Short Communication

Synthesis of fluorescent di-dansyl substituted ethoxy compound: A selective sensor for antimony and thallium metals detection

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\textbf{A B S T R A C T}

Fluorescence assays have been widely engaged to assess the affinity of metallic ions. Dansyl chloride or 5-(dimethyl amino)-naphthalene-1-sulfonyl chloride is considered to be the reagent having potential to react with amino groups to yield stable sulfonamide adducts. A fluorescent sensor associated with crown ether moiety could have a potential to be developed as metal ions radar; cations, anions and other biological moieties. This can be further employed to observe relevant biotic processes. The reaction of dansyl sulfonyl chloride with di-ethoxy amine 1 chain in presence of potassium carbonate base resulted in a formation of compound 2. No change was observed on addition of aliquots of anions with compound 2. However, cation binding studies was performed using the series of metallic cations of constant concentration and its influence on a series of cations has been monitored using fluorescence spectrometry. This has been recorded that highest quenching effect was observed for antimony (Sb) and thallium (Tl) while other anions and cations were having no effect. The fluorescent compound 2 was further confirmed with proton-nuclear magnetic resonance (\textsuperscript{1}H NMR) spectroscopy, \textsuperscript{13}C NMR spectroscopy and ultra violet spectroscopy. It has been concluded that compound 2 is very much selective for the detection of toxic metals like antimony (Sb) and thallium (Tl) even at parts per billion (ppb) levels. This study could be considered as a contemporary development in design and applications of fluorescent investigations containing crown ethers.

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1. Introduction

A fluorochrome (fluorophore) is a fluorescent chemical material that can re-emit light on excitation. Fluorophores mainly contain cyclic, planar or groups of aromatic compounds containing conjugated π-bond in a system. The fluorescent compounds are mainly based on ‘Donor and Acceptor’ moieties or a bridge (spacer) is used in between to connect them [1,2]. These fluorescent compounds have advantages over non-fluorescent due to their low cost, selectivity, sensitivity, easy detection, selective recognition from a bulk solution and wide range to cover in UV–visible spectrum region. Such fluorescent mechanism can be explained due to photo-induced electron transfer (PET), photo-induced charge transfer (PCT) and excimer formation. The selective recognition of cations, anions and neutral molecules is an important area of research, which has wide applications in biology, environment and industries. There is great need to design cation based sensors for the application in industries, biological samples and while anions are ubiquitous in biological environment. Extraction of precious and toxic metals is two important perspectives of research to be explored with simple, cost effective and rapid detection using fluorescent moieties [3–5]. Dansyl fluorophore have also been used along with other groups due to their selective recognition of metal cations, toxic metals like mercury [6–8], lead [9,10], copper [11–15], zinc [12], cyanide [16] and halogen anions [17,18]. Most of these transition metal cations are known to be hazardous pollutants with toxic effects for the living organisms in the environmental system. The antimony (Sb), thorium (Th) and selenium (Se) are classed as toxic metals for aqueous environment and their excessive presence in an occupational work place causes severe health hazards [19]. The selenium toxicity is an environmental concern because of bioaccumulation attributable to industrial refining, petroleum and irrigation of slenoforous soil and the presence of selenium (Se) in lakes causes’ great harm to the aquatic living organisms [20]. Talanov group has published calixarene based Fluorescent molecules for selective extraction of toxic metal Mercury ion (Hg²⁺) in acetonitrile solution and others [21].

The lead (Pb) based chemical sensors were developed on Calix[4]arene dansyl moieties [22] while Ummuhan has reported series of selective extraction of cations using benzyl substituted dansyl calix[4]arenes and its un-substituted one [23]. Steed group has described the effect of intramolecular hydrogen bonding of dansyl substituted calix[4]arene and their further effects on addition of spherical halogen, y-shaped anions and also their single crystal structures [17]. The remarkable early work of Pederson further followed by Lehn and Izzat’s crown ether macrocycles were well known for the selective recognition of cations [24–26]. The factors which affect the cation binding/recognition are the size and type of the cation, cation cavity match, the type of donors present in the crown ether and the crown properties [27]. The objective of this study is to design fluorescent donor with ethoxy chain through amide linkage for having selectivity for toxic metals.

