Published in final edited form as:

Anal Chim Acta. 2007 August 29; 598(2): 295–303.

Optical Fluoride Sensor Based on Monomer-Dimer Equilibrium of Scandium(III)-Octaethylporphyrin in a Plasticized Polymeric Film

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Abstract

A fluoride-selective optical sensor based on scandium(III) octaethylporphyrin (Sc(III)OEP) as an ionophore within a plasticized PVC film is described. The presence of fluoride ion in the aqueous sample phase increases the formation of a difluoro-bridged Sc(III)OEP dimer species in the polymer film. The ability of the Sc(III) porphyrin to form the dimeric structure in the presence of fluoride is confirmed by UV-Vis spectroscopy and X-ray crystallography. For more practical sensing applications, a pH chromoionophore (ETH 7075) is added to the plasticized PVC film along with Sc(III)OEP and the observed optical response is based on co-extraction of protons with sample phase fluoride to create the dimeric porphyrin and a protonated chromoionophore species. The selectivity pattern observed is $F^- \gg ClO_4^-, SCN^-, NO_3^- > Br^-, Cl^-$. Only organic salicylate is a significant interferent. Fast and reversible fluoride response is observed over the range of $10^{-4} \sim 10^{-2}$ M fluoride, allowing use of the sensing film in a waveguide configuration for flow-injection measurements.

1. Introduction

Fluoride measurements are receiving continuous attention from sensor research communities due to the clinical importance of fluoride level in drinking water [1-4] and potential applications in enzyme-coupled sensors for detecting a wide range of substrates that liberate hydrogen peroxide in the presence of selective oxidase enzymes (the peroxide generated can oxidize fluorophenol compounds in the presence of peroxidase enzyme to liberate free fluoride ion [5]). Fluoride ion can also be liberated enzymatically or by inorganic catalysts from toxic fluorophosphate species, including the nerve gases such as soman and sarin [6,7]. Although the most useful fluoride ion selective sensor is based on a LaF_3 crystal (solid-state ion-selective electrode) [8], development of very inexpensive fluoride selective devices is of interest, especially using liquid polymeric membrane/film configurations to create potentiometric or optical devices [9,10]. However, the very negative Gibbs free energy of hydration of fluoride ion (-366.5 kcal/mol) makes the fluoride one of the most difficult anions to be solvated within the organic polymeric phase of such sensors. In order to compensate for this unfavorable partitioning, a fluoride selective ionophore in the organic phase must exhibit exceptionally strong yet reversible binding with fluoride ion.

Recently, a number of new ionophores have been suggested for detection of fluoride, either potentiometrically or optically, using polymer membranes/films doped with lipophilic metal ion-ligand complexes. Initially, gallium(III) porphyrins were found to exhibit non-Hofmeister selectivity patterns when used as ionophores in polymeric membrane electrodes, with potentiometric fluoride response significantly improved [11]. Subsequently, various zirconium

(IV) porphyrins were found to also exhibit greatly enhanced selectivity toward fluoride when employed to prepare membrane electrodes [12]. These ionophores have been thoroughly studied in terms of response mechanisms, optimized polymeric matrices as well as fundamental studies of ligation and dimerization reactions using mass spectrometry [13-16]. Beyond porphyrin complexes, Schiff-base complexes of Ga(III) or Zr(IV) have also demonstrated potentially useful selectivity for fluoride when employed as ionophores to construct polymer membrane electrodes [17,18].

The most selective ionophores reported to date for detection of fluoride are aluminum(III) porphyrins [19,20]. Aluminum(III) octaethylporphyrin (Al(III)OEP) was found to provide unmatched selectivity for fluoride over all other anions when used in an optode configuration to quantify fluoride in the range of $10^{-7} \sim 10^{-3}$ M. The polymer film used in this earlier work included a pH chromoionophore along with the Al(III) porphyrin, and optical detection was based on a co-extraction principle [21]. Use of Al(III) porphyrins in polymeric films to create highly selective potentiometric fluoride sensors has also been reported, with the optimal potentiometric response being achieved using a sterically hindered picket fence type Al(III)-tetraphenylporphyrin structure [22]. Al(III)-salophenes as well as other porphyrin structures have also been examined for creating optical and electrochemical fluoride sensors [23,24].

It is important to understand how metalloporphyrins of group IIIA metal ions exhibit their selective ligation with given anions. Although In(III)-porphyrins exhibit good selectivity for chloride sensing [25,26], and sensors based on Ga(III)-porphyrins exhibit much improved fluoride response, Al(III)-porphyrin ionophores exhibit unrivaled selectivity for fluoride in both optical and potentiometric transduction modes. This trend is consistent with the hard-soft acid-base convention [27]; if hardness of the central metal ion increases (i.e., $\text{Al}^{3+} > \text{Ga}^{3+} > \text{In}^{3+}$), its porphyrin complex exhibits higher selectivity for fluoride, since fluoride is a hard base. This idea is further supported by the fact that high-valent non-transition metal ion (hard acid) complexes, such as zirconium(IV) porphyrins, have also been shown to be useful for developing fluoride selective sensors [12,14].

