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Rapid detection of fluoride in potable water using a novel fluorogenic compound 7-O-tert-butyldiphenylsilyl-3-cyano-4-methylcoumarin

Akumu Edwin Otieno* and Kebenei J. Sellah
[1]Department of Physical and Biological Sciences, Kabarak Univeristy,
Private Bag 20157 Kabarak, Kenya

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Abstract
The study presents the synthesis of a new fluoride sensor 7-O-*tert*butyldiphenylsilyl-3-cyano-4-methylcoumarin (Si-CHMC) that imparts a blue fluorescence to an aqueous solution in the presence of fluoride ions. Si-CHMC has excellent sensitivity and selectivity towards fluoride. The results further indicate that fluoride concentrations as low as 0.01M can be accurately detected within almost instantly as the response time is within a second. Fluoride testing with Si-CHMC is simple and relatively rapid compared to the conventional methods that require skilled personnel. Hence, the method presented herein can be applied and is particularly useful for monitoring the quality of portable water among communities.

Key words: Fluoride, Detection, Coumarin, chemosensor, fluorescence

Introduction

The development of highly selective and sensitive compounds to for recognition and sensing of anions has received considerable interest in recent years as an important and interest in research topic because of their important roles Wu, Sedgwick, Gunnlaugsson, Akkaya, Yoon, & James, 2017) in biological (Jiao, Zhu, Chen, & Duan, 2015), (Huang, 2014) environmental (Chavali, 2015), and industrial processes (Huang, 2014). The detection of anions especially fluorides by fluorescence is rapidly becoming more established due to their high sensitivity, selectivity and ease of operation (Chavali, 2015). A fluoride ion is a classic example of double-edged sword to the animal health: Fluoride protects teeth from decay by demineralization and remineralization (Neel, Aljabo, Strange, Ibrahim, Coathup, Young & Mudera, 2016).

However, too much fluoride leads to both dental and skeletal fluorosis which damage bones (Sabti, Al-Yahya, Al-Sumait, Akbar, & Qudeimat, 2019). This makes is an attractive target for sensor design. Fluoride sensors that possess various functional groups with varied abilities to initiate resonance have proven to be particularly effective in this regard as they are able to bind anions using directional hydrogen bonding interactions (Boiocchi, Del Boca,Esteban, mez, Fabbrizzi, Licchelli and Monzani 2004) when attached to suitable fluoromophores (Langton, Serpell, & Beer, 2016). This in turn increases the sensitivity (Wu, Wang, Yang, Tian, Liu, & Sun, 2019) of luminescent sensors to display binding information either by a color change (Singhal & Jha, 2019), (Ghosh & Adhikari, 2006) fluorescence (Tang, Zhu, Liu, Ni, Qiu, Han, & Wang, 2019) or both.

* *Corresponding author: oakumu@kabarak.ac.ke*

In the face of the significant development in this field of study, the search for simple, novel with has recently been of keen interest. In pursuit of this, the study present a Photo induced Electron Transfer (PET) based (Jiao et al., 2015) new coumarin derivative chemosensor with Schiff base (–C≡ N) for the selective recognition of anions which is detectable by the naked eye, upon binding of anions (Yang, 2013).

Experimental Method

Materials

All the chemicals and commercial reagents required for the synthesis and testing were purchased from Kobian Scientific Kenya Ltd. and used without further purification unless otherwise mentioned.

Physical measurements

NMR spectra were recorded at 500 MHz, using Agilent/Varian Inova two-channel spectrometer. Proton chemical shifts are reported in ppm (δ) downfield from tetramethylsilane (TMS) or in reference to the solvent methanol (δ ^{1}H-NMR 3.31, ^{13}C-NMR 49.1). Coupling constants (J) are reported in hertz (Hz). Electronic absorption spectra were recorded on an MRC UV-11 Model UV–Vis spectrophotometer. Fluorescence spectra were taken by using a Biobase-BKF93 Model F2000 fluorospectrometer at room temperature.

Synthesis of 7-O-tert-butyldiphenylsilyl-3-cyano-4-methylcoumarin

3-cyano-7-Hydroxy-4-methylcoumarin (2 g, 0.01mol) was dissolved in 100 mL of THF and stirred under nitrogen atmosphere till a clear solution was obtained. Imidazole (0.68 g, 0.01mol) was dissolved in 30 mL of dry dichloromethane (DCM) -Tetrahydrofuran (THF) solvent mixture (3:1). The two solutions were mixed and stirred. *Tert*-butyldiphenylsilylchloride (TBDPSCl, 2.4g, 0.01mol) was dissolved in 30 mL of DCM and added slowly dropwise over a period of 1h with continuous stirring. The reaction was then allowed to stir for 3 h under nitrogen at room temperature. The reaction mixture was then filtered through a short bed of celite and was washed with 200 mL water and 100 mL brine. The organic layer was dried with anhydrous sodium sulphate, filtered and concentrated under reduced pressure to give the crude product. The crude residue was purified by column chromatography using varied ratios of hexane: ethyl acetate as eluent. The product was obtained as a light yellow paste compound (Fig 1). The product was further purified by subjecting it to pTLC using hexane-ethylacetate (3:7) solvent system to yield 3.59 g (81.7 %).

