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Stibonium Ions for the Fluorescence Turn-On Sensing of F^- in Drinking Water at Parts per Million Concentrations

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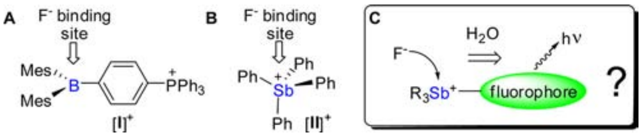
Ⓢ *Supporting Information*

ABSTRACT: The 9-anthryltriphenylstibonium cation, $[\mathbf{1}]^+$, has been synthesized and used as a sensor for the toxic fluoride anion in water. This stibonium cation complexes fluoride ions to afford the corresponding fluorostiborane **1**-F. This reaction, which occurs at fluoride concentrations in the parts per million range, is accompanied by a drastic fluorescence turn-on response. It is also highly selective and can be used in plain tap water or bottled water to test fluoridation levels.

Fluoride anion salts are commonly added to drinking water supplies and toothpaste because of their beneficial effects in dental health. In the U.S., this practice has been the center of some discussions because of the adverse effects that excessive fluoride intake may trigger. The recent lowering of the U.S. Department of Health and Human Services recommended fluoride levels from 1.2 to 0.7 ppm[1] has sparked a renewed interest in Lewis acidic main-group compounds that can be used to sense low concentrations of this anion, especially in aqueous media.[2] Examples of such Lewis acidic compounds include cationic boron compounds[3] such as $[\mathbf{I}]^+$ which react with fluoride ions to form the corresponding zwitterionic fluoroborates (Chart 1A).[4] Although the fluoride ion affinity of these cationic boranes enables sensing at the parts per million level in aqueous media, the anion binding event is accompanied by a fluorescence turn-off response, thus limiting the analytical practicality of these derivatives.[4] Some of these boranes also show evidence of slow decomposition in aqueous media. Because of these drawbacks, we are now searching for alternative fluoride ion binding platforms. Inspired by the emerging use of pnictogen-based Lewis acids in various areas of chemistry,[5] we have now turned our attention toward pnictonium ions ($[R_4Pn]^+$, Pn = pnictogen), which react with fluoride ions to form the corresponding fluoropnictoranes (R_4PnF). For example, tetraalkylphosphonium ions combine with fluoride ions to form fluorophosphoranes, albeit in strictly anhydrous and nonpolar media.[6] A higher fluoride ion affinity is displayed by stibonium ions such as $[Ph_4Sb]^+$ ($[\mathbf{II}]^+$), which, as documented in earlier reports, binds fluoride in biphasic water/CCl_4 mixtures (Chart 1B).[7] Following a recent study in which we observed fluoride binding at the antimony center of cationic transition-metal stibine complexes,[8] we decided to investigate the use of organostibonium ions as water-compatible fluoride sensors (Chart 1C). Another important objective of this study was the incorporation of a fluorescent turn-on reporter.

Chart 1



To initiate this study, we first decided to investigate the fluoride ion affinity of $[Ph_4Sb]^+$ in organic solvents. Addition of tetra-*n*-butylammonium fluoride (TBAF) to an acetonitrile solution of $[Ph_4Sb]Br$ resulted in a blue shift of the phenyl $S_2 \leftarrow S_0$ transition, a phenomenon assigned to the formation of the fluorostiborane Ph_4SbF. Fitting of these spectral data on the basis of a 1:1 binding isotherm afforded a fluoride binding constant greater than 10^6 M^{-1} (see the Supporting Information). Analogous experiments carried out with $[Ph_4P]^+$ and $[Ph_4As]^+$ and monitored by both UV−vis and NMR spectroscopy indicated that these two cations do not associate with fluoride anions under these conditions. Thus, the Lewis acidity trend observed for these tetraphenylpnictonium ions ($[Ph_4P]^+ \approx [Ph_4As]^+ \ll [Ph_4Sb]^+$) is reminiscent of that observed for halogen-bonded complexes, which become more stable as the group is descended.[9] This analogy suggests that the increased acidity observed on going from Pn = P to Sb originates from the increased polarizability and electropositivity of Sb in comparison with P and As. The larger size of the element and its ability to accommodate more ligands in its coordination sphere may also be contributing factors. These results were corroborated by DFT calculations (BP86/basis sets: 6-31G(d) for H and C; 6-31+G(d) for F, and CRENBL ECP for Pn, PCM/MeCN), which indicated that the fluoride anion affinity of $[Ph_4Sb]^+$ exceeds those of $[Ph_4P]^+$ and Ph_4As^+ by 23.2 and 15.9 kcal/mol, respectively.

