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ZINC METAL COMPLEX AS SENSOR FOR SIMULTANEOUS DETECTION OF FLUORIDE AND HSO4⁻ IONS

Jasminder Singh^a, Manisha Yadav^b, Ajnesh Singh^a, Narinder Singh^{a*}

Schiff base based tripodal receptor was synthesized and was complexed with zinc metal ion (n17) using very easy single step process. The resulting complex was fully characterized by CHN and single crystal XRD. The real time application of the complex in aqueous media was devised by preparing its ONP and their sensor activity was tested with various anions by observing changes in fluorescence profile of n17. It was observed that ONP of n17 responded excellently for fluoride and sulfate producing two different signals, with a detection limits of 4.84×10^{-12} M and 5.67×10^{-9} M respectively, without having any interference from each other. The real time application of the sensor was also tested using various samples collected from various daily utility items and found to respond exceptionally well.

Introduction

Anionic receptors are an important research area¹ because of the considerable importance of anions in nature, as agricultural fertilizers and industrial raw materials and their corresponding environmental concerns²⁻⁷. The importance of anions can be estimated from the fact that more than 70% of substrates and cofactors involved in biological processes carry a net negative charge⁸⁻¹⁰. Anions are profoundly involved in catalysis reactions involving Carboxypeptidase, RNase, ATP synthases, DNA polymerase, Citrate synthase etc¹¹.Extremely high levels of sulphates are toxic as it increases the acidity of the atmosphere and form acid rain. So, anions are also of important environmental concerns. Therefore, in recent times, supra-molecular chemists have devoted considerable effort to design systems capable of recognizing, sensing and transporting negatively charged species. However, the detection of anionic species is still a challenging task compared to cationic determination. The reason behind this lies on the following: 1. Anionic species donot have uniform shapes like cations¹², 2. in case of anionic species, electrostatic interactions¹³ are less effective, 3. pH window¹⁴ is narrower(this is an important issue in aqueous environment). Anion recognition in water is an extremely challenging task for a number of reasons, the main reason being that anions are strongly hydrated and any complexation process that involves anion dehydration will have to pay a large energy price by an overall increase in the entropy¹⁵. Therefore, it is particularly difficult to develop an anion recognition system that forms hydrogen bonded complexes in an aqueous solvent, for the obvious reason that the water competes strongly for the hydrogen bonding sites¹⁶. The selectivity of a chemo-sensor for an anionic species is related to its discrepant ability to interact with the receptor site through intermolecular hydrogen bonding (HB).

The simultaneous detection of 2 anions is a rarely reported case in the literature so far. In view of this, it is promising to visualize the use of such a system in a range of sensing applications as well as in other situations, such as anion transport and purification¹⁷. Metal complex-based carriers can have unique anion selectivity based on characteristic coordination chemistry¹⁸. Therefore, recently metal complexes have been used as anionic sensors as they have vacant binding sites to bind specific anions or have pendant arms containing anion receptor units. Transition metal complexes have their own specific colors due to different electronic structures and coordinating directly to anions results in alterations in their electronic structures and hence color changes. These changes can be measured quantitatively and qualitatively by different spectroscopic techniques like UV-Visible and fluorimetry. In the presented work, a poly-nuclear zinc complex was developed. Zinc can function as active site of hydrolytic enzymes, where it is ligated by hard donors (N or O). It has long been recognized as an important co-factor in biological molecules, either as a structural template in protein folding or as a Lewis acid catalyst that can readily adopt the coordination numbers 4, 5, or 6¹⁹⁻²¹. The metal zinc was selected for the complexation because of its importance in biological systems. It is the only metal which appears in all enzyme classes

including carbonic anhydrase and carboxypeptidase, which are essential for the processes of carbon dioxide (CO₂) regulation and digestion of proteins, respectively²²⁻²⁴. Zinc is stored and transferred in metallothioneins that are responsible for the absorption of zinc .However, inadequate or excessive zinc intake can be harmful and excess zinc particularly impairs copper absorption because metallothionein absorbs both metals²⁵. To be an effective anion receptor, the metal complex had the combination of strong hydrogen bonding (O–H or N– H) moieties and positively charged groups such as Zn^{+2} . This receptor simultaneously²⁶ detected multiple anions in the aqueous medium.

