ORIGINAL PAPER

The First Bifluoride Sensor Based on Fluorescent Enhancement

Kaku Dutta · Ramesh Ch. Deka · Diganta Kumar Das

Abstract The first fluorescent sensor for HF_2^- anion, N^1, N^3-di(naphthalene-1-yl)isophthalamide **(L)** has been derived from α-Naphthylamine and isopthaloyl chloride. In 1:1 (v/v) $DMSO:H_2O$, **L** exhibits high selectivity towards HF_2^- anion with a 4-fold enhancement in fluorescent intensity. Very little enhancement in fluorescence intensity is observed for F^-, Cl^-, Br^-, I^-, SCN^-, PO_4^{3-}, SO_4^{2-}, and CH_3COO^- anions. The stoichiometry interaction between **L** and HF_2^- is found to be 1:1 from fluorescence and UV/Visible spectral data. DFT calculation shows that binding between HF_2^- and **L** is 1:1 and increases the relative planarity between the two naphthyl rings causing fluorescence enhancement. A shift of 0.080 V in oxidation potential of **L** is observed on interaction with HF_2^- by cyclic voltammetry and square wave voltammetry.

Keywords Bifluoride · Fluorescence · Sensor · Voltammetry · DFT

Introduction

Anions play important role in biological as well as industrial processes and hence designing of anion sensors has been of great interest to chemists for many years [1, 2]. Designing anion sensor is also a challenging task in supramolecular and biological chemistry [3, 4]. Fluorescence anion sensing has been widely used in recent times due to its simplicity and low detection limit [5]. Generally the sensors possess suitable anion binding sites such as amine, guanidinium, amide groups or involve the covalent linking of an optical-signaling chromophoric fragment to a neutral anion receptor. The receptor may contain subunits like urea, thiourea, amide, phenol, pyrrole etc. which can provide one or more H-bond donor sites for selective binding and sensing of anions [4, 6–8]. The chromophores are generally indoles [9], bisindole [10], carbazole [11], nitrophenyl [12], quinine [13, 14], and nitrobenzene/azo groups [15] and other electron-withdrawing moieties [16] covalently attached to an anion receptor. Napthalene derived chromophoric supramolecular materials have found utmost utility amongst anion sensors because of their spectroscopic and electrochemical properties [17–20].

The hydrogen bifluoride anion, HF_2^-, is of significant structural and theoretical interest. It is a classic example of semi-ionic, three-center, four-electron bonding and exhibits the strongest known hydrogen bonds [21]. HF_2^- is used in insecticides [22], etching borosilicate glasses [23], fluorescence detection of beryllium in occupational hygiene samples [24], synthesising borane derivatives [25], understanding supramolecular interaction [26], preparation of molten salts [27] etc.. Interestingly there has not been any report on fluorescence or/and electrochemical detection of HF_2^- anion.

In this paper we report a novel sensor N^1,N^3-di(naphthalen-1-yl)isophthalamide (L), synthesized from α-Napthylamine and isopthaloyl chloride for sensing bifluoride anion (HF_2^-). In 1:1 (v/v) $DMSO:H_2O$ solution **L** showed 4-fold increase in fluorescence intensity upon binding HF_2^- anion. The interaction between **L** and HF_2^- was also confirmed by electrochemical studies and DFT calculations.

Experimental Section

Chemicals and Spectroscopic Measurements

All the chemicals were purchased from Merck (all halides are ammonium salts). The metal salts were

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recrystallized from water (Millipore) and their solutions (10^{-4} M) in aqueous medium were prepared. A 10^{-4} M solution of L in 1:1 (v/v) DMSO:H_2O (phosphate buffer solution, pH 7.0) was used in these experiments. Fluorescence experiments were performed on a Hitachi F-2500 spectrophotometer at room temperature using quartz cuvette.

The UV/Visible spectrum was recorded on a Shimadzu UV/Vis -1800 spectrophotometer. ^1H NMR spectra were recorded using a Bruker Ultrashield 300 MHz NMR spectrometer in room temperature. Chemical shifts are expressed in ppm (in DMSO-d6, with TMS as internal standard) and coupling constants (J) in Hz. ^1H NMR of **L** in d^6 DMSO showed peaks at δ values (ppm) 6.576, 7.576, 7.769, 7.791, 7.875 and 7.899 due to CH of 1-Napthalene; at 8.798 due to –NH of secondary amide; at 8.322, 8.156, 8.06 and 7.992 due to CH of 1- Benzene (Fig. 7).