Structural determination was done using NMR spectroscopy analysis and the following data was obtained: **^{1}H-NMR (500 MHz, CD_3OD):** δ (ppm): ^{1}H NMR: δ 0.74 (9H, s), 2.6 (3H, s), 6.76 (1H, dd, *J* = 8.1, 1.4 Hz), 6.90 (1H, dd, *J* = 1.4, 0.5 Hz), 7.35 (2H, tt, *J* = 7.7, 1.4 Hz), 7.41-7.37 (8H, 7.38 (dddd, *J* = 7.8, 7.5, 1.7, 0.5 Hz), 7.32 (dtd, *J* = 7.5, 1.6, 0.5 Hz)), 8.31 (1H, dd, *J* = 7.9,

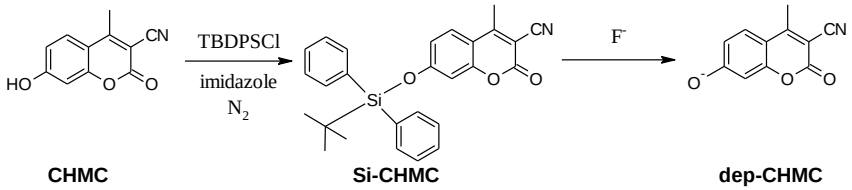
0.5 Hz). **^{13}C-NMR (500 MHz, CD_3OD):** δ (ppm): 165.3, 156.0, 154.3, 150.2, 137.3, 134.2, 130.9, 130.2, 130.0, 122.1, 116.4, 115.2, 101.3, 97.7, 32.9, 19.5, and 18.2.

Fluoride testing

A series of test samples with varying concentrations of fluoride ranging from 0.1 to 100 mg/L were prepared by dissolving 0.2210 g of NaF in 1 L of de-ionized (DI) water and diluted as per the required concentration. 1ml of varying concentrations of 7-O-*tert*-butyldiphenylsilyl-3-cyano-4-methylcoumarin solution ranging from 0.01 to 0.1mg/L prepared in THF was then added to 1 mL of each of these solutions. Fluorescence spectra were obtained for each of these solutions with corresponding excitation and emission wavelengths of 360 nm and 450 nm, respectively. Samples were tested in triplicates.

Interference testing

A series of test samples were prepared with different anions that include F^-, Cl^-, Br^-, I^-, NO_3^- and AcO^- Each of the anion solutions were prepared in DI water and maintained at a specific concentration of 5 mg/L 40 mL of the test solution prepared in THF was then added to 1 mL of each of these solutions. Fluorescence spectra was obtained for each of these solutions with corresponding excitation and emission wavelengths of 360 nm and 450 nm, respectively.



Scheme 1. Schematic of protection and deprotection of CHMC

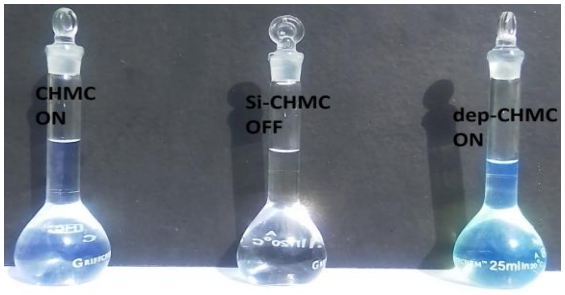


Fig 1. Effect of TBDPSC and F- on the fluorescence of CHMC

Results and discussion

The addition of fluoride ions to Si-CHMC results in its dissociation into TBDPS-F and CHMS. This emits a blue fluorescence confirming the presence of fluoride in solution (scheme 1). An interaction between the CHMC and UV-VIS light showed excitation and emission at 349 nm and 400nm in acetone respectively. When 0.01M of F^-, was added to the CHMC the fluorescence wavelength shifted from 400 nm to 487 nm indicating a red shift of 87 nm (Fig. 2). CHMC had

no colour change in the presence of Cl^-, Br^-, NO_3^-, and AcO^- anions (fig. 4). This result shows that the CHMC exhibits a selective recognition of F^-. Fig. 1 shows the effect of protection and F^- ions on the fluorescence wavelength of CHMC. The fluorescence intensity increased with increase of the fluoride ions (fig. 3). Fig. 5 represents the fluorescence emitted by each of these solutions. It can be noted that no noticeable fluorescence was visualized for any other anions other than fluoride indicating a highly specificity Si-CHMC on fluoride ions.