Results and Discussions

Synthesis of the sensor

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The tripodal ligand (H_3L_1) was primed by the reaction of 2-Hydroxy-5-nitrobenzaldehyde with Tris (2-aminoethyl) amine in methanol, with refluxing of one and half hour with zinc perchlorate as catalyst. H_3L_1 thus formed was copiously characterized with ¹H NMR, ¹³C NMR (Figure S1 & S2) and CHN analysis. H_3L_1 was further used for complexation with zinc metal ion using zinc acetate in acetonitrile, carried out at increased temperature on water bath for about 2 hrs. Solid separated out was collected and washed with small volume of acetonitrile; the separated brownish yellow product was recrystallized in HPLC grade acetonitrile by slow evaporation method and verified the structure using single crystal XRD data.



Structure Determination of Zn complex of $H_3L_1\,(n17)$ using single crystal XRD

The structure of complex **n17** was unambiguously determined by single crystal X-ray determination. X-ray structure determination revealed that the complex **n17** crystallizes in the triclinic crystal system ($P\bar{1}$) and the asymmetric unit consists of one neutral complex [$Zn_3(C_{18}H_{24}N_7O_6)_2$]/ [$Zn_3(L_1)_2$] and four acetonitrile molecules as solvent of crystallization, out of these two are disordered. The molecular structure of **n17** is shown in **Figure 1**.

The complex n17 is a trinulear Zn(II) complex where three Zn(II) metal ions are crystallographically different. All metal centres are octahedrally surrounded by N and O donor atoms originating from two tripodal ligands (H_3L_1). In outer Zn (II) metal ions octahedral coordination is completed by three sp² hybridized N atoms and three phenolate O atoms while

coordination of central zinc metal atom (Zn2) is satisfied by six bridged phenolate oxygen atoms. It is also interesting to note that all the phenolate oxygen atoms are acting as bridged ligand between Zn (II) metal centres. The zinc atoms, Zn (1) and Zn (3) have slightly distorted octahedral coordinations.



Figure 1: ORTEP diagram of compound n17 with 40% probability thermal ellipsoids and the atom-numbering scheme (hydrogen atoms and solvent molecules are removed for clarity).

The maximum deviation from the regular octahedral geometry is 15.86° and 16.72° in cis-N-Zn-N [N(4)-Zn(1)-N(2)=105.86°, $N(11)-Zn(3)-N(13) = 106.76^{\circ}$] angles while in trans N/O-Zn-N/O angles, maximum deviation is of 22.39° and 24.29° $[(N(13)-Zn(3)-O(13)=155.71^{\circ})]$ N(4)-Zn(1)-O(4)=157.61(6)respectively in Zn(1) and Zn (2). In case of central Zn (2) atom, the extent of distortion is less as compared to other two Zn (II) atoms. The average Zn-N, Zn-O distances and O/N-Zn-O/N bond angles around Zn(II) octahedrons are comparable to other similar reported Zn(II) complexes.³⁴ The selected bond lengths and bond angles are given in supporting information as Table 2. When crystal packing is viewed down a -axis, the complex moieties are arranged in form of set of two complex moieties packed like bricks in a wall (as shown in Figure 2). The different moieties are held together by weak C-H...N and C-H...O interactions (hydrogen bonding interactions are given in supporting information as Table 3). Most of oxygen atoms of the nitro groups are involved in hydrogen bonding interactions with neighbouring moieties. The solvent molecules of crystallization (acetonitrile) are providing more robustness to the crystal structure by hydrogen bonding and C-H... π interactions (C55-H55C...Cg=3.061Å and angle C55-H55C...Cg=127.24° where Cg is centroid of ring defined by atoms C1-C6) with metal complex moieties. To further support the interaction of zinc metal ion with the receptor, IR studies were carried out. It is clearly visible from the IR spectra of receptor and complex of metal ion with receptor that zinc metal ion interacts with -C=N of the complex leading to shift in the schiff's base peak from 1627 cm⁻¹ to 1608 cm⁻¹ (**Figure S3**).