FTIR data were measured on a KBr pallet, using a Perkin Elmer spectrophotometer (RX1). FTIR spectra of **L** showed the peak for $\nu_{C=O}$ stretching at 1,650 cm^{-1}, peak for ν_{N-H} stretching at 3,405 cm^{-1}, peak for $\nu_{aromatic\ C-H}$ stretching at 3,203 cm^{-1} and 3,006 cm^{-1} and peak for ν_{C-C} stretching at 1,535 and 1,596 cm^{-1}.

Electrochemical experiments were carried out at room temperature using CHI 600B Electrochemical Analyzer (USA) in a conventional three electrode system with Ag/AgCl (3 M KCl) as the reference electrode, a platinum wire as the counter electrode and a glassy carbon disc (GC) as working electrode. Tetrabutylammonium perchlorate (0.1 M) solution was used as supporting electrolyte. Nitrogen gas was purged through the electrolytic solution for at least 5 min to remove any dissolved oxygen before every experiment. Nitrogen atmosphere was maintained over the electrolytic solutions during each experiment. Prior to every experiment the GC electrode was cleaned as reported [28].

Synthesis of N^1,N^3-di(Naphthalen-1-yl)Isophthalamide (L)

L (Scheme 1) was prepared by dissolving 4 mM (0.57 g) of α-Naphthylamine in 30 mL DCM. 2 mL triethylamine was added to the above solution and stirred for 15 min at 0 °C. Then 2 mM (0.30 g) of isopthaloyl chloride was added to the solution and stirred for another half an hour at 0 °C to get solid product. The product obtained was filtered, dried and washed with 2 % HCl water to convert the excess triethylamine into its hydrochloride salt. Triethylamine hydrochloride salt was removed by washing with water. The light pink amorphous product obtained was dried. Yield, 68.9 %; melting point, 90 °C; solubility, DMSO.
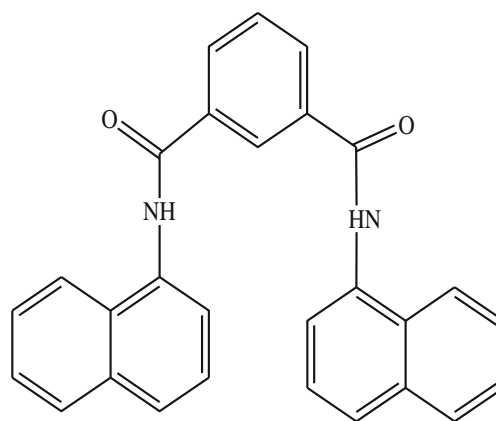
Scheme 1 N^1,N^3-di(naphthalen-1-yl)isophthalamide