Following this initial survey, we considered the incorporation of a fluorescence reporter that would turn on upon anion binding. Inspired by the pioneering work of Yamaguchi and Tamao, who showed a fluorescence turn-on response upon conversion of Ant_3P and Ant_3SiF into Ant_3PF_2 and $[Ant_3SiF_2]^-$ (Ant = 9-anthryl), respectively,[10] we prepared the triflate salt of 9-anthryltriphenylstibonium ion, $[\mathbf{1}]$OTf. This salt was characterized by ^1H and ^{13}C NMR spectroscopy, elemental

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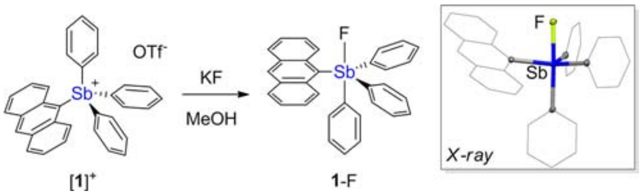
Scheme 1



analysis, and single-crystal X-ray diffraction (see the Supporting Information), which revealed that the stibonium cation adopts a tetrahedral structure comparable to those reported for other tetraarylstibonium ions. Treatment of [**1**]OTf with KF in methanol afforded an essentially quantitative yield of the corresponding fluorostiborane, **1**-F, which was also fully characterized. The presence of an Sb−F bond was confirmed by the detection of a ^{19}F NMR resonance at −75.8 ppm in CDCl$_3$, a value comparable to that for Ph$_4$SbF (−81.4 ppm in CDCl$_3$). The crystal structure of **1**-F was also determined and indicated that the more sterically demanding anthryl substituent occupies an equatorial site, while the fluoride anion adopts an axial position as in Ph$_4$SbF (Scheme 1).[11] Having established the facile conversion of [**1**]$^+$ into **1**-F, we decided to investigate the photophysical properties of each compound. The low-energy part of the absorption spectrum of [**1**]$^+$ in CHCl$_3$ is dominated by absorption bands from the anthryl substituent, as confirmed by the characteristic vibronic progression (Figure 1). Interestingly, this compound is only weakly fluorescent, with an anthryl-based emission band at λ_{fluo} = 427 nm and a quantum yield of Φ = 0.7% for [**1**]OTf. Conversion of [**1**]OTf into **1**-F by addition of TBAF induced a blue shift of the anthryl-based absorption as well as a drastic increase in the fluorescence intensity of the anthryl fluorophore from Φ = 0.7% for [**1**]OTf to Φ = 9.5% for **1**-F (λ_{ex} = 375 nm in CHCl$_3$) (Figure 1). However, no shifts in the emission spectra were observed, thus suggesting that the 0−0 transition energy is virtually the same in the two complexes. As summarized in Table 1, **1**-F becomes a brighter emitter primarily because of a decrease of the nonradiative decay channel (k_{nr}). These changes may result from (i) the decrease in chromophore−solvent interactions that would accompany the conversion of an inherently highly solvated cation ([**1**]$^+$) into a neutral compound (**1**-F) and (ii) the disappearance of any intramolecular anthryl → Sb charge transfer processes in **1**-F that would otherwise quench the excited state of the anthryl chromophore. It is also possible that changes in intramolecular aryl−aryl interactions may be involved, as previously invoked by Yamaguchi and Tamao.[10]

Table 1. Photophysical Properties of [1]OTf, 1-F, and Anthracene (for Comparison) Measured in CHCl$_3$

	τ (ns)	Φ (AQY)	k_r (s^{-1})	k_{nr} (s^{-1})
[**1**]OTf	<0.15	0.007	4.67×10^7	6.62×10^9
1-F	3.85	0.095	2.47×10^7	2.35×10^8
Ant	1.99	0.107	5.38×10^7	4.49×10^8

