Communication

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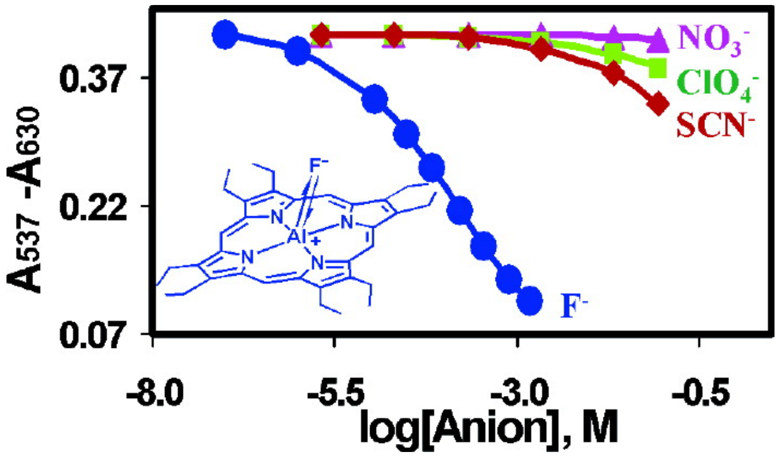
J. Am. Chem. Soc., **2005**, 127 (15), 5318-5319• DOI: 10.1021/ja0500153 • Publication Date (Web): 26 March 2005



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

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Highly Selective Optical Fluoride Ion Sensor with Submicromolar Detection Limit Based on Aluminum(III) Octaethylporphyrin in Thin Polymeric Film

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Over the past 35 years, considerable success has been realized in the development of electrochemical (potentiometric ion-selective electrodes) and optical sensors with selective response to given cations using various natural antibiotics (e.g., valinomycin), crown ethers, calixarenes, and other ionophore type structures within thin polymeric membranes/films.[1−6] However, the design of analogous anion selective sensors has been far more difficult owing to the lack of suitable lipophilic host molecules that exhibit specificity for interaction with given anions. Especially challenging are organic membrane/film type sensors with selective response to fluoride because of the very negative Gibbs free energy of hydration of this anion relative to others (−436 kJ/mol).[7] Hence, achieving fluoride extraction into low dielectric constant polymeric films with selectivity over anions with much more positive free energies of hydration (e.g., perchlorate, −201 kJ/mol) requires an exceptionally high degree of anion binding discrimination by the host molecule to overcome the favorable single ion partition coefficients associated with such interferent anions.[8] Herein we demonstrate that a new, fully reversible optical sensor with extraordinary selectivity for fluoride ion can be prepared using thin polymer films containing aluminum(III)octaethylporphyrin (Al[OEP]) and a lipophilic pH indicator.

A variety of metal−ligand complexes, particularly metalloporphyrins and related structures, have been examined as potential ionophores in organic membranes/films to prepare useful anion sensors,[6,9,10] using both optical and potentiometric modes of detection. Selectivity is achieved based on the relative binding interactions of anions as axial ligands with the metal ion−ligand complexes within the organic films. Very recent work has suggested that films doped with gallium(III) and zirconium(IV) porphyrins display an enhanced degree of selectivity for fluoride ion when tested in a potentiometric measurement mode,[11−13] although sensitivity is less than desired for certain applications (e.g., detecting fluoride levels in municipal drinking waters) and selectivity over some anions is still marginal for practical applications.