It is known that scandium(III) exhibits similar complexation chemistry as Al(III). For example, among the group IIIB cations in the periodic table, the coordination number of Sc(III) is same as Al(III) (i.e., ≤ 6) and less than that of other group IIIB cations (i.e., > 6) [28]. In addition, Sc(III) can form the cryolite phase, Na_3ScF_6 , which is the chemical equivalent of the naturally occurring cryolite Na_3AlF_6 [29]. This fact suggests that Sc(III) complexes may behave like Al(III) complexes in terms of their interaction with fluoride. Herein, we examine the chemistry of Sc(III) octaethylporphyrin (Sc(III)OEP) in plasticized polymeric films in an effort to devise an optical fluoride selective sensor. It will be shown that very high selectivity for fluoride over other inorganic anions can be achieved based on formation of a unique difluoro-bridged dimer when fluoride is present in solutions that contact polymeric films doped with Sc(III)OEP.

2. Experimental

2.1 Reagents

Hydroxo(2,3,7,8,12,13,17,18-octaethylporphyrinato) scandium(III) (Sc(III)OEP-OH) was prepared according to previous literature reports [30,31]. 4',5'-Dibromofluorescein octadecyl ester (ETH 7075), high molecular weight poly(vinyl chloride) (PVC), o-nitrophenyl octyl ether (o-NPOE), and bis(2-ethylhexyl) sebacate (DOS) were used as received from Fluka (Ronkonkoma, NY). Tetrahydrofuran (THF) was from Sigma-Aldrich (St. Louis, MO) and distilled before use. Glycine was obtained from Fisher Scientific (Cincinnati, OH). Acids (phosphoric acid and hydrofluoric acid (35 wt. % in water)), sodium salts of anions (bromide, chloride, nitrate, perchlorate, phosphate monobasic, salicylate, and thiocyanate), and trans-1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid (CDMA) were obtained from Sigma-Aldrich.

2.2. Film preparation

Optical film cocktails were prepared by dissolving Sc(III)OEP-OH (1.0 mg), ETH 7075 (100 mol% relative to Sc(III)OEP-OH), a given plasticizer (66 mg), and PVC (33 mg) in 5 mL THF. The films used in the transmission mode were manually cast using a pipette on a glass slide (ca. 50 mm × 9 mm × 1 mm) or on a silica glass slide (77 mm × 25 mm × 1 mm; Chemglass, Vineland, NJ). The films used for the waveguide experiments were spin-coated on the silica glass slide, using a spin coating device (model SGS-G3-8; Cookson Electronics, Providence, RI): 150 μ L of cocktail was loaded on the substrate and spun at 1000 rpm for 20 s. The film was dried overnight and used within 1 ~ 3 days. The film should be kept in the dark to minimize any loss by photo-decomposition.

2.3. Optical measurements

Optical studies of the dimer-monomer chemistry of Sc(III)OEP were performed in the transmission mode. In this arrangement, a UV-Vis spectrophotometer (model Lambda 35; Perkin-Elmer, Boston, MA) was employed with a polymer film-coated glass slip in the quartz cuvette [25] or with a flowcell made of the fused silica glass coated with the optical sensing film, a teflon gasket (0.18 mm thickness), and another fused silica glass slide with inlet and outlet holes. Continuous flow of buffer (1 mL/min) was achieved via a peristaltic pump (Miniplus-3; Gilson, Middleton, WI).

Optical response for fluoride sensing was assessed by determining the degree of deprotonation (α) of the ETH 7075 chromoionophore or the degree of dimerization of Sc(III)OEP in the polymer sensing film. According to the coextraction principle of bulk optode [21], when an analyte anion in the aqueous phase is introduced into the organic phase and tightly binds with an ionophore, a cation is transferred into the organic phase at the same time to maintain charge neutrality in both phases. When ETH 7075, a proton binding chromoionophore, is doped in the organic phase, it is the proton that partitions into the film along with anions. Therefore, degree of anion transfer can be monitored by looking at protonation ($1-\alpha$) (or deprotonation (α)) of the ETH 7075, and the degree of protonation (or deprotonation) is correlated to the activity of analyte anion in the aqueous phase. Since Sc(III)OEP employed as the ionophore also changes its Soret band by binding with fluoride, absorbances of ETH 7075 and dimeric Sc(III)OEP have been measured simultaneously to evaluate the degree of deprotonation (α) and dimerization, respectively.

Optical anion sensors based on the coextraction mechanism generally achieve better detection limit by decreasing pH since the anionic response depends on the product of the concentration of anion and the concentration of protons in the aqueous phase. In this work, all the measurements were done at pH 3.0 where about 60% of fluoride exists as HF ($pK_a = 3.17$) and the content of fluoride is described in terms of total concentration of fluoride, which is the sum of anionic fluoride and neutral hydrogen fluoride in the aqueous phase.