2. Material and methods

All the chemicals, solvents and metal perchlorates (vacuum dried over blue silica gel) were of highest quality available. ¹H NMR spectra were recorded on a Varian 400 spectrometer, using CDCl₃ with TMS as the internal reference. IR spectra were recorded on a Perkin-Elmer FTIR spectrometer frontier model 2010. The absorption spectra of the solution were recorded using spectro 210 plus manufactured by Analytica Jena. A photon Technologies International Quanta Mater Spectrofluorimeter (model QM-4/2006) was used for all the fluorescence measurements.

Ligand 1 (Fig. 1) was synthesized by Pederson’s synthetic procedure [23] and compound 1 (1.40 ml, 6.74 mmol) of diamine was further dissolved in dry acetone and purged under nitrogen atmosphere in a Schlenk system connected to a vacuum line. A solution of dansyl sulfonyl chloride (0.700 g, 2.58 mmol) and potassium carbonate (0.700 g, 6.50 mmol) was mixed together with in 10 ml of acetone and stirred at room temperature for 2 h of reaction mixture as reported earlier [17]. The reaction mixture was monitored using thin layer chromatography and product was eluted in petroleum ether and chloroform fraction leaving for a longer time. The crude product was washed with slight amount of ether, petroleum ether, to remove the unwanted impurities and dried in an oven. Absorption spectra of the ligand 2 with a concentration of 2.032 × 10⁻⁶ M in ethanol:water (1:1, v/v) containing 10 M equivalents of appropriate metal perchlorate salt were measured using 1 cm absorption cell. Fluorescence spectra of the constant ligand solutions of 2.032 × 10⁻⁶ M were measured in 1 cm quartz cell. Excitation wavelength was 345 nm. Fluorescence emission spectra were recorded in the range 360–800 nm with silt width 1.0 nm. Fluorescence spectrophotometric titration measurements were recorded on addition of perchlorates

![Fig. 1 – Structures of synthetic compounds 1 and 2.](image-url)
of metal cations and anions having the fixed constant concentration of $(2.032 \times 10^{-5}$ M). The stoichiometry of the complexes was determined by using the molar-ratio method. The stability constant was calculated according to the procedure described in literature [28].

### 3. Results and discussion

The simple reaction of ethoxy amine with dansyl sulfonyl chloride in presence of potassium carbonate base resulted in the formation of fluorescent compound 2 that was confirmed with the help of thin layer chromatography (TLC). The crude product was showing green fluorescent under UV–visible light at 365 nm and washed small amount of petroleum ether and ether solvent to remove the excess of impurities from product. The proton NMR and carbon NMR have shown spectrum with characteristic peaks: $^1$H NMR (400 MHz, CDCl$_3$), 1.60 (t, 4H, OCH$_2$), 2.90 (s, 12H, NCH$_3$), 2.95 (m, 4H, OCH$_2$), 3.60 (m, 4H, OCH$_2$), 3.70 (m, 4H, OCH$_2$), 3.80 (m, 4H, OCH$_2$), 5.80 (Br, 2H, NH), 7.00 (t, 2H, Napth), 7.35 (m, 4H, Napth), 8.20 (d, 2H, Napth), 8.30 (d, 2H, Napth), 8.5 (d, 2H, Napth); $^{13}$C NMR [22] (400 MHz, CDCl$_3$): 28.90, 29.03, 32.11, 38. 9, 39.04, 40.90, 45.23, 68.81, 69.14, 69.8, 69.9, 70.2, 70.3, 114.93, 119.1, 119.2, 123.02, 127.9, 128.9, 130, 135.33, and 152] of N substituted dimethyl at 2.90, amide NH proton at 5.80, series of naphthalene region from 7.00 to 8.50 and as usual ethoxy region is covered in the area of 1.60–3.80 ppm. The presence of amide linkage, lone pair on nitrogen attached with naphthalene ring, electron withdrawing nature of sulfonyl moiety, amide linkage bond and ethoxy chain in fluorescent compound 2 was making an interested fluorescent ligand to study for cation and anion binding studies. Our proposed study is to follow systematic understanding of metal:ligand complexation studies using ultra violet and fluorescence spectrophotometry. The concentration of anion, cations were constant $(2.032 \times 10^{-5}$ M) and ligand 2 $(2.032 \times 10^{-6}$ M) in all fluorescence spectrophotometric titrations. The absorption spectra of the ligand in ethanol:water system (1:1, v/v) display strong π–π* absorption bands at 222, 254 and 340 nm having absorption 2.5, 1.64 and 0.57, respectively; which are characteristic peaks of naphthalene and sulfonamide. The absorption coefficients are 2492, 1612 and 558 cm$^{-1}$ M$^{-1}$ in these wavelengths, respectively (Fig. 2).

