to study the copolymerization of styrene with the synthesized dye. Experiments for the copolymerization of styrene with AFTN was carried out in bulk with 0.1 wt % of the corresponding dye and 0.5 wt % DBP according to a procedure described elsewhere [16,18]. To confirm polymerizability of dye, we used polystyrene as a transparent polymer and studied its copolymerization with the synthesized dye.



copolymer (St - AFTN)

Scheme 2: Structure of copolymer (St – AFTN).

After the copolymerization of Styrene with **AFTN**, solid and transparent yellow polymer with an intense yellow-green fluorescence was obtained. The polymer was purified after repeated, successive, and selective dissolving and precipitation in proper solvents (CHCl_3 , $\text{CH}_3\text{CH}_2\text{OH}$), and colored copolymer was isolated. Then the copolymer retained its color and/or fluorescence, and this indicated that **AFTN** was chemically bonded to the polymer chain. The difference between dye and its copolymer was determined by FTIR spectroscopy. Their FTIR spectra show considerable difference in the spectral range of $720\text{--}790\text{ cm}^{-1}$, $1600\text{--}1700\text{ cm}^{-1}$ and $3300\text{--}3500\text{ cm}^{-1}$. The out-of-plane bending vibrations of C-H of the dye are observed at 780 and 730 cm^{-1} . The rocking vibrations $(\text{CH}_2)_n$ of polystyrene appears as a doublet in the solid state at 697 and 755 cm^{-1} . The FTIR spectrum of copolymer (St - **AFTN**) indicates the overlapping of these two types of vibration in the studied range. The stretching vibration of C=C of allyl group of the **AFTN** is at 1688 cm^{-1} and this type of vibration disappear in the spectrum of copolymer (St - **AFTN**). Also the bands at 3337 cm^{-1} and 3446 cm^{-1} are assigned to the stretching vibration of NH in the dye

and the copolymer (St - **AFTN**); it is disappeared in polystyrene spectrum (Figure 1).

3.2. Spectroscopic evaluation **AFTN** in the presence of anions group

The luminescent properties of **AFTN** were investigated in acetonitril solution using different anions. The absorption spectrum of **AFTN** in the absence of anions showed two main spectral regions at shorter wavelengths $260\text{--}298\text{ nm}$, assigned to the $\pi\text{--}\pi^*$ transition, and a second region centered at 436 nm ($\epsilon = 15.79 \times 10^3\text{ L M}^{-1}\text{ cm}^{-1}$) assigned to the internal charge transfer (ICT) character of the fluorophore, which arises due to the push-pull nature of the donating amine and the withdrawing diimide [20]. When **AFTN** was titrated with anions, no significant changes were observed using, Cl^- , Br^- , I^- , NO_3^- , HSO_4^- , ClO_4^- and only very minor changes for AcO^- or H_2PO_4^- were observed in the absorption spectra. This is to be expected as the thiourea anion receptor is separated from the fluorophore by the ethylene spacer.

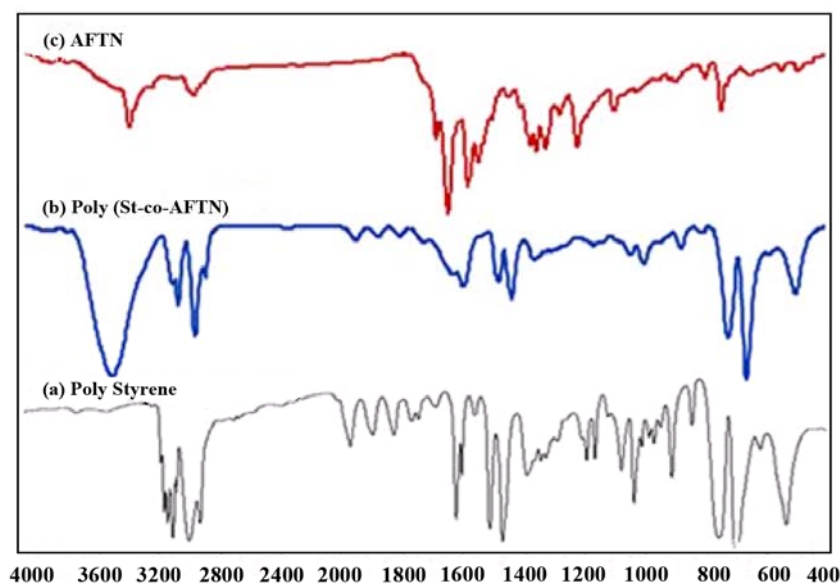


Figure 1: FTIR spectrum of **AFTN**, copolymer (St - **AFTN**) and polystyrene.