While selectivity was studied in the same transmission mode, reversibility, response time measurements, and flow injection analysis (FIA) of several samples containing fluoride were carried out using a waveguide optical sensing configuration [32]. The same flow-cell used in the transmission mode was fixed horizontally with two light-coupling prisms placed on the waveguide (a fused silica glass slide spin-coated with the fluoride sensing polymer film on one side). The light from a deuterium-tungsten lamp (DT-1000; Ocean Optics, Dunedin, FL) was guided into one prism by an optical fiber connected with a collimating lens at the end. The light coming out from the second prism was collected into another optical fiber by a collimating lens. A CCD detector (USB 2000; Ocean optics) was connected to the optical fiber and the spectrum was digitized from 200 to 800 nm. In the FIA arrangement, a 50 μ L injection loop

was used and the cell volume was ca. 40 μL . The optical response at 550 nm was recorded simultaneously every 0.5 seconds.

For most of experiments, a 0.05 M glycine-phosphate buffer (pH 3.0) was used as the background electrolyte. This buffer was prepared by adjusting the pH of a 0.05 M glycine solution with phosphoric acid. For FIA experiments for commercial mouth wash samples, total ionic strength adjustor buffer was prepared from 0.5 M glycine, 1 M NaCl, and 2.9 mM CDMA with the pH adjusted to 3.1 by adding phosphoric acid. Anion solutions were prepared by dissolving corresponding sodium salts in the same buffer. A stock fluoride solution (1 M) was prepared by dilution of hydrofluoric acid solution with the buffer and the pH was adjusted to ca. 3 by addition of sodium hydroxide. For selectivity experiments, 50 mL of buffer was pumped into the flow-cell and its outlet was introduced back into the buffer reservoir. The concentration was adjusted by adding increasing volumes of the test anion salt solution to the reservoir. For response time measurements, a two-way flow configuration with a switch valve [32] was employed in order to minimize the concentration gradient between the two concentrations that were being tested.

2.4 X-ray crystallography

The single crystal of the bis(μ -fluoro) Sc(III)OEP dimer was prepared by dissolving Sc(III) OEP-OH (5 mg) in dichloromethane (5 mL) and equilibrating with 2 M fluoride solution (ca. pH 3) several times. The organic phase was then dried with sodium sulfate and filtered. Hexanes were carefully added to the filtrate and then this dichloromethane/hexanes solution was left partially open to air for a couple of days in the dark as crystals were formed at 22 $^{\circ}\text{C}$.

A crystal of dimensions $0.36 \times 0.34 \times 0.04$ mm was mounted on a standard Bruker SMART CCD-based X-ray diffractometer equipped with a LT-2 low temperature device and normal focus Mo-target X-ray tube ($\lambda = 0.71073$ Å) operated at 2000 W power (50 kV, 40 mA). The X-ray intensities were measured at 123(2) K; the detector was placed at a distance 4.969 cm from the crystal. A total of 2525 frames were collected with a scan width of 0.5° in ω and ϕ with an exposure time of 30 s/frame. The integration of the data yielded a total of 23732 reflections to a maximum 2θ value of 49.64° of which 5309 were independent and 3834 were greater than $2\sigma(I)$. The final cell constants were based on the xyz centroids of 4623 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection; the data were processed with SADABS and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 6.12) software package, using the space group $P1\bar{1}2_1$ with $Z = 1$ for the formula $\text{C}_{72}\text{H}_{88}\text{N}_8\text{Sc}_2$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. The molecule lies on an inversion center in the crystal lattice. The fluoride bridging atoms are disordered over two positions and were refined with partial occupancy atoms constrained to sum to one. Full matrix least-squares refinement based on F^2 converged at $R1 = 0.0730$ and $wR2 = 0.2347$ [based on $I > 2\sigma(I)$], $R1 = 0.1050$ and $wR2 = 0.2500$ for all data [33].

3. Results and Discussion

3.1 Bis(μ -hydroxide) dimer and bis(μ -fluoro) dimer of Sc(III)OEP

Metalloporphyrins can be utilized not only as anion-selective ionophores but also as chromophores that exhibit optical changes upon binding of target anions. One of the best examples reported in the literature is an optical chloride sensor based on a dimer-monomer equilibrium of indium(III) porphyrin where a hydroxo-bridged dimer of In(III)OEP is broken into corresponding monomeric species as chloride replaces hydroxide as an axial ligand of the metalloporphyrin. This results in a simultaneous optical shift of the Soret absorption band [25]. Scandium(III) porphyrins are also known to form dimers that exhibit a hypsochromic

shift of the Soret band from monomeric scandium(III) porphyrins. Gouterman et al. [30] reported the X-ray structure of the μ -oxo-dimer of Sc(III)OEP and the observed a blue shift of the Soret band for this dimer species (vs. monomer) and this observation was discussed from a theoretical structural standpoint. Arnold et al. [31] argued that the bis(μ -hydroxide) dimer of Sc(III)OEP (see Figure 1a) could be observed, depending on the degree of hydration during crystal growth. However, there have been no previously reported studies of dimer-monomer chemistry of Sc(III)OEP as a (chromo)ionophore for sensing purposes. In the present work, the dimer-monomer equilibrium of Sc(III)OEP is utilized for the detection of fluoride using organic polymer phases doped with this metalloporphyrin.