Fluorescence spectra of the ligand were recorded in ethanol:water system (1:1) and excited at 345 nm that show characteristic emission wavelength 525 nm that is the typical peak of dansyl fluorophore. In order to search selectivity and sensitivity of ligand to metal, we have recorded its influence against many anions and cations of alkali, alkaline earth metals, transition metals, metalloids and non-metalloids and anions. The ligand was titrated with series of anions like fluoride ($F^-$), chloride ($Cl^-$), bromide ($Br^-$), iodide ($I^-$), hydrogen carbonate ($HCO$_3^-$), hydrogen sulfate ($HSO$_4^-$), sulfate ($SO$_4^{2-}$), acetate ($OAC^-$), nitrate ($NO$_3$), nitrite ($NO$_2$), phosphate ($PO$_4^{3-}$) and oxalate ($C$_2$O$_4^{2-}$) and no change was observed on addition aliquots of anions. In search of compatible anions, we have performed anion binding studies with compound 2 suggesting that there is no effect of anion on compound 2, which could be due to non-presence of suitable cavity, a suitable spacer and the presence of urea pendant group reported earlier [17,18,27]. The ligand 2 was further titrated with series of cations like lithium ($Li^+$), potassium ($K^+$), beryllium ($Be^{2+}$), magnesium ($Mg^{2+}$), calcium ($Ca^{2+}$), strontium ($Sr^{2+}$), barium ($Ba^{2+}$), copper ($Cu^{2+}$), silver ($Ag^+$), zinc ($Zn^{2+}$), cadmium ($Cd^{2+}$), cobalt ($Co^{2+}$), iron ($Fe^{2+}$), manganese ($Mn^{2+}$), scandium ($Sc^{3+}$), yttrium ($Y^{3+}$), chromium ($Cr^{3+}$), molybdenum ($Mo^{6+}$), vanadium ($V^{5+}$), thallium ($Tl^{3+}$) and antimony ($Sb^{3+}$) has been monitored using fluorescence spectrometry. This has been recorded that highest quenching effect was observed for antimony ($Sb$) and thallium ($Tl$) while other cations were having no effect as shown in Figs. 3–5.

![Fig. 2 – Absorption spectrum of compound 2 showing the characteristics pattern of the peaks.](image1)

![Fig. 3 – Fluorescence spectrum of compound 2 showing the characteristic peaks of fluorescence emission on addition of metal cations.](image2)

![Fig. 4 – Fluorescence spectrum bar graph of compound 2 showing different metal ion complexation fluorimetric strength at 450 nm.](image3)
However, highest selectivity and quenching effect was recorded with antimony (Sb) and thallium (Tl) as shown in Figs. 3–6. The cation binding fluorescence titration was performed using antimony cation (Sb) where there was subsequent quenching effect was recorded on addition small aliquots of antimony (Sb) cation [29–32]. The binding constant is calculated which was found 4.68 × 10−4. Stability constants and stoichiometry’s for complexation of Sb3+ with ligand 2 (Fig. 6) were determined by fluorimetric titration [28]. The titration experiments were performed by adding solution with various concentrations of metal percolate in ethanol:water mixture to solutions of the ligand 2 in ethanol:water mixture. The concentration of the ligand 2 was held constantly at 2.032 × 10−6 M.

4. Conclusions

Based on fluorescent dansyl groups linked by ethoxy chains, a novel compound has been synthesized and its impact on various metallic moieties has been examined using sophisticated analytical techniques. It has been concluded that the synthesized compound is very much beneficiary for detection of toxic metals particularly antimony (Sb) and thallium (Tl) in environment even at ppb levels. For future prospects, the study could be direction toward development with respect to design and applications of fluorescent studies encompassing crown ethers.

**Fig. 5** – Fluorescence spectrum of compound 2 (2.032 × 10−6 M) on addition of Sb3+.

**Fig. 6** – Stability constant for complexation of Sb3+ with ligand 2.

**Conflicts of interest**

The authors declare no conflicts of interest.

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