The fluoride sensing film described here employs the principles of anion/proton co-extraction chemistry to achieve optical response.[14] A thin polymeric film (2−5 μm; *o*-nitrophenyl octyl ether (*o*-NPOE) plasticized poly(vinyl chloride)) doped with chloro (Al[OEP]) as the fluoride recognition element and a lipophilic pH indicator (ETH-7075; 4′,5′-dibromofluorescein octadecyl ester) (see Figure 1S in Supporting Information) is cast on a quartz slide. The casting cocktail contains 72 mmol/kg Al[OEP], 33 wt % PVC, 66 wt % *o*-NPOE, and 100 mol % (relative to fluoride ionophore) ETH-7075. The lipophilic pH chromoionophore transduces the binding event of the fluoride ion to the Al[OEP] in the form of an optical signal. As shown in Figure 1, when a buffer (0.1 M β-alanine adjusted to pH 3.6 using phosphoric acid) without any fluoride is flowed over the film (using flow-through configuration similar to that reported in ref 15), the deprotonated form of the indicator dye (C^-) ($\lambda_{max} = 537$ nm) is the predominant absorbance band observed in the wavelength range of 450−550 nm. As fluoride is added to the buffer, the deprotonated band decreases in intensity, and the protonated form (CH) increases in absorbance ($\lambda_{max} = 470$ nm). Interestingly, there is also a large change in the Soret band of the porphyrin itself ($\lambda_{max} = 410$ nm) (data not shown), with a substantial decrease in absorbance observed at low fluoride ion concentrations. However, use of the optical signal from the pH indicator ($\lambda_{max} = 537$ nm) provides a more reproducible and stable optical response for the film. Indeed, films prepared with Al[OEP] and 100 mol % of sodium tetrakis[bis(3,5-trifluoromethyl)phenyl]borate in place of the pH indicator showed a very slow and irreversible optical response toward fluoride ion using changes in the Soret band absorption for transduction purposes. Addition of the pH chromoionophore to the film dramatically reduces the response times and enhances reversibility of the system.

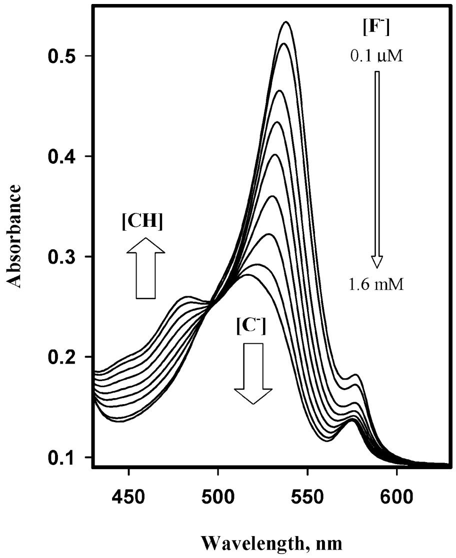

Figure 1. Spectral change of Al[OEP]/ETH-7075 based fluoride optical sensitive thin film prepared using PVC−*o*-NPOE when exposed to different concentrations of fluoride ion: 0.10, 1.0, 11, 31, and 71 μM and 0.17, 0.36, 0.80, and 1.6 mM.

The high binding affinity of aluminum ions with fluoride is well-documented in the literature.[16,17] The observed fluoride optical response is likely due to selective binding of fluoride to the Al(III) center of the porphyrin in the organic film. To maintain charge neutrality, a proton is co-extracted to protonate the pH chromoionophore (see scheme in Figure 2S, Supporting Information). Indeed, a large number of cation-selective optical sensing films have been prepared previously by co-incorporating pH chromoionophores with classical cation ionophores in polymer films. In such cases, proton exchange occurs to maintain charge neutrality within the organic film, thereby yielding the optical response.[6,14]

Figure 2 shows the optical response of the Al[OEP]/ETH-7075 doped film toward changes in fluoride, as well as a host of other