When Sc(III)OEP(OH) is incorporated within a plasticized film, a similar UV-Vis spectral change is observed. The dimeric band is observed within a plasticized polymeric film before contact with solutions containing fluoride, and this species is believed to be the bis(μ -hydroxide) dimer (Figure 1a) since the organic phase in contact with aqueous phase (no fluoride) is saturated with water. The formation of the bis(μ -hydroxide) dimer of Sc(III)OEP does not require any ionic sites in the organic phase since it is a neutral species. This is in contrast to Ga(III)OEP and In(III)OEP, where dimerization results in positively charged single hydroxo-bridged dimers only in the presence of anionic additives (e.g., tetraphenylborate derivatives) within the organic phase [34]. Hence, the degree of dimerization will be a function of the initial concentration of Sc(III)OEP-OH in the organic polymer film phase if there are no ligands present other than OH⁻. Indeed, when Sc(III)OEP-OH alone is doped within plasticized (o-NPOE as a plasticizer) PVC films at high concentrations (3 wt%, 50 mmol/kg), the observed Soret band is at 393 nm (see Figure 2a). At lower concentrations (0.7 wt%, 12 mmol/kg), the observed Soret band is at 408 nm. Since it is known that the corresponding dimer and monomer species in chloroform exhibit Soret bands at 390 nm and 405 nm, respectively [30], it is reasonable to assign the 393 nm band observed in the PVC film as a dimer and the 408 nm band as originating from a monomer.

When similar PVC films (Sc(III)OEP-OH(1 wt%)/o-NPOE(66 wt%)/PVC(33 wt%)) are exposed to fluoride ion in the bathing solution (pH 3.0 buffer), as the fluoride concentration is increased, the absorbance at 393 nm increases and the absorbance at 408 nm decreases (see Figure 2b). Since the band at 393 nm in Figure 2a is believed to originate from a dimeric structure, the data shown in Figure 2b suggests fluoride binding may initiate the conversion of monomeric porphyrin to the dimeric porphyrin within the polymeric film, even when the porphyrin is present at concentrations where only minimal bis(μ -hydroxide) dimers form spontaneously in the absence of fluoride.

To prove that fluoride can promote the formation of a dimer Sc(III)OEP species, an organic phase solution of dichloromethane containing 1 mg/mL of Sc(III)OEP-OH was equilibrated with an aqueous phase of 2 M fluoride solution at pH 3.0. The organic phase was separated, dried with sodium sulfate, and filtered. Hexane was added into the clear and dark red filtrate. This hexane-dichloromethane mixture was left in the dark and allowed to slowly evaporate, which led to formation of crystals. Single crystal X-ray diffraction analysis of these crystals yielded the dimer structure shown in Figure 3. The structure shows the N₄ planes (consisting of four nitrogen atoms in each porphyrin) are parallel to each other and slightly off center, and clearly bridged via two fluoride ions. These structural features are quite similar to the reported bis(μ -hydroxide) dimer [31]. The structural parameters are summarized in Table 1. The only difference is that the bis(μ -fluoro) dimer has slightly shorter bond lengths between the Sc(III) and fluorides, a larger F-Sc-F angle, and a smaller Sc-F-Sc angle compared to the bis(μ -hydroxide) dimer species. As a result, the distance between two N₄ planes of bis(μ -fluoro) dimer is 4.910 Å, which is 0.15 Å shorter than that of bis(μ -hydroxide) dimer (5.06 Å). These dimeric structures are fairly distinctive from μ -hydroxo-dimeric structures of Ga(III)OEP and In(III)OEP [34], which have previously been utilized as ionophores. The most prominent

difference of the Sc(III)OEP-dimers from the μ -hydroxo-dimers is orientation of the two porphine ring planes (Table 1). That is, ring planes of Sc(III)OEP dimers are essentially parallel with only a small torsion angle (2.09°), while those of In(III)OEP dimers are tilted with a torsion angle of 22.85° .

Even with these configurational variations, similar hypsochromic shifts of the Soret band are observed for bis(μ -fluoro) dimer species of Sc(III)OEP as observed for the μ -hydroxo dimers of In(III)OEP and Ga(III)OEP. These blue shifts can be explained conceptually by exciton coupling theory [35]. When two dyes are placed in parallel, an energy level of an excited state splits into two energy levels; the lower level is with two transition dipole moments aligned in a opposite direction, which is optically inactive, and the higher level is the one with the two dipole moments in a same direction and, therefore, optically active. The energy gap between these two levels is varied by the distance and the relative orientation between the two dyes.

