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Fluorescence detection by thiourea based probe of physiologically important sodium ion

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ABSTRACT

A thiourea base receptor **1** was synthesized and characterized with ^{1}H NMR, ^{13}C-NMR, and mass spectroscopy. The receptor **1** has shown judicious fluorescence enhancement in the intensity (at 385 nm) on binding with the sodium cation compared to other surveyed metal ions. The rationale behind the design of sensor lies in the fact that the sensor has sodium-binding recognition site, coupled with a fluorophore having the correct spectral and electron-accepting properties. Thus, the thiourea compound is a promising system for the development of new fluorescent probes for the detection of Na^{+} cation.

1. Introduction

In last decades, fluorescence-based detection methods have gained much attention because of their simplicity, low cost, selectivity and sensitivity [1–5]. Significant advances have been made in the development of fluorescent cation probes based on different chemical reactions between probes and cations. The cleavage strategy is of immense attention because probes display excellent selectivity and high sensitivity toward cations with off–on fluorescence signalling [6–9]. The quantification of physiologic cation such as sodium is vital in clinical identification [10–12]. Traditionally, ion-selective electrodes were used to moniter the level of these analytes in blood serum; however, with the unpredictable growth of near-patient devices used at the hospital bedside, there is increasing require for portable systems utilizing small disposable sensors capable of whole-blood measurements [13–15]. Therefore, the progress of realistic and cheap optical sensor and system for the clinical resolve of these analyte in whole blood stay a significant area of research [16–19].

We are interested in the development of a novel thiourea based chemosensor for sodium ion detection based on the mechanism of electron transfer. We present the development of a sodium sensor capable of analyte estimation over a broad concentration range and without interference from any other cations in this study.

2. Experimental

^{1}H and ^{13}C NMR spectra were obtained on a Bruker AVANCE DMX400 spectrometer in DMSO-d_6 as solvent. The fluorescence and UV–visible spectra were recorded respectively on a Fluoromax-4 spectrofluorometer and a Shimadzu UV-24500 spectrophotometer. The solvents were distilled before used. Commercially available reagents were used without further purification unless otherwise.

2.1. Synthesis of receptor *1*

To a solution of 1-isothiocyanatobenzene (1 mmol) in acetone (25 mL), solution of naphthalen-2-amine (1 mmol) in acetone (25 mL), both solution mixed at room temperature. Further the reaction mixture was stirred and refluxed for 2 h. The reaction mixture was cooled and the precipitate was filtered. The pinkish white precipitate was washed with cold ethanol and dried under vacuum 84% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ=7.08–715 (t, 1*H*, Ar–H), 7.28–7.35(t, 2*H*, Ar–H), 7.46–7.62 (m, 6*H*, Ar–H),

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7.82–7.88 (t, 1*H*, Ar–H), 7.82–7.88 (t, 1*H*, Ar–H), 7.39–7.97 (m, 2*H*, Ar–H), 8.00 (s, 1*H*, –NH), 8.02 (s, 1*H*, NH) ppm. ^{13}C NMR (100 MHz, DMSO-d_6,): δ=123.6, 124.2, 122.3, 125.4, 126.2, 126.5, 127.2, 128.6, 130.6, 134.3, 135.5, 140.0, 181.8 ppm; LC–MS ($M+H^+$): Found 279.63 Calculated 279.10.Elemental analysis (calcd %) for $C_{16}H_{13}N_2S$: C, 72.42, H, 4.94, N, 10.56; found: C, 72.20, H, 4.60 and N, 10.67.

2.2. UV–visible and fluorescence spectral measurements

For UV–visible and fluorescence spectroscopy, the metal ion Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Ba^{2+}, Cs^+, Bi^{3+} Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Th^{4+}, Ag^+ were added as their nitrates, Sr^{2+}, Cr^{3+}, Mn^{2+} were added as their chlorides, Zr^{4+} was added as its oxychloride while U^{6+} was added as its sulphate. The solutions of metal salts were prepared in CH_3CN containing 1% H_2O (c=1 mM) for analysis with receptor **1**. The solution of receptor **1** was freshly prepared in CH_3CN containing 1% H_2O (c=0.1 mM). The excitation was carried out at 278 nm for receptor **1** with 5 nm emission slit widths in fluorometer. For absorbance and fluorescence measurements 1 cm width and 3.5 cm height quartz cells were used.

3. Result and discussion

Receptor **1** was synthesized through a reaction of 1-isothiocyanatobenzene and naphthalen-2-amine to form thiourea based receptor (Scheme 1). The receptor **1** was obtained with good yield and has appearance of pinkish white powder. The synthesized receptor was characterized with spectroscopic techniques such as ^{1}H-NMR, ^{13}C-NMR and mass spectroscopic methods (Fig. S1–S3, Supporting information [SI]). The spectral analysis is consistent for structure of receptors **1**.