Figure 2: Packing diagram of compound n17 along a-axis. Metal canters are shown with help of green polyhedral

Formation of ONP of Zinc complex of H₃L₁

Organic compounds suspended in a fine particle size ranging from 10 nm to 1 µM in aqueous medium are termed as organic nanoparticles³⁵. Various methods of ONP formation has been developed and explored due to their developing demands in widespread fields of modern world like electronics, photonics, conducting materials, sensors, etc. Various physio-chemical parameters and properties like binding sites, solubility of compound and environmental factors such as pH, temperature, and salt strength³⁶ of the organic compound are considered for development and workability of ONP in various applications. Single step re-precipitation method developed by Fessi³⁷ due to its ease, economical and reproducibility is being implemented for formation of ONP of n17 instead of other two steps techniques. In re-precipitation approach, organic compound solution prepared in organic solvent (1mL) is injected slowly to the bulk of aqueous medium (99 mL) without prior emulsification. Influence of water on photophysical properties of the complex was studied using fluorescence spectroscopy. Emission spectrum of n17 was having a broad peak at 430 nm with DMF as a solvent, while a solvatochromic change in the peak was observed as peak shifted bathochromically to around 470 nm, when water (1:99) was taken as solvent (Figure 3). The ratio was optimized as no ONP were formed in concentration less than this or settled down in concentration more than this. Shift in the fluorescence can be attributed to the reason that two types of aggrgates are formed during nanoparticle formation 'J' type and 'H' type. Two chromophore units when get parallel aligned in aggragtes or nanoparticles causing formation of two new exciton bands. Transition only to lower exciton band leads to red shift in the spectra and blue shift in case of transition to higher exciton band.³⁸



Figure 3: Emission profile of n17 in 1: 99, DMF: water system and in pure DMF system.

Particle size of **n17** was analysed using DLS (Dynamic Light Scattering) and of nano-aggregates of **n17** with a narrow size distribution of ranging from 15-20 nm (**Figure 4a**). The particle size distribution of the prepared nano-aggregates was also confirmed using transmission electron microscopy (TEM) (**Figure 4b**). The emission profile of prepared ONPs were also tested over a period of 8 days and it was observed that prepared ONPs show nearly same fluorescence profile, without much decay in the fluorescence (**Figure S5**).



Figure 4: (a) Characterization of ONPs of n17 with DLS and (b) Transmission electron microscopy (TEM)

Recognition properties

The anion binding ability of **n17** was evaluated by observing the changes in emission profile of **n17** caused by addition (100 μ M) of tetrabutylammonium salts of various anions (F⁻, Cl⁻, Br⁻, I⁻, HSO₄⁻, ClO₄⁻, PO₄²⁻, CH₃COO⁻, NO₃⁻, CN⁻)to prepared ONPs of **n17**. It was noticed that most of the anions did not cause any significant change in the emission spectrum of the **n17** except Fluoride and HSO₄⁻ (Figure 5), when excited at a wavelength of 300 nm. The addition of HSO₄⁻ caused hypsochromic shift in the fluorescence spectra of the complex i.e. fluorescence peak got shifted to 370 nm which was earlier at 470 nm. The changes caused by addition of HSO₄⁻ ions can be detected chromogenically even with the naked eye as it leads to change from yellow to colourless (**Figure 6**). The same behaviour was observed with emission photography (**Figure S4**).