Figure 2 showed the absorption spectral changes of compound **AFTN** after addition of various anions, from which a good selectivity of compound **AFTN** toward F^- and AcO^- over other anions was clearly seen.

Upon addition of F^- , the intensity of the band at 538 nm increased at the expense of the 436 nm transition. Furthermore, a new band at 341 nm and two clear isobestic points were observed at 469 and 389 nm, respectively (Figure 3). The yellow to deep purple color change is clearly evident to the naked eye (Figure 4). We propose that these changes are consistent with the anions binding to the thiourea moiety through hydrogen bonding [19-21]. It is also possible that the proton of the 4-amino moiety helps binding the anion

and that these combined binding modes give rise to enhanced ICT character with concomitant color changes [19]. The changes in the 538 nm band of **AFTN** as a function of increasing concentration of F^- (as $-\log[F^-]$) were observed. This is characteristic of 1:1 binding and simple equilibrium. The thiourea functional group is essential to successful anion sensing and consequent color changes. However, it is worth noting that at higher F^- concentrations there were distinctive changes in the absorption spectra that we assign to the deprotonation of the 4-aminonaphthalimide moiety and the formation of bifluoride (HF_2^-) [22].

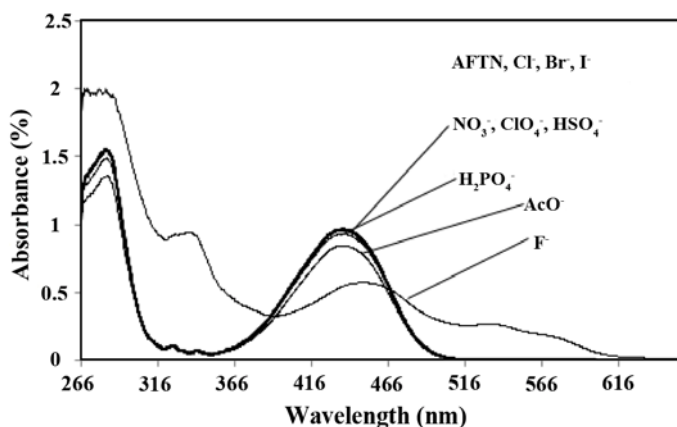


Figure 2: The absorption spectral changes of compound **AFTN** (5.0×10^{-5} M) after addition of various anions.

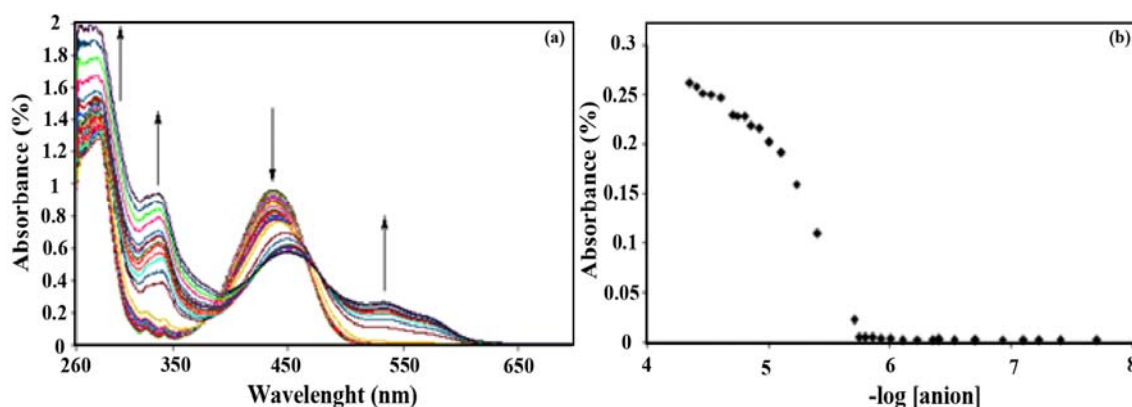


Figure 3. Left (a): The absorption spectra of **AFTN** change upon addition of F^- in DMF solution Right(b): shows the changes at 538 nm as a function of $-\log[\text{anion}]$: F^- .