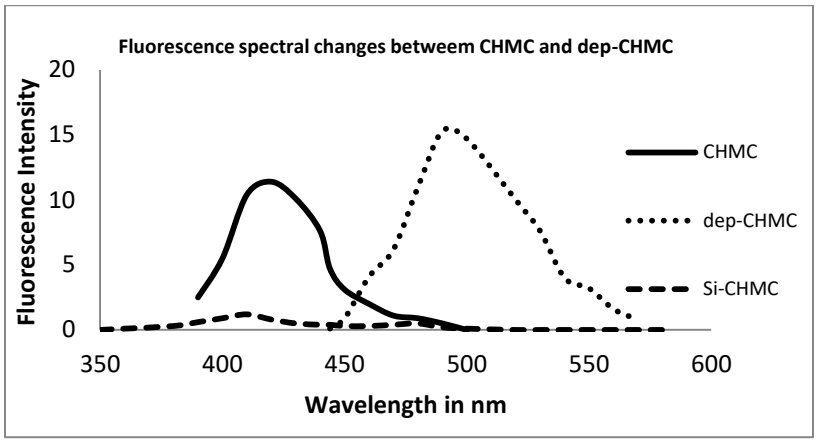


Fig 2. Effect of protection and F^- ions on the fluorescence wavelength of CHMC

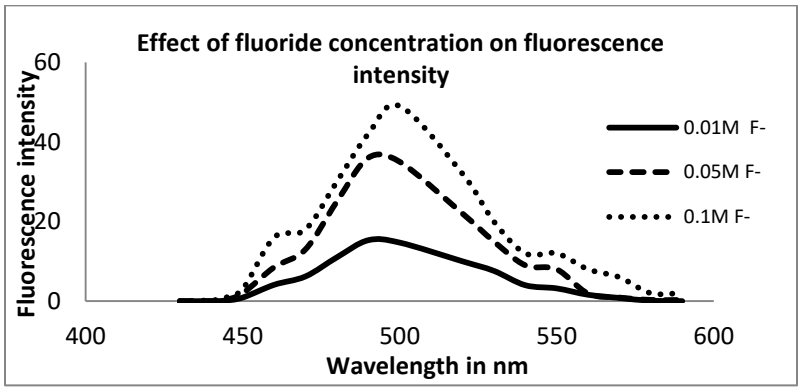


Fig 3. Effect of fluoride concentration on fluorescence intensity of dep-CHMC

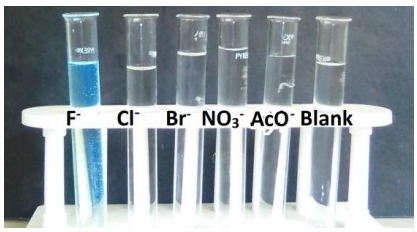


Fig. 4. Fluorescence upon addition of 0.01M of different anions to a solution of Si-CHMC

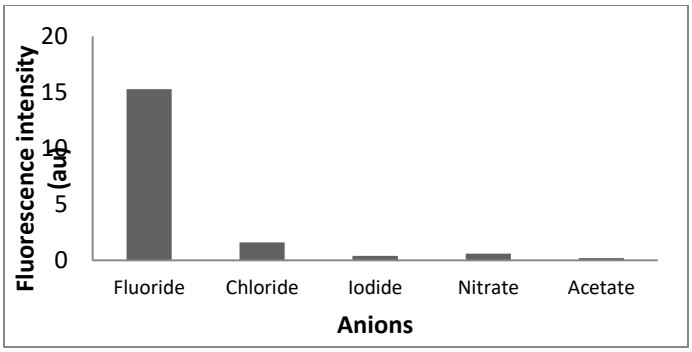


Fig. 5. Fluorescence intensity comparison between differentl anion solutions after reacting with Si-CHMC at 25 C for 1 h.

No fluorescence was observed in samples without fluoride ions. To test the specificity of this compound towards fluoride, several anion solutions were prepared with standard concentrations of 0.01M that included Cl^-, Br^-, NO_3^-, and AcO^-. A mixture of 10 mL of each of these anions and 10 mL of F^- was added to the Si-CHMC in THF to check for interference from either of these compounds towards fluoride testing.

Conclusion

In order to develop a rapid and selective method for fluoride testing in potable water, a successful design and synthesis of a novel fluorogenic compound 7-O-tert-butyldiphenylsilyl-3-cyano-4-methylcoumarin has been achieved. A detailed synthetic procedure and characterization of the compound has been presented. Test analysis on the compound with different concentrations of various anions including F^- Cl^-, Br^-, NO_3^-, and AcO^- in water reveals high selectivity for fluoride ions. Such ease of the test method would allow any untrained user to conduct the test and assess the quality of water. This test method has a great potential and can be applied in fluoride testing in portable water. This will assist in excess fluoride consumption as fluoride levels can be easily be monitored using this novel product obtained from the study.

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