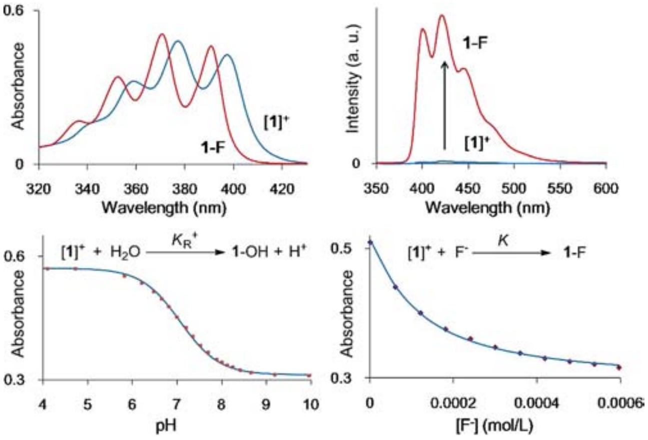


Figure 1. Top left: absorption spectra for [**1**]OTf (blue) and **1**-F (red) in CHCl$_3$. Top right: emission spectra of [**1**]OTf (blue) and **1**-F (red) in CHCl$_3$. Bottom left: spectrophotometric acid−base titration curve for [**1**]OTf in a 9:1 (v/v) H$_2$O/DMSO solution containing CTAB (10 mM) and sodium phosphate (10 mM). The absorbance was measured at 381 nm and fitted to K_{R^+} = [**1**-OH][H$^+$]/[[**1**]$^+$] with ε([**1**]OTf) = 8130 M^{-1} cm^{-1}, ε(**1**-OH) = 4460 M^{-1} cm^{-1}, and pK_{R^+} = 7.07 ± 0.05. Bottom right: fluoride titration of [**1**]OTf in a 9:1 (v/v) H$_2$O/DMSO solution containing CTAB (10 mM) and pyridine (10 mM) at pH 4.8. The absorbance was monitored at 381 nm and fitted to a 1:1 binding isotherm with K = 12000 ± 1100 M^{-1}, ε([**1**]OTf) = 8130 M^{-1} cm^{-1}, and ε(**1**-F) = 4850 M^{-1} cm^{-1}.

Initial evidence for the water compatibility of [**1**]$^+$ was provided by the observation that addition of fluoride to a solution of [**1**]OTf in 9:1 (v/v) H$_2$O/dimethyl sulfoxide (DMSO) resulted in rapid precipitation of the fluoride complex. To prevent the formation of this precipitate and to study this reaction at equilibrium, we decided to use cetyltrimethylammonium bromide (CTAB) (10 mM) as an additive. As indicated by UV−vis spectroscopy, [**1**]OTf exists as the free cation up to pH 5. Above this pH, the UV−vis spectrum undergoes a distinct blue shift, suggesting binding of hydroxide anion to the antimony center. To parametrize this phenomenon, an acid−base spectrophotometric titration was carried and afforded a pK_{R^+} value[4a] of 7.07 ± 0.05 (Figure 1). This pK_{R^+} value, which can be regarded as the pH at which [**1**]OTf is 50% neutralized by hydroxide anions, indicates that [**1**]OTf should serve as an efficient fluoride anion sensor at slightly acidic pH. Indeed, a fluoride titration experiment carried out in 9:1 (v/v) H$_2$O/DMSO (CTAB, 10 mM) at pH 4.8 (pyridine buffer, 10 mM) indicated that [**1**]OTf binds fluoride anion with a binding constant of 12000 ± 1100 M^{-1}, making this compound compatible for the detection of fluoride in the parts per million range (Figure 1). Gratifyingly and as observed in CHCl$_3$, an increase in the fluorescence intensity was also observed on going from [**1**]OTf to **1**-F, as indicated by Φ = 2.2% for [**1**]OTf and Φ = 14.1% for **1**-F (Figure 2) in aqueous solution. This assay is remarkably selective and does not produce any response to other anions such as Cl$^-$, Br$^-$, I$^-$, NO$_3^-$, N$_3^-$, HCO$_3^-$, and HSO$_4^-$. Because of this lack of interference, this compound can be used with untreated tap water. For example, this assay returned a value of 1.04 ± 0.01 ppm for a tap water sample (College Station, TX) and a value of 0.14 ± 0.01 ppm for bottled water (Evian, France). To confirm the accuracy of these measurements, the two samples were also tested independently using a fluoride-selective electrode, which returned comparable values (1.07 and 0.16 ppm for the tap and bottled water samples, respectively). Last but not least, the fluorescence turn-on response can be detected with the naked eye in under 1 min for concentrations of at least 1 ppm (Figure 2).

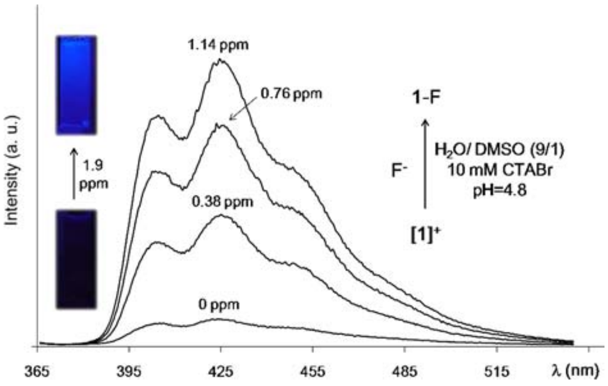


Figure 2. Fluorescence spectra of [**1**]OTf (5.0 μM) in 9/1 (v/v) H_2O/DMSO at pH 4.8 (10 mM CTAB/pyridine buffer) before and after addition of fluoride. The inset shows the visible fluorescence changes (under a hand-held UV lamp) accompanying the addition of 1.9 ppm F^-.

In conclusion, we have described an original approach to the detection of aqueous fluoride anions in water at the parts per million level. This approach is based on the discovery that stibonium ions are sufficiently fluorophilic to bind fluoride anions in highly competing solvents such as water. The stability, selectivity, and optical turn-on response of this new sensor should make it especially useful for analytical applications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional experimental and computational details and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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