However, there was an evident and sharp increase in the fluorescence intensity upon addition of F⁻ ions. The spectral profile of n17 showed 2 folds of enhancement on addition of 100 µM of fluoride ions. It is quite evident from the spectral profile changes caused by HSO₄⁻ and F⁻ that the receptor binds with both in a different manner can be attributed to different binding sites for both the anions i.e. fluoride ions get coordinated with in the cavity formed by the complex, leading to separation in the two aromatic nitro rings causing cancellation of photo induced electron transfer (PET)³⁹, eventually resulting in enhancement in the fluorescence intensity at same wavelength. On the other hand HSO₄ ions gets coordinated with the metal ions of the complex leading to modulation of internal charge transfer⁴⁰, which in turn leads to shift in the fluorescence (Figure 5) as well as in UV-Visible absorption profiles (Figure S6) i.e. n17 had two peaks at 310 and 422 nm respectively. On addition of fluoride only peak at 422 nm showed the enhancement, while on adding HSO_4^- ions the peak gets shifted to 373 nm. The peak at 422 nm can be attributed to charge transfer band between -OH and -N=C groups.⁴¹This assignment has been concluded on the basis that both the parents i.e. aldehyde and amine lack this band and this band appears only upon -C=N linkage.⁴² Further, no change in peak position on addition of fluoride ions confirms the photo induced electron transfer mechanism, as being an excited state phenomenon would not be visible in UV-Visible spectrum.43 On the contrary, addition of HSO₄⁻ ions caused modulation of internal charge transfer, causing the shift in both fluorescence and UV-Visible spectra (ICT is a ground state phenomenon).⁴⁴



Figure 5: Fluorescence emission spectra of the receptor **n17** upon addition of a particular anion (F⁻, Cl⁻, Br⁻, I⁻, HSO₄⁻, ClO₄⁻, PO₄²⁻, CH₃COO⁻, NO₃⁻, CN⁻) of tetrabutylammonium salts



Figure 6: Chromogenic naked eye detection of HSO₄ ions using ONP's of **n17**

To explore more about the binding affinity of the complex as a receptor for HSO₄ and F, fluorescence titration was carried out separately for both Fluoride and HSO_4 , by subsequent additions 10 mL of 5 mM solution of the respective anion to a total volume of 5 mL. The fluorescence intensity of n17 increased gradually with each successive addition of fluoride ions (Figure 7 a), while in case of HSO_4^- ions, initially there is slight change in the spectra initially up to 40 mL but later the fluorescence peak shifts from 470 nm to 370 nm and increases gradually with each successive addition of HSO₄⁻ ions (Figure 8 a). The calibration curves for both the anions were plotted on the basis of changes observed in spectral profile of n17 on successive addition of respective anions. It was observed that calibration plot of fluoride ions showed excellent linear regression upto 200 nM with r² value of 0.9946 and a detection limit of 4.84×10^{-12} M (Figure 7 b).



Figure 7: (a) Changes in the fluorescence spectrum of **n17** after the subsequent additions of fluoride ion in ONP of **1**(b) Calibration plot for successive addition of Fluoride ion to ONP of **n17**

While calibration plot for HSO_4^- ions showed a linear regression range from 35-200 nM with r² value of 0.9907 and a detection limit of 5.67×10^{-9} M (**Figure 8b**).



Figure 8: (a) Titration of HSO₄⁻.Changes in the fluorescence spectrum of the complex after subsequent additions of HSO₄⁻ (0–200 μ L) (b) Calibration plot for successive addition of HSO₄- ion in ONP of **n17**