10.1021/ja0500153 CCC: $30.25

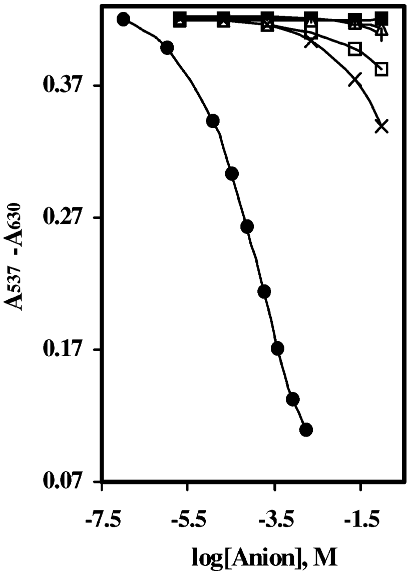

Figure 2. Response of Al[OEP]/ETH-7075 based fluoride optical sensor toward different anions: fluoride (●), thiocyanate (×), perchlorate (□), nitrite (+), nitrate (Δ), chloride, bromide, and sulfate (■). Spectral change was monitored at λ_{max} = 537 nm vs background absorbance at 630 nm.

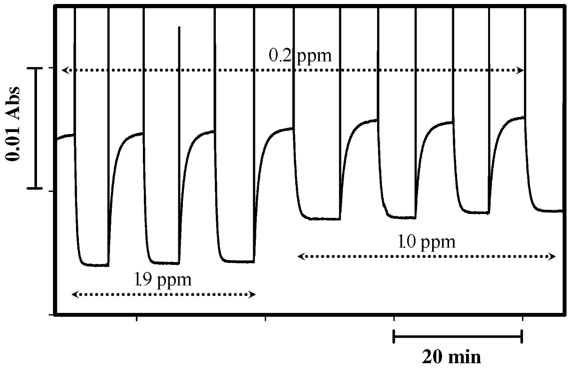

Figure 3. Response and recovery time trace for Al[OEP]/ETH-7075 based fluoride sensing film measured when alternating flow solutions containing 0.2, 1.9, and 1.0 ppm total fluoride. Absorbance at 537 nm is monitored.

anions tested under the same conditions. Optical response toward fluoride is observed over the range of 0.1 μM to 1.6 mM (or 1.9 ppb to 30 ppm) total fluoride. As also shown, selectivity for fluoride over sulfate, chloride, nitrate, nitrite, and bromide is extraordinarily high (log $k_{F,X}^{opt} < -5$), and selectivity over highly lipophilic anions such as perchlorate and thiocyanate is also unusually large (log $k_{F,X}^{opt} \leq -4$). Only hydroxide ion is a major interference, necessitating the use of low pH buffer to achieve low detection limits toward fluoride.

The response to fluoride is completely reversible in the low concentration regime. Figure 3 illustrates the absorbance signal for the deprotonated form of the chromoionophore when alternating flow solutions containing 0.2, 1.9, and 1.0 ppm total fluoride (film containing 16 mM/kg Al[OEP] and 100 mol % ETH-7075 was used in this experiment). This would be the concentration range required for monitoring fluoride in drinking water.[18] Even greater optical responses can be obtained if the films are employed as thin coatings on optical waveguides to obtain a longer effective path length for the absorbance measurements.

The selectivity achieved with this new optical fluoride sensor rivals or exceeds that reported for the classical solid-state fluoride selective membrane electrode that is based on a single crystal of lanthanum fluoride (LaF_3).[19] Use of the LaF_3 crystal type electrode is now considered the reference method for monitoring fluorination of water supplies.[20] We believe that the use of the aluminum(III) porphyrin/pH chromoionophore doped films provides a very inexpensive optical sensor with the potential for equivalent or even improved analytical performance for fluoride detection. More importantly, the ability to selectively extract fluoride into an organic film over a host of other anions is a fundamental advance and suggests that studies of this and other aluminum complexes may be fruitful for the development of polymer membrane type potentiometric fluoride selective electrodes. Such studies are now ongoing in this laboratory.

Acknowledgment. This research was supported by a grant from the National Institutes of Health (EB 000784). I.H.A.B. would like to thank Ain Shams University, Cairo, Egypt, for granting a sabbatical leave.

Supporting Information Available: Detailed scheme for the co-extraction chemistry from the aqueous sample solution into the membrane phase and chemical structures of the pH-chromoionophore and Al[OEP]. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA0500153