Considering the fact that most of axial anion ligation reactions with monomeric metalloporphyrins do not cause a significant shift in the Soret band $\lambda_{\max}$ by more than 5 nm, and that the crystal structure obtained in the presence of fluoride is the bis(μ -fluoro) dimer, it is likely that the optical fluoride response of Sc(III)OEP observed in the polymeric films, as shown in Figure 2b, can be attributed to dimer formation in the organic phase induced by the presence of fluoride in the aqueous solution. The reaction can be expressed by the following equilibrium:

where L denotes the Sc(III)OEP species in the polymer film. Species in the aqueous phase are denoted with the subscript (aq) and species in the film are denoted without any subscript. In principle, the direct dimerization reaction based on the presence of fluoride in the aqueous phase can be utilized to devise a highly selective fluoride sensor. However, such an approach to obtain a practical optical sensor for fluoride has certain limitations. Indeed, the bis(μ -fluoro) dimer is not optically distinguishable from the bis(μ -hydroxide) dimer, and some small amount of the bis(μ -hydroxide) dimer can form in the polymer film, depending on the initial concentration of Sc(III)OEP used to cast the film. In addition, it is not easy to fully assess the sensor selectivity pattern by using polymer films doped with only the Sc(III)OEP species since the monomer absorption bands can shift somewhat in location, depending on which anions are present as counter-anions within the polymer (based on anion exchange of initial hydroxide ligand with sample phase anions). Therefore, to further evaluate the use of Sc(III)OEP as an ionophore for optical fluoride sensing, a lipophilic pH chromoionophore, ETH 7075 (see Figure 1b), was also added to the polymeric film (at 100 mol % of Sc(III)OEP level) to prevent any initial formation of the bis(μ -hydroxide) dimer and to determine selectivity patterns by monitoring intensity of the absorbance band corresponding to the protonated form of the ETH 7075 species (i.e., based on co-extraction of protons along with fluoride ion).

3.2 Optical fluoride sensor

All experiments to evaluate the more practical fluoride sensing films (with Sc(III)OEP and ETH 7075 together in the polymeric film) were carried out in a flowing system (~ 1 mL/min) using either a spectrophotometer for selectivity determinations, or a waveguide-configuration for reversibility and response time studies. Each anion response was obtained in a 0.05 M Glycophosphate (pH 3.0) buffer, and the optical signal was measured as the degree of protonation ($1-\alpha$) of ETH 7075 in the polymer film (see Experimental Section). It should be noted that while only the absorbance changes of the ETH 7075 dye are used for sensing purposes, the Soret band $\lambda_{\max}$ for the Sc(III)OEP species also shifts to a lower wavelength (393 nm) when

fluoride is extracted into the films, indicating that the dimeric porphyrin species still forms in the presence of the added ETH 7075 species (see below, Figure 6 (a)).

3.2.1 Selectivity—As shown in Figure 4, the Sc(III)OEP/ETH7075-based films yield favorable optical response toward both fluoride and salicylate when $1-\alpha$ is plotted as a function of anion concentration equilibrated with the films (in the flowing solutions). Responses to all other anions are far less, even for highly lipophilic anions such as ClO_4^- , SCN^- , and NO_3^- . This selectivity pattern (i.e., $\text{Sal}^-, \text{F}^- \gg \text{ClO}_4^-, \text{SCN}^-, \text{NO}_3^- > \text{Br}^-, \text{Cl}^-$) deviates significantly from the classical Hofmeister series [36]. The hardness of fluoride as a base suggests that hard acids have higher affinity for fluoride than soft acids. Previous success in using Al(III) porphyrin and salen complexes [19,20,22,23] as well as zirconium(IV) complexes [12-14,17] as ionophores to devise fluoride selective sensors (electrochemical and optical) is consistent with this “hard-soft acid-base” concept. Sc(III) porphyrins should, therefore, be good candidates for devising fluoride sensors and the selectivity pattern illustrated in Figure 4, clearly supports this prospect.

It is known that the ligation properties of metal cation-ligand complexes are dependent on the surrounding solvation environment of the interacting species within the organic polymeric phase. Hence, the nature of the plasticizer (e.g., dielectric constant) can also play a significant role in altering the strength of interaction between the Sc(III)OEP ionophore and fluoride, as well as other anions. Therefore, the response and selectivity of the optical fluoride sensor was examined using two different plasticizers, o-NPOE ($\epsilon = 21$) and DOS ($\epsilon = 2.4$) [37]. As shown in Figure 4a, the films prepared with DOS exhibits slightly better selectivity over most lipophilic anions (ClO_4^- , SCN^- , NO_3^-) than films prepared with o-NPOE, while selectivity for salicylate shifts only slightly (less selective) (see also Table 2). At the same time, the detection limit for fluoride in using DOS as the plasticizer is lower than when o-NPOE is employed. This behavior can be explained based on the dielectric constant of plasticizers tested. In general, the higher dielectric constant of o-NPOE should support greater affinity toward fluoride, and thus better response for fluoride is expected when using this plasticizer. However, fluoride is not the only species that is solvated by the membrane solvent. Sc(III)OEP and ETH 7075 are also dissolved in the “organic liquid” film. Given the highly symmetric structure of the bis(μ -fluoro) dimer species, it is expected that this dimer would have lower polarity than Sc(III)OEP monomers. Thus, it is likely that the bis(μ -fluoro) dimer is more stable in the low dielectric constant medium than the ligated monomer. Hence, lower detection limits and improved selectivity over most lipophilic anions (ClO_4^- , SCN^- , NO_3^-) using the DOS plasticized film may be attributed to the lower polarity of the bis(μ -fluoro) dimer.