The most important result from our current study is that upon addition of anions such as F^- , the emission of **AFTN** (5.0×10^{-5} M) was substantially reduced in intensity. The mechanism for this quenching is via PET, which takes place between the receptor and the fluorophore. Unlike many PET sensors for cations, the fluorescence of **AFTN** is “switched off” rather than “switched on” upon ion recognition [16].

Figure 5 shows fluorescence changes of dye **AFTN** after addition of various anions. Addition of anions such as Cl^- , Br^- , I^- , NO_3^- , HSO_4^- and ClO_4^- to **AFTN** in acetonitrile only caused very slight fluorescence changes, however, considerable fluorescence quenching was observed for F^- and AcO^- under the same condition [23].

The result shows that this quenching process is due to the following mechanism; prior to the recognition

process, the excited state of the fluorophore is not, or only to a minor extent, quenched by electron transfer from the receptor to the fluorophore. However, after the addition of the anion, and the formation of the anion-receptor hydrogen bonding complex, the reduction potential of the receptor is increased, making the electron transfer more feasible. This subsequently gives rise to enhanced fluorescence quenching [24]. This is clearly demonstrated in Figure 6 for the addition of F^- to **AFTN** in DMF. Here the fluorescence emission of **AFTN** is effectively quenched or completely “switched off” after the addition of 80 mM of F^- . Addition of MeOH (ca. 10% v/v) to this solution “re-switched on” the emission, demonstrating that the process was fully reversible, i.e. the hydrogen bonding interactions were broken [25].



Figure 4: The yellow to deep purple color of **AFTN** change upon titration with F^- .

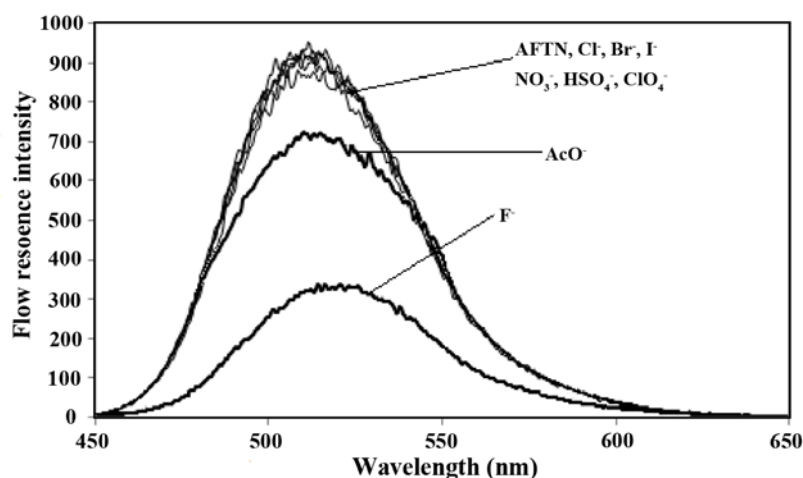


Figure 5: The fluorescence changes of **AFTN** after addition of various anions.

3.3. ^1H NMR Study of AFTN in the presence of anions group

The binding of AFTN to a series of anions was investigated by monitoring the changes in the ^1H NMR spectra of DMSO- d_6 solutions of AFTN upon addition

of F^- , Cl^- , Br^- and I^- . However, the additions of either I^- , Br^- and Cl^- afforded only minor changes in the ^1H NMR spectrum and we concluded that very weak, if any, binding of these anions occurred.

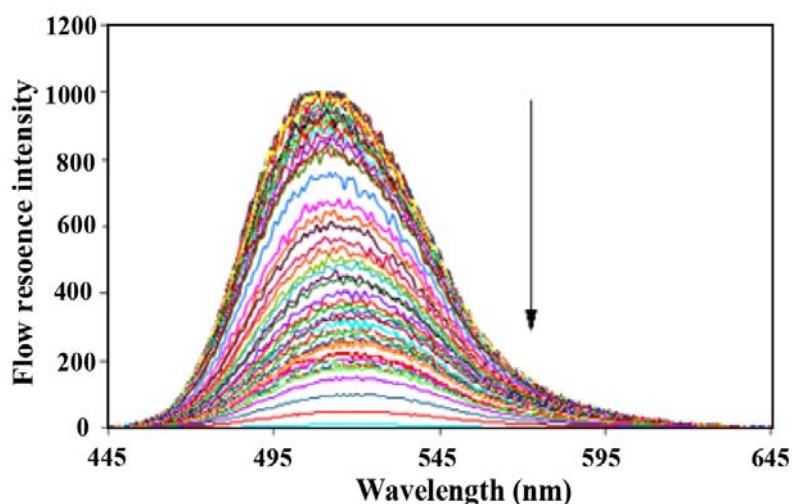


Figure 6: The changes in the fluorescence emission spectrum of AFTN upon titration with F^- , showing the quenching by enhanced PET from the fluoride bound receptor.