Simultaneous Detection

To explore the use of proposed sensor for simultaneous determination of HSO4⁻ and F⁻ ion in same solution, experiments were performed. Calibration plot was again plotted for the same by successive additions of one (0-200 nM) and keeping the concentration of other constant (100 nM) in ONP solution of n17, to check their possible interference in each other's determination. It was observed that the slope of calibration plot 5.6694 and 0.9628 for HSO4 and F ion respectively remains the same (Figure 9 a & 9 b) as was observed in determination of each anion independently i.e. 5.6882 and 0.9605 (Figure 7 b & 8 b). This concluded that the sensor can be used for determination of both the anions simultaneously without any interference from each other in aqueous samples. The binding constant and stoichiometry of the complexes was calculated using Lehrer-Chipman equation.⁴⁵ Plotted curves (Figure S7 & S8) clearly show a stoichiometry of 10:1 for fluoride and 2:1 for HSO₄⁻ ions, having a binding constant of 4.2×10^4 M⁻¹ and 2.5×10^4 M⁻¹ respectively. Such high molecularity can be explained on the basis that organic nanoparticles have number of exposed sites for interaction with analyte of interest.



Figure 9: Calibration plot of interference studies of (a) fluoride ions in presence HSO_4^- ions (b) HSO_4^- ions in presence of fluoride ions.

Recyclability

The recyclability of complex was tested by treating it with 0.1 mM of Na₂CO₃. The complex on treatment with fluoride and hydrogen sulphate ions showed a remarkable increase in fluorescence intensity and shift in fluorescence peak respectively. After respective treatment of anions a solution of 0.1 mM Na₂CO₃ was added to the solution under constant sonication. The resultant mixture after addition of 1 equivalent of Na₂CO₃ was tested for its fluorescence intensity. It is quite evident from the fluorescence obtained that Na₂CO₃ was able to remove the anions from the complex generating the original fluorescence profile. The resulting solution was again exposed to respective anions producing their respective signals, with no much loss in the intensity (**Figure 11**). The whole process can be used for recycling of the receptor and ensures its reusability.⁴⁶



The proposed sensor was also compared with the reported sensors for fluoride and HSO_4^- ions (**Table 1**). It is quite evident from the comparison that the proposed sensor offers a considerable enhancement in detection limit and allows the determination of two analytes simultaneously.

S.	Authors	Solvent	Simultaneou	Detectio	Ref.
No.		System	s Studies	n Limit	
-	K. V. Gothelf	DMSO-Water	F ⁻ ions	50 µg	47
1.	et al			mL^{-1}	
2.	L. Weber et	Cyclohexane	F ⁻ ions	-	48
	al	& THF			
	M. G.	Chloroform	F ⁻ ions	-	49
3.	Davidson et				
	al				
4.	D. Chellappa	Acetonitrile-	F ⁻ ions	8.52 nM	50
	et al	Water			
5.	Z. Bai et al	Water	F ⁻ ions	580 nM	51
	N. Singh et al	Water	F ⁻ ions &	4.84 pM	Propos
6.	_		HSO ₄ ⁻ ions	& 5.67	ed
				nM	Sensor
7.	A. Mallick et	Acetonitrile-	F⁻ ions &	-	52
	al	Water (5:1)	HSO4 ⁻ ions		
8.	A. Wu et al	Methanol	HSO4 ⁻ ions	1.39 mM	53
9.	A. Kuwar et	Water	HSO4 ⁻ ions	0.25 mM	54
	al				
10.	N. Kaur et al	Water	HSO ₄ ⁻ ions	37 mM	55
11.	N. Kaur et al	Water	HSO ₄ ⁻ ions	1.12 mM	56

Table 1: Comparison of proposed sensor with the reported sensors in the literature

Real Sample Analysis

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Sulphate and fluoride are found in various daily practice products like body wash, shampoo, toothpaste and various oral care products and are commercially available in market. Some such products were identified and tested using the proposed sensor (Figure 10). Thus obtained results were compared with the calibration plot for estimation of the concentration of sulphate and fluoride present in the samples (Table 2). The proposed sensor performed exceptionally well with all the samples showing substantial signal enrichment in case of fluoride and alteration in spectral maxima for sulfate, it was quite discernible over here that proposed sensor was able to detect amount of sulfate and fluoride present together in various commercially available samples.