Results and Discussion

L in 1:1 (v/v) DMSO:H_2O solution showed fluorescence emission spectra in the range 300 nm to 650 nm with λ_{max} at 430 nm when excited with 255 nm photons. The effect of the anions HF_2^-, F^-, Cl^-, Br^-, I^-, SCN^-, PO_4^{3-}, SO_4^{2-}, and CH_3COO^- on the fluorescence intensity of **L** in 1:1 (v/v) DMSO:H_2O solution was investigated. A steady and smooth enhancement in fluorescence intensity of **L** was observed on addition of HF_2^- anion (from 0.99×10^{-4} M to 14.0×10^{-4} M) which saturates at 1.0 equivalent concentration (Fig. 1). A red shift of λ_{max} was also observed from 430 nm to 450 nm. The overall enhancement in fluorescence intensity was found to be 4 fold at saturation to that of fluorescence intensity when no HF_2^- anion was added. The plot of I/I_o where I is the intensity at a given concentration of HF_2^- anion and I_o is the intensity at zero HF_2^- anion concentration was found to increase linearly with HF_2^- anion concentration till the
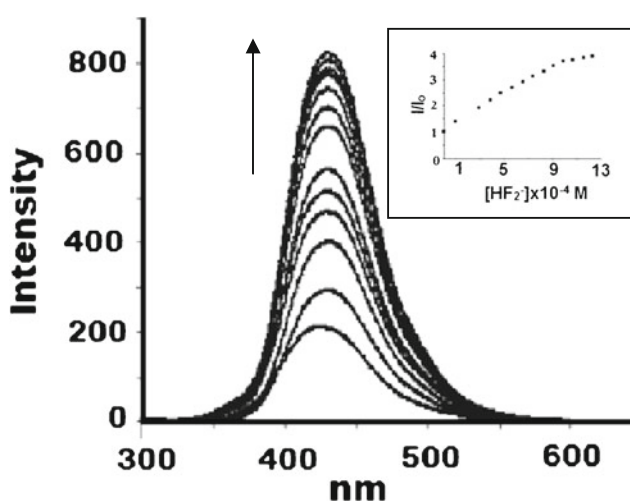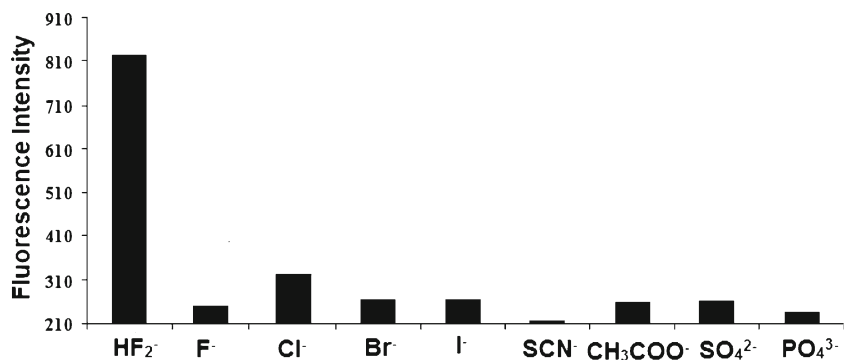
Fig. 1 Changes in fluorescence spectra of **L** as a function of added HF_2^- anion concentration in 1:1 (v/v) DMSO: H_2O solution ($\lambda_{ex}=$ 255 nm; $\lambda_{emi}=300–650$ nm; Inset: Plot of I/Io as a function of HF_2^- anion concentration)

Fig. 2 Bar diagram showing change in fluorescence intensity of **L** upon addition of 1equivalent (14×10^{-4}M) of various anions in 1:1 DMSO: H$_2$O

concentration of HF$_2^-$ anion became 12×10^{-4}M concentration (inset of Fig. 1) and remained constant thereafter.

Figure 2 is the bar diagram profile of the effect of different anions at 14.0×10^{-4}M concentration on the fluorescence intensity of **L**. From the figure it is clear that fluorescence intensity enhancement is much higher for interaction between **L** and HF$_2^-$ anion compared to the other anions. Further we recorded the fluorescence intensity of **L** as a function of HF$_2^-$ anion with all the other anions present in the solution at a concentration of 0.01 M each. A fourfold enhancement in fluorescence intensity was observed at 1:1 concentration ratio of **L** and HF$_2^-$. This proves that **L** has much higher affinity towards HF$_2^-$ compared to the other anions.

To calculate the binding constant and the stoichiometry of binding, $\log[(I-I_o)/(I_{max}-I)]$ was plotted against $\log[HF_2^-]$ where I is the fluorescence intensity of L at $\lambda_{max}=430$ nm for a given added concentration of HF$_2^-$, I$_o$ is the fluorescence intensity of **L** when no HF$_2^-$ was added and I$_{max}$ is the maximum fluorescence intensity at saturated concentration of HF$_2^-$. The plot was found to be linear and has been shown in Fig. 3. A least squares fitting of data yielded the slope as 1.044 indicating a 1:1 binding between **L** and HF$_2^-$. The binding constant was calculated to be log β=3.43 [29].