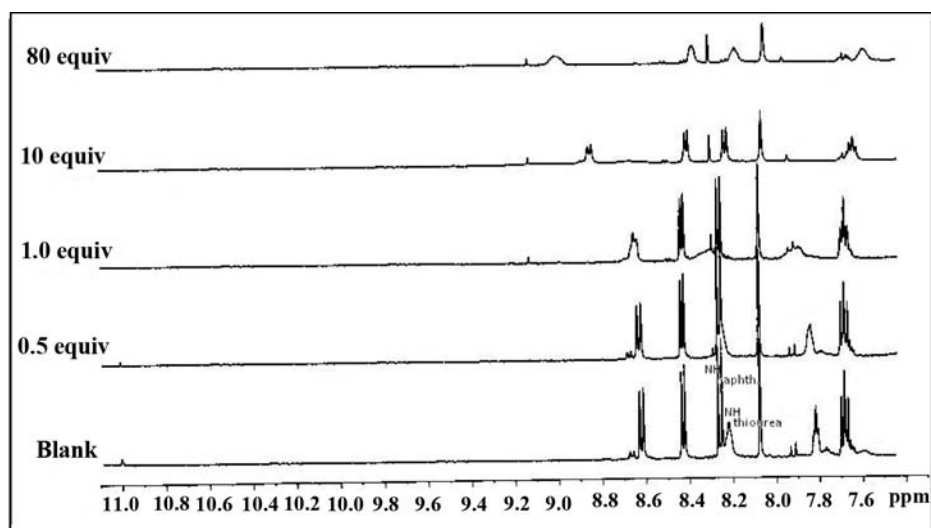


Figure 7: ^1H NMR spectra of sensor AFTN in DMSO- d_6 in the presence of F^- .

In the case of F⁻, however, the naphthalimide N–H signal became significantly broadened after the addition of only small quantities of the anion and completely disappeared after the addition of only 1.0 equiv. While 1.0 equivalent of F⁻ was added to the solution of compound **AFTN** in DMSO-d₆, the signals of 4- amino NH proton and thiourea protons were respectively shifted from 8.27 to 8.67 ppm and from 8.27 to 9.18ppm, and the other thiourea protons completely disappeared. After another one equivalent of F⁻ was added, the signal of 4- amino NH proton further downfield shifted from 8.30 to 9.10 ppm along with a great broadening, and the thiourea NH signals completely disappeared. Concomitant with this disappearance was a distinct, visible color change from fluorescent yellow/green to deep red/ purple [10]. In contrast, the other protons of the naphthalimide ring underwent an up field shift (0.10 ppm) due to the effect of through bond propagation. The significant changes of chemical shifts attributed to 4-amino NH and thiourea NH showed that multiple hydrogen bonding interactions were responsible for the binding of F⁻[24]. Figure 7 shows the stack plot of ¹HNMR spectra (in DMSO-d₆) of **AFTN** after addition of various quantities of F⁻.

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4. Conclusions

The synthesis of new polymerizable fluorescent PET sensor (**AFTN**) for the sensing of F⁻ has been achieved in a few steps and in good yields. We have demonstrated that this sensor show ideal PET behavior for F⁻, where the absorption spectra do not change to any significant degree upon binding to the ion. In contrast, the emission spectra changed dramatically; being quenched or ‘switched off’ significantly for this sensor. Importantly, **AFTN** show high selectivity for F⁻ ions, even in the presence of other halide ions. To have structural insight into to the receptor-anion effect, the interaction of **AFTN** with fluoride anions by the ¹HNMR spectroscopy titration method. To the best of our knowledge this is the first examples of such polymerizable PET sensor for F⁻ that give rise to high selectivity for F⁻.

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