Figure 10: Real sample analysis of fluoride and ${\rm HSO_4}^{\rm -}$ ions in various items of daily utility

Table 2: Estimated values of fluoride and sulfate ions in various items of daily utilities, calculated using respective calibration plots.

S.	Sample Name	Estimated	Estimated
No		Fluoride (nM)	Sulfate (nM)
1.	Bodywash (B1)	-	169.37 ± 0.25
2	Bodywash (B2)	-	134.04 ± 0.21
3	Toothpaste (T1)	215.52 ± 0.2	220.27 ± 0.33
4	Toothpaste (T2)	80.24 ± 0.3	46.86 ± 0.2
5	Dentifrices waste (F1)	190.73 ± 0.18	-
6	Dentifrices waste (F2)	153.53 ± 0.17	-
7	Dentifrices waste (F3)	107.98 ± 0.2	-

Conclusions

A new receptor **n17** i.e. Zn complex of tripodal ligand was formed and characterized using various techniques like ¹H, ¹³C NMR and mass spectroscopy. The structure of the complex was determined using single crystal XRD. To use the prepared complex in real time application ONP of the complex were prepared and found their use in simultaneous and effective detection of HSO_4^- and F^- ions in the real time samples in aqueous media. The results were verified using various commercial samples from our daily chores and calibration curve plotted in the experiment is being used for determination of their concentration and concluded that the proposed sensor can be used to determine both the anions in same solution with utmost ease and accuracy without any interference and without any pre-treatment of the solution.

Experimental

All precursor chemicals for the reaction scheme were purchased from Aldrich and SD Fine, India. All solvents were dried by standard methods. Unless otherwise specified, chemicals were purchased from commercial suppliers and used without further purification. ¹H and ¹³C NMR spectra were recorded on Avance-II (Bruker) instrument, which operated at 400 MHz for ¹H NMR and 100 MHz for ¹³C NMR (chemical shifts are expressed in ppm). The fluorescence measurements were performed on a Perkin Elmer LS55 Fluorescence. IR spectra of H_3L_1 and n17 were recorded using a Bruker Tensor 27 spectrometer with KBr discs. IR spectra is used to confirm the bonding of metal ion with -C=N of H_3L_1 to form n17. The TEM images were recorded with Hitachi (H-7500) instrument worked at 120 kV. A 400-mesh formvar carbon-coated copper grid was used for sample preparation. This instrument had the resolution of 0.36 nm (point to point) with 40-120 kV operating voltage. The particle size of nano-aggregates was determined with Dynamic Light Scattering (DLS) using external probe feature of Metrohm Microtrac Ultra Nanotrac Particle Size Analyzer.

Synthesis of (H₃L₁)

 H_3L_1 was prepared from Tris(2-aminoethyl)amine (146 mg, 1.0 mmol) was stirred with 5-nitro-2-hydroxy benzlaldehyde (534.4 mg, 3.2 mmol) in the presence of traces of zinc

perchlorate as catalyst in methanol^{27, 28}. The color of the solution changed immediately to yellow and precipitate separated out in quantitative yield. These precipitates were filtered, washed with methanol and dried. Yield = 90.2 % (535.37 mg). mp = 197 °C. $C_{27}H_{27}N_7O_9$: C, 54.64; H, 4.59; N, 16.52. Found: C, 54.58; H, 5.51; N, 16.61.

Synthesis of Zn acetate+ ACN+ H₃L₁ (n17)

An acetonitrile solution of Zn acetate (27.76 mg, 1.5 eq) was added to a solution of H_3L_1 (50mg, 1 eq) in acetonitrile. The solution was refluxed for two hours during which the color of the solution changed slightly. After the completion of reaction, the solution was filtered and kept for crystallization by slow evaporation. Brownish-yellow colored crystals were obtained having yield of 92.43% (36.22 mg). The crystal structure was obtained by single x-ray crystallography.