In order to confirm the binding stoichiometry of HF$_2^-$ with L and the binding constant, the UV/Visible spectra of **L** was recorded at different added concentration of HF$_2^-$ anion (Fig. 4). The UV/Visible spectra of **L**, in absence of HF$_2^-$
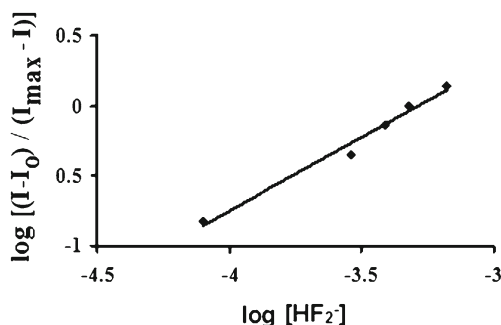
anion, showed a peak at λ_{max} value 420 nm. Addition of HF$_2^-$ anion found to decrease the absorbance of the 420 nm peak. The absorbance at 420 nm was recorded as a function of HF$_2^-$ anion concentration. The plot of $\log[(A_o-A_s)/(A_s-A_\infty)]$ versus $\log[HF_2^-]$ was found to be linear (Inset of Fig. 4). Where A$_o$ is the absorbance of **L** at zero HF$_2^-$ anion concentration, A$_s$ is the absorbance at intermediate HF$_2^-$ anion concentration, A$_\infty$ is the absorbance at saturated HF$_2^-$ anion concentration. The least squares fitting of data shows that the slope is 1.17 confirming 1:1 stoichiometric binding between **L** and HF$_2^-$ which is in agreement with that obtained from fluorescence data. A$_\infty$ was determined from the intercept of the plot of $1/(A_o - A_s)$ versus $1/[HF_2^-]$. The binding constant was calculated and found to be log β= 3.58 which is close to that obtained from fluorescence data [29].

It is already known that if analyte binding brings a molecule to more planarity the fluorescence intensity of the molecule enhances [30]. Therefore to know whether the interaction of HF$_2^-$ with **L** has any effect on the relative planarity of the two naphthalene rings on **L**, we carried out
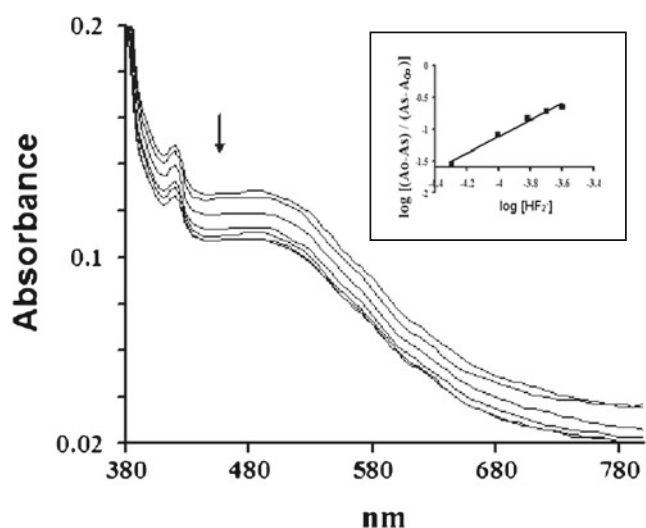

Fig. 3 Plot of $\log[(I - I_o)/(I_{max}-I)]$ versus $\log[HF_2^-]$ for fluorescence titration of **L** against HF$_2^-$ ion in 1:1 DMSO: H$_2$O

Fig. 4 UV/Visible spectral titration of **L** against HF$_2^-$ anion in 1:1 (v/v) DMSO: H$_2$O. (Inset: Plot of $\log[(A_o-A_s/A_s-A_\infty)]$ as a function of log $[HF_2^-]$)

density functional theory (DFT) calculations. DFT calculations were carried out using BLYP functional and DNP basis set. Several initial structures were generated using Materials Studio software and the most stable structures of **L** and **L**.HF_2^- were considered for DFT calculations. Vibrational calculations were also performed to confirm stability of **L** and **L**.HF_2^- and no imaginary vibrational frequency was found confirming that they are stable structures on the potential energy surface. The optimized structures of **L** and **L**.HF_2^- are shown in Fig. 5. The dihedral angles between the two naphthalene rings are calculated for both **L** and **L**.HF_2^- and they are found to be 63^0 and 45^0, respectively in complex **L** and **L**.HF_2^-. Our DFT results indicate that addition of HF_2^- species in **L** reduces the dihedral angle bringing it to more planarity.