The anion selectivity of the Sc(III)OEP/ETH 7075 doped films can be estimated more quantitatively by comparing the concentrations of anions required to achieve $\alpha = 0.5$. The complete response functions of the anions for which relatively small optical responses are observed can be projected by extrapolating curves if the exact response function is known. The response function varies depending on the specific equilibrium that takes place for each anion with the Sc(III)OEP species and chromoionophore, in the polymer phase. For the fluoride response, the following equilibrium is expected:

When total concentration of the porphyrin and the chromoionophore is identical, the corresponding response function is given by:

$$[Y^-]_{(aq)} = \left(\frac{1}{\sqrt{2} L_T K_F [H^+]_{(aq)}} \right) \frac{(1 - \alpha)^{3/2}}{\alpha^2} \quad (\text{eqn. 1})$$

where α is degree of deprotonation, K_F is equilibrium constant, and L_T is total concentration of ionophore. However, as can be seen in the Figure 5, the experimental data fits best with the function:

$$[F^-]_{(aq)} \propto \frac{(1 - \alpha)}{\alpha} \quad (\text{eqn. 2})$$

One of the possible equilibria that yields eqn. 2 is:

This equilibrium suggests not only an interaction between the Sc(III)OEP (L^+) and the chromoionophore (C^-) (e.g., strong π - π type interaction, as suggested for ETH 7075 and Al(III)OEP [19]), but also a certain degree of affinity between the dimeric porphyrin and the protonated ETH 7075 in the film. Further effort to identify such complexes formed in the plasticized film is ongoing. Therefore, rxn. 3 should remain as a hypothetical equilibrium at this point.

The response curve for salicylate follows eqn. 2, which suggests the following equilibrium:

However, for most inorganic interferent anions tested (see Figure 4), the response function fits well with the form:

$$[Y^-]_{(aq)} \propto \frac{(1 - \alpha)^2}{\alpha} \quad (\text{eqn. 3})$$

and eqn. 3 suggests the following equilibrium reaction:

To quantify the selectivity coefficient from different response functions, the concentration of anions that yield $\alpha = 0.5$ are compared. Table 2 summarizes the optical selectivity coefficients for anions relative to fluoride based on the absorbance change of ETH 7075 at 550 nm. As can be seen in Table 2, the Sc(III)OEP/ETH 7075-doped film exhibits the best response toward fluoride and salicylate (nearly equal), but extremely high selectivity over all other anions tested, using either o-NPOE or DOS as the plasticizers for the film. It also reports the detection limits for each type of film, as defined by the limiting sensitivity (a slope 1/5 of the maximum) of the response function. As suggested above, slightly improved detection limits are obtained using DOS, the lower polarity plasticizer.

It should be pointed out that if the absorbance of the dimer band at 393 nm is also monitored, only fluoride binding yields an observable optical change. As can be seen in Figure 6, fluoride response increases absorbance at 393 nm which corresponds to a dimeric Sc(III)OEP complex, whereas salicylate increases 408 nm which corresponds to a monomeric Sc(III)OEP complex. Considering that most of anions except for fluoride and hydroxide form monomeric complexes and that deprotonated ETH 7075 prevents hydroxo-dimer formation, the absorbance change

at 393 nm is an evidence of fluoride in the sample phase. Therefore, by monitoring fluoride-specific response (393 nm) and non-specific anionic response (550 nm) simultaneously, selectivity for fluoride could potentially be further improved.

3.2.2 Reversibility, response time, and lifetime—Rapid and fully reversible optical response toward fluoride of both the DOS and NPOE plasticized Sc(III)OEP/ETH 7075-doped PVC films are clearly shown in Figure 7 (monitoring at $\lambda = 550$ nm, the λ_{max} of the deprotonated ETH 7075 species). This figure illustrates response between two fluoride levels; $[F_{\text{total}}]_{\text{(aq)}} = 10^{-2}$ M ($\alpha \sim 0.2$) and $[F_{\text{total}}]_{\text{(aq)}} = 10^{-4}$ M ($\alpha \sim 0.8$) in a flow system (flow rate 1 mL/min) using a waveguide based optical sensor configuration. For the o-NPOE plasticized film, the t_{90} response times (time required to reach 90% of full equilibrium) were measured as ~ 6 sec and ~ 4 sec when changing from blank buffer to 10^{-4} M fluoride and 10^{-2} M fluoride, respectively. The t_{90} values of the reverse optical response were measured as ~ 6 sec and ~ 9 sec in going from 10^{-4} M and 10^{-2} M to the blank buffer, respectively. Response times for the DOS plasticized fluoride sensing films are 25 $\sim$ 33 % longer than the corresponding o-NPOE plasticized films, owing to the higher viscosity of DOS [38]. Compared to previously reported Al(III)OEP/ETH 7075-doped films [19,20], the Sc(III)OEP/ETH 7075 system exhibits a higher detection limit but faster response times. This suggests that Sc(III)OEP-F binding is not as strong as Al(III)OEP-F, and that reversible ligation of fluoride to Sc(III)OEP is kinetically more facile, making them more suitable as detection systems for flow-injection type measurements.