X-Ray Crystallography

The X-ray diffraction data for n17 were collected on a Bruker X8 APEX II KAPPA CCD diffractometer at 293 K using graphite monochromatized Mo-K α radiation ($\lambda = 0.71073$ Å). The crystals were positioned at 50 mm from the CCD and the diffraction spots were measured using a counting time of 10 s. Data reduction and multi-scan absorption were carried out using the APEX II program suite (Bruker, 2007). The structures were solved by direct methods with the SIR97 program²⁹ and refined using full-matrix least squares with SHELXL-97.³⁰ Anisotropic thermal parameters were used for all non-H-atoms. The hydrogen atoms of C-H groups were with isotropic parameters equivalent to 1.2 times those of the atom to which they were attached. All other calculations were performed using the programs WinGX³¹ and PARST.³² The molecular diagrams were drawn with DIAMOND.33 Final R-values together with selected refinement details are given in supporting information as Table 1.

Preparation of Organic Nanoparticles of n17 (ONP 1)

The organic nano particles (ONP) of n17 were prepared by reprecipitation single step method. Solution of the ligand was dissolved in 1 mL DMF with various concentrations. The working solution was slowly injected into water (100 mL) under sonication and size of the ONP formed were analyzed using DLS probe after every injection. It was observed after using various concentrations of ligand that concentration having 0.1mM of complex in 1.0 ml of DMF gave the optimum sized ONP. Prepared ONP were sonicated again for 10-15 minutes, making sure the temperature of the solution containing ONP do not rise above 10 °C and was later again observed under DLS for particle size to confirm stability and size of ONP. It was observed that at concentration higher than this generated agglomeration caused by considerable increase in particle size and suspension settled down in the beaker even though sonication was done during the whole process, while at concentration minor than the optimum concentration, no ONP were observed as the material simply settles down without giving any suspension.

Anion Binding Studies

The anion binding affinity of the **n17** was determined by observing the changes in the photo-physical properties of ONPs in the presence of different anions. The binding studies were performed at $25\pm1^{\circ}$ C, and the solutions were shaken for a sufficient time before recording the spectra. The working concentration of ONPs for all experiments was kept 0.01 µM. For anion binding assay 100 µL of tetrabutylammonium salts (10 µM) of 10 different anions were selected namely, F⁻, Cl⁻, Br⁻, I⁻, $HSO_4^{2^-}$, CIO_4^{-} , $PO_4^{2^-}$, CH_3COO^- , NO_3^{-} , CN^- in aqueous medium and changes in the photo-physical properties of ONP n17 were determined by Fluorescence spectroscopy. Further, simultaneous detection of the 2 anions (F⁻ and HSO₄⁻) was carried out so as to determine any interference caused by the 1 ion in the detection of the other anion by adding 100 μ L of one ion as interferent anion and doing successive addition of 10 µL as anion being determined. The effect of ionic strength was explored by recording the spectra at different concentration of tetrabutylammonium perchlorate (0-100 equivalent). The pH titrations were accomplished to comprehend the effect of pH on the recognition profile of ONP n17.

Real Sample Analysis

Real time application of the proposed sensor was tested using commercially available samples of HSO_4^- and F^- ions i.e. B1 and B2 are the commercially available body wash (0.5g in 100 mL water) having sodium lauryl sulfate as their major ingredient, T1 and T2 are the two major toothpaste brands having both sulfate and fluoride in them (0.250 g in 100 mL of water) in form of sodium fluoride and sodium lauryl sulfate and F1-3 are taken from dentifrices waste taken from different dentists, which is quite rich in fluoride content and is used without further dilution. All samples were taken in aqueous form.

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^a Chemistry Department, Indian Institute of Technology Ropar (IIT Ropar), Rupnagar, Panjab, India, 140001.

^b Centre for Converging Technologies, University of Rajasthan, Jaipur, India, 302004.

nsingh@iitrpr.ac.in

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Complex of tripodal receptor with zinc metal ion (ONPs) were used for simultaneous determination of F^- and HSO₄⁻ ions.