Existence of a number of twisted conformations in a molecule can lead to fluorescence quenching due to redistribution of internal energy among the conformations [31, 32]. **L** can posses such conformational structures due to rotation around C-N bonds. According to our DFT calculation HF_2^- fits well into the space between the two N atoms and interacts with H bound to N through hydrogen bonding. This is likely to increase the energy barrier between the different conformational barriers increasing stability of photoexcited states and enhancing fluorescence.

The interaction between **L** and HF_2^- anion was also investigated by electrochemical studies. Cyclic voltammogram of **L**

$(10^{-4}M)$ in 1:1 DMSO:H_2O at GC electrode and Ag-AgCl as the reference was found to be irreversible with an oxidation peak at 0.830 ± 0.005 V at scan rate 0.09 Vs^{-1}. The current of the peak was found to increase linearly with square root of scan rates indicating a diffusion controlled process. Addition of aqueous solution of HF_2^- anion into the electrolytic medium found to shift the oxidation peak of **L,** in negative direction, to 0.750 ± 0.005 V at HF_2^- anion concentration 0.74 mM (Fig. 6a). The plot of redox potential versus concentration of HF_2^- anion profile was linear. The results obtained by cyclic voltammetry experiments were confirmed by square wave voltammetry experiments. Figure 6b shows square wave voltammogram of **L** at zero and 0.74 mM concentration of HF_2^- and the redox potential values obtained were in good agreement with that obtained by cyclic voltammetry. The plot of redox potential versus HF_2^- anion concentration is found to be linear. Cyclic voltammogram and square wave voltammogram of **L** was also recorded in presence of 1.0 mM, F^-, Cl^-, Br^-, I^-, SCN^-, PO_4^{3-}, SO_4^{2-}, or CH_3COO^- anions alone or together but no significant effect in either the cyclic voltammogram or square wave voltammogram was observed.

^{1}H NMR data supports the theoretical results. Figure 7 compares the ^{1}H NMR spectra of **L** in absence and in presence of HF_2^- anion in d^6 DMSO. The peak at δ value 8.798 ppm which is due to –NH proton of **L** becomes a