The lifetime of the Sc(III)OEP/ETH 7075-doped films is limited by leaching of active compounds and photo-bleaching of optically active species. Over a few hours of continuous flow-through measurements, loss of Sc(III)OEP from the film is observed. Based on the absorbance changes of Sc(III)OEP and ETH 7075, loss of Sc(III)OEP is about 13%/h and loss of ETH 7075 is about 4%/h. However, such loss is anticipated using the waveguide configuration, where extremely thin polymeric films are employed ($< \text{ca. } 0.5 \mu\text{m}$) in conjunction to achieve fast response times with a flow-through arrangement [32]. If thicker films were employed, at the expense of response time, greater stability would be possibly achieved. The optical drift that occurs due to continuous loss of active species from the sensing film can be corrected for by frequent monitoring of background absorbances at the detection wavelengths during FIA experiments.

Another important effect that limits the operational lifetime of the sensors based on ScOEP/ETH 7075-doped films is photo-bleaching of the Sc(III)OEP species. When the film is exposed to the ambient light, Sc(III)OEP slowly decomposes and loses its optical properties. Such photodegradation occurs over a 2-3 day period, and results in loss of the Soret band and Q-bands, which are characteristic absorption bands of metalloporphyrins. This can be prevented by storing films in the dark before use. Given the extremely low cost of the polymeric sensing films, changing flow through detectors after a given period of use can overcome this photobleaching issue, as well as loss of active components by continuous use in the flow-injection analysis mode.

3.3 Preliminary Applications

Commercial samples of mouth wash were tested with the FIA configuration. Each of the samples were diluted 10 times with total ionic strength adjustor buffer (0.5 M Glycine-phosphate buffer, pH 3.1 with 1 M NaCl and 2.9 mM CDMA) before measurement. Potentiometric measurements using LaF₃ electrode were done with same samples as well. For example, one sample with fluoride (PhosFlur, Colgate, $[F_{\text{total}}] = 0.01112$ M ($n = 3$, standard deviation (s) = 0.00004, measured by LaF₃ electrode) yielded both absorbance changes at 393 nm and 550 nm and $[F_{\text{total}}]$ was measured to be 0.0114 M ($n = 6$, $s = 0.0002$) based on the

absorbance change at 550 nm. Another sample without fluoride (biotene, Laclede, Inc) showed absorbance change only in 550 nm, indicating fluoride level is less than the lower detection limit. However, in the other sample (ACT, Johnson & Johnson, $[F_{\text{total}}] = 0.013 \text{ M}$ by LaF_3 electrode), absorbance change at dimer band is too high compared to the change of ETH 7075 band. It has been confirmed that lipophilic cationic species such as cetylpyridinium chloride (anti-septic reagent) were responsible for this observation; not only protons but also lipophilic cations facilitated fluoride coextraction into the film and this increased the level of bis(μ -fluoro) dimeric band. Currently, further studies are underway to resolve this lipophilic cation interference effect.

4. Conclusions

A new fluoride selective optical sensing polymeric film based on using a Sc(III)OEP ionophore is described. Fundamental studies of the dimer-monomer chemistry of the Sc(III)OEP species within the plasticized films suggests that this species forms a difluoro-bridged dimer when the film is bathed in sample solutions containing fluoride ion. Addition of a chromoionophore (ETH 7075) to the films helps stabilize the response, and provides an alternate wavelength to monitor optical fluoride response. Based on this dimer-monomer equilibrium, an optical fluoride sensor has been evaluated in terms of selectivity, reversibility, response time, and lifetime. The response range of the optimized film for fluoride is about $10^{-4} \sim 10^{-2} \text{ M}$ and selectivity for fluoride over ClO_4^- , SCN^- , NO_3^- , Br^- , Cl^- is quite high. Only salicylate is a major interference. Fully reversible and fast response of the sensing film enables this configuration to be employed as an optical fluoride selective detector in an FIA system. These studies suggest that films doped with Sc(III)OEP and ETH 7075 may provide an alternative to previously reported Al(III)-porphyrins and salens for the preparation of simple fluoride selective optical and possibly potentiometric sensors.

Acknowledgements

We greatly acknowledge the National Institute of Health, for supporting this work (EB-000784) and Dr. Ibrahim H. A. Badr for his valuable comments.