The thermal behaviour of receptor **1** was recorded on TGA and DSC as shown in Figs. S4 and S5 (SI). The sharp onset decomposition peak was obtained at 189.5 °C that may be attributed to cleavage of thiourea linkage. Further small peak observed at 223.6 °C is attributed to decomposition of sulphur. The DSC curve of the receptor **1** showed two peaks, which are similar to two decomposition points as seen in TGA of the same compound. The DSC revealed the sharp endothermic peak at 174.9 °C corresponding to the melting point of receptor **1** which is in concordance with the same obtained by open capillary method. The endothermic small peak observed at 206. 8 °C is due to the melting point of sulphur which may be quite lowered due to presence of other moieties.

We tested the binding affinity of chemosensor **1** by mixing the solution of it with Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Ba^{2+}, Cs^+, Sr^{2+}, Bi^{3+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Th^{4+}, Zr^{4+} and U^{6+} metal ions in CH_3CN containing 1% H_2O. The pure chemosensor **1** exhibited week fluorescence emission at 385 nm upon excitation at 278 nm. However, the fluorescence intensity of **1** was selectively and significantly enhanced in the presence of Na^+ ion. On the other hand, there was no such significant fluorescence turn on observed in emission outline of receptor **1** in the presence of other tested metal ions, which indicated the high selectivity of receptor **1** for Na^+ ion (Fig. 1). The enhancement of fluorescence was attributed to occurrence of the strong complexation of Na^+ with receptor **1**, resulting in the electron transfer between C=S moiety and sodium ion.

The spectrofluorometric response of receptor **1** towards various metal ions was recorded and depicted in Fig. 2. Receptor **1** shows significant florescence enhancement compared to other surveyed metal ions. To study the influence of other metal ions on Na^+ binding with receptor **1,** we performed competitive metal binding experiments with other metal ions (2 equiv.) in the presence of Na^+ (1 equiv.) (Fig. 3). The observed fluorescence enhancement for mixtures of Na^+ with surveyed metal ions was similar to that was observed for Na^+ alone. Thus no other metal ion appeared to interfere with the fluorescence of the **1**.Na^+. These results indicate that receptor **1** shows a good sensitivity and selectivity towards Na^+ ion over other competitive metal ions. The effect of increasing concentration of Na^+ ion on the emission intensity of receptor **1** is pictured in Fig. 4a. The quantum yield of receptor **1** and receptor **1** on binding with Na^+ was found to be 0.20 and 0.70. The successive addition of Na^+, leads to enhanced emission intensity and ultimately, reached saturation (with 20-fold enhancement at 385 nm) upon complete addition of 1 equiv. (200 μL) of Na^+ and the enhancement is due to cancelation of PET channel upon complexation of Na^+. Further the titration is progressed up to 600 μL (3 equiv.) from which it is concluded that no further significant enhancement or quenching is taking place which is beneficial to the sensing. From the titration, it is clear that receptor **1** is almost non-fluorescent and addition of Na^+ provided judicious pathway for photoelectron transfer (PET) between the Na^+ ion and receptor **1**. The significant sensing of Na^+ ion with receptor **1** may be attributed to the compatible size of sodium cation with the pseudocavity within the synthesized key receptor.

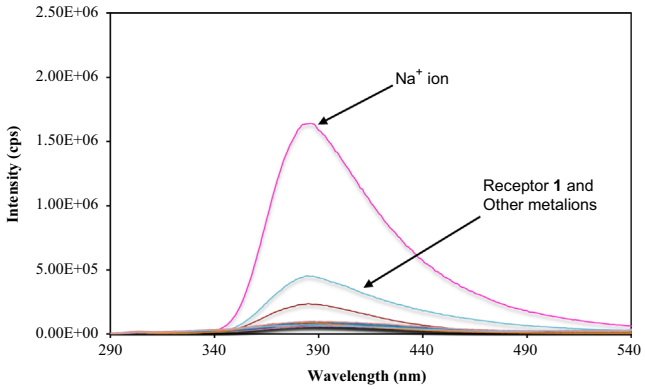
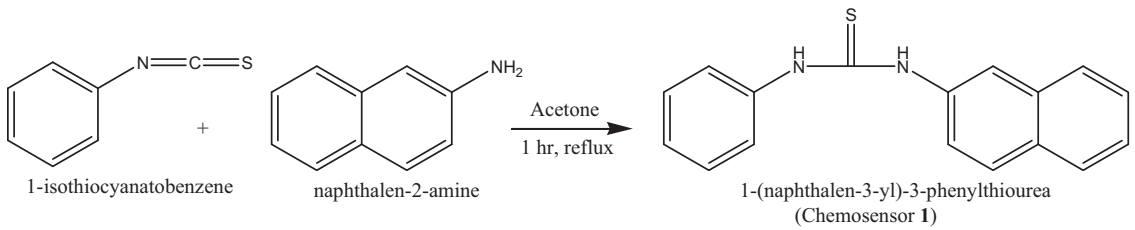


Fig. 1. Fluorescence emission spectra of receptor **1** (0.1 mM) in the presence of different ions (1 mM). The excitation was at 278 nm, and the emission was at 385 nm, excitation and emission slit 5 nm.



Scheme 1. Synthesis of receptor **1**.