Fig. 5 The optimized structures of **L** and **L**.HF_2^- obtained from DFT Calculations which indicates that addition of HF_2^- species in **L** reduces the dihedral angle (from 63^0 to 45^0) bringing it to more planarity
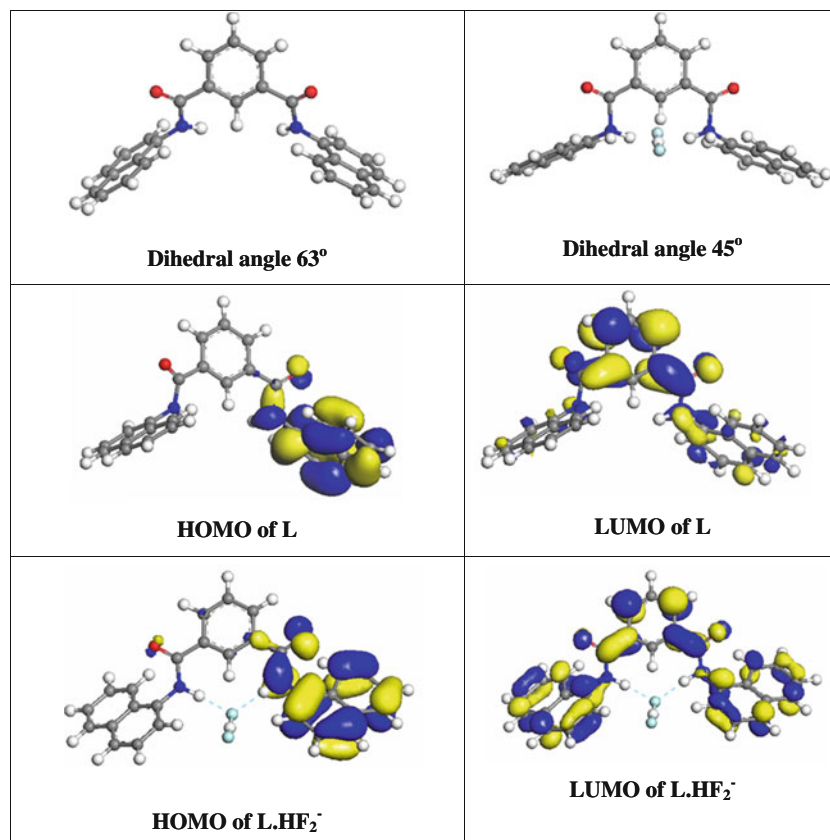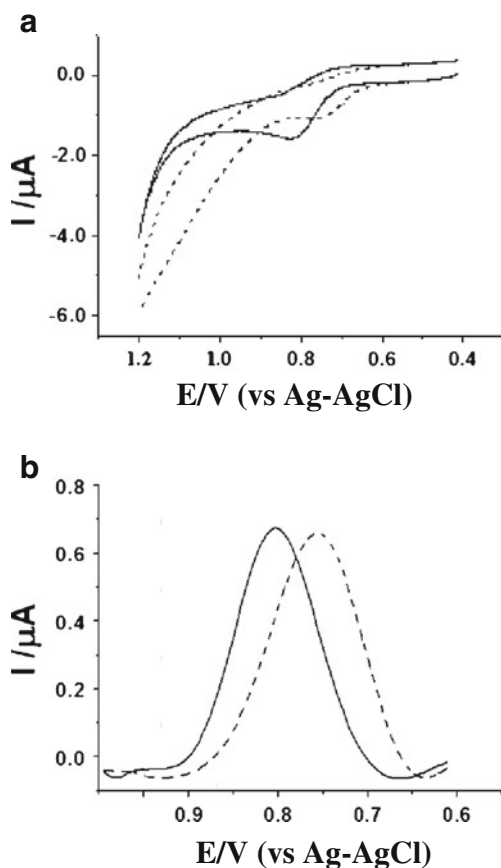
Fig. 6 Cyclic voltammetric (**a**) and Square Wave voltammetric (**b**) response of **L** (10^{-4}M) in 1:1 (v/v) DMSO:H_2O in presence of 0 mM HF_2^- (——) and 0.74 mM HF_2^- (-----) at scan rate 0.09 Vs^{-1}
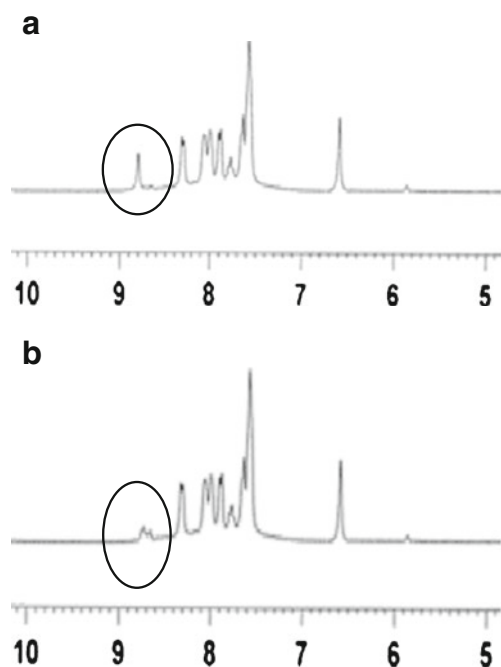
Fig. 7 a ^{1}H NMR spectra of **L** in d^6 DMSO; **b** ^{1}H NMR spectra of **L** in presence of HF_2^- anion in d^6 DMSO

doublet on interaction with HF_2^- ion. In **L**.HF_2^-, the anion interaction causes a small difference in the relative orientation of the two NH protons and hence the doublet results.

Conclusion

In summary, we have shown that the prepared sensor **L** acts as a fluorescent sensor for HF_2^- anion in aqueous medium by switch "on" mode. A host of anions F^-, Cl^-, Br^-, I^-, SCN^-, PO_4^{3-}, SO_4^{2-}, and CH_3COO^- has no interfering effect. The interaction between **L** and HF_2^- anion is further confirmed by ^{1}H NMR data, electrochemistry and DFT calculations.

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