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33. Crystallographic data for [Sc(III)OEP]₂(μ-F)₂: C₇₂H₈₈F₂N₈Sc₂, M = 1193.42 g mol⁻¹, orange plate, size 0.36 × 0.34 × 0.04 mm³, triclinic, space group P-1, a = 10.940(4) Å, b = 13.072(5) Å, c = 13.303(5) Å, α = 117.987(5)°, β = 99.495(6)°, γ = 103.240(6)°, V = 1551.0(10) Å³, Z = 1, T = 123(2) K, ρ_{calcd} = 1.278 Mg/m³, μ = 0.275 mm⁻¹, 23 732 reflections, 1.80° ≤ θ ≤ 24.82°, 5309 independent reflections, R_{int} = 0.0780, 3834 reflections with I ≥ 2σ(I), 397 parameters, R1 = 0.1050, wR2 = 0.2500 (all data), GOF = 1.097, Crystallographic data can be obtained free of charge as CCDC 645795 from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or 12 Union Road, Cambridge CB2 1EZ, U.K.
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Figure 1.
Structures of (a) bis(μ-hydroxide) dimer of Sc(III)OEP and (b) ETH 7075.

Figure 2.

(a) Absorbance of Sc(III)OEP in different concentrations in the o-NPOE/PVC films when the film is conditioned pH 3.0 Gly-phosphate buffer (0.05 M). (b) Absorbance change of Sc(III)OEP upon fluoride response at pH 3.0 with the film Sc(III)OEP(OH) (1 wt%)/o-NPOE (66 wt %)/PVC (33 wt%).

Figure 3. crystal structure of bis(μ-fluoro) dimer of Sc(III)OEP (left). Diagram of structural characteristics of $[\text{Sc}(\text{III})\text{OEP}]_2(\mu\text{-F})_2$ (right).

Figure 4.

Response curves for anions (chloride (■), bromide (×), nitrate (*), thiocyanate (●), perchlorate (◆), salicylate (▲), and fluoride (+)) in (a) DOS/PVC film and (b) o-NPOE/PVC film. Black points represent experimental data points, and grey lines are based on best-fitting curves for

each response. Film compositions : Sc(III)OEP(OH) (1 wt%)/ ETH 7075 (100 mol%) / plasticizer (DOS or o-NPOE 66 wt%)/ PVC (33 wt%).

Figure 5. Fluoride response (●) at different total fluoride concentration in the 0.05 M Gly-phosphate buffer (pH 3.0) with the film composition : Sc(III)OEP (1 wt%)/ETH 7075 (100 mol%)/o-NPOE (66 wt%)/PVC(33 wt%) and theoretical response curves based on rxn. 2 and rxn. 3.

Figure 6. Spectral shift of Sc(III)OEP/ETH 7075/NPOE/PVC film upon (a) fluoride and (b) salicylate responses. Absorbance change at 550 nm is attributed to both anions, while absorbance change at 393 nm is solely by fluoride response.

Figure 7. Reversible response (550 nm) to fluoride between 10^{-4} M and 10^{-2} M in (a) DOS/PVC film and (b) o-NPOE/PVC film.

Table 1
Comparison of the various dimeric structures of metalloporphyrins

	[Sc(III)OEP] ₂ (μ-F) ₂ [33]	[Sc(III)OEP] ₂ (μ-OH) ₂ [31]	[Ga(III)OEP] ₂ (μ-OH) ⁺ [34]	[In(III)OEP] ₂ (μ-OH) ⁺ [34]
Distance (Å)				
Metal to N ₄ -plane	0.796	0.84	0.225	0.42
Metal to N	2.188	2.203	2.033	2.136
Metal to O/F	2.046	2.078	1.945	2.119
N ₄ -plane to N ₄ -plane	4.910	5.06	3.43 ^a	3.76 ^a
Angle (°)				
Dihedral ^b	0.00		15	23
Torsion ^c	2.09		22.23	22.85
Metal-O/F-Metal	108.96	109.90	151.96	114.45
O/F-Metal-O/F	71.04	70.12		

^a Closest distance between two carbons in two porphyrin macrocycles [33].

^b The angle between the two porphyrin mean planes.

^c Average N-M-M'-N' torsion angle.

Table 2

Selectivity coefficient calculated from theoretical response curves for anions and detection ranges for fluoride.

Selectivity ($\log k_{\text{opt}}F,Y$)			
DOS		o-NPOE	
Sal ⁻	0.2	F ⁻	0
F ⁻	0	Sal ⁻	-0.1
SCN ⁻	-3.0	SCN ⁻	-2.7
NO ₃ ⁻	-3.2	ClO ₄ ⁻	-3.1
ClO ₄ ⁻	-3.8	NO ₃ ⁻	-3.5
Br ⁻	-5.0	Br ⁻	-4.7
Cl ⁻	-5.5	Cl ⁻	-4.9
Detection range for F ⁻			
$3.4 \times 10^{-5} \sim 1.1 \times 10^{-2} \text{ M}$		$7.7 \times 10^{-5} \sim 2.5 \times 10^{-2} \text{ M}$	