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Preparation of a highly fluorophilic phosphonium salt and its use in a fluorous anion-exchanger membrane with high selectivity for perfluorinated acids

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ABSTRACT

Fluorous solvents are the most nonpolar, nonpolarizable phases known, whereas ions are inherently polar. This makes it difficult to create salts that are soluble in a fluorous solvent. Here we present the synthesis and characterization of a new fluorophilic phosphonium salt, tris{3,5-bis[(perfluorooctyl)-propyl]phenyl}methylphosphonium methyl sulfate. The salt has a solubility of at least 14 mM in perfluoro(perhydrophenanthrene), perfluoro(methylcyclohexane), and perfluorohexanes. It also shows immediate potential for use as a phase-transfer catalyst in fluorous biphasic catalysis, but in this work it is used as an anion-exchanger site in the first potentiometric fluorous-membrane anion-selective electrode. The membrane sensor exhibited the exceptional selectivity of 3.9×10^{10} to 1 for perfluorooctanesulfonate over chloride, and of 2.5×10^{7} to 1 for perfluorooctanoate over chloride. With improvements to the sensor's detection limit and lifetime, it has the potential to be an attractive alternative to the expensive, time-consuming methods currently employed for measurement of perfluorinated acids.

1. Introduction

Ion-selective electrodes are chemical sensors that respond to the activity of a specific ionic species in a sample solution by generating an electrical potential [1–6]. These sensors have found wide application in the clinical setting, especially for measurement of inorganic ions such as K^+, Na^+, Ca^{2+}, and Cl^-, where they are used to make over a billion measurements per year. Recent improvements have allowed these sensors to achieve picomolar detection limits [7–9], and an ongoing effort to design new receptors has led to the development of sensors for over 60 analytes [2,3,10]. In an attempt to prepare ion-selective sensors with enhanced selectivities and improved resistance to biofouling, we first described cation-selective electrodes employing fluorous matrixes instead of conventional lipophilic matrixes [11–13]. These fluorous membranes incorporated a highly fluorophilic anion, such as tetrakis[3,5-bis(perfluorohexyl)phenyl]borate (**1**), as an anionic site, enabling the sensors to respond to ions of the opposite charge (Fig. 1). Both receptor-free and receptor-doped fluorous-membrane sensors exhibited enhanced selectivity.

In order to extend the fluorous sensor system to be able to measure not only cations but also anions, a highly fluorophilic cationic site was needed. Such a cation has to be soluble in a fluorous matrix even when paired with highly hydrophilic ions such as Cl^-, F^-, or HPO_4^{2-}. However, very few fluorophilic cations have been reported in the literature. Neumann and co-workers described a fluorinated ammonium cation, $[CF_3(CF_2)_7(CH_2)_3]_3CH_3N^+$ (**2**), which was used as a phase-transfer catalyst for a polyoxometalate catalyst with a −12 charge [14]. Unfortunately, when the cation is paired with a monoanion, we observed that for our purposes it is not soluble enough in fluorous solvents even when the anion has such a low hydrophilicity as iodide [15]. An array of phosphonium cations, each with four fluorous ponytails, was recently reported in work by Gladysz and co-workers (**3** was among the most fluorophilic) [16]. However, even the most fluorophilic of them was reported to be only sparingly soluble in perfluoro(methylcyclohexane) at room temperature when paired with $CF_3SO_3^-$ or I^-. To the best of our knowledge, the most fluorophilic cation ever reported in the literature was described by Maruoka and co-workers. Their quaternary ammonium cation **4** was reported to be soluble in perfluorohexanes when paired with Br^- [17]. Unfortunately, the 11-step synthesis required to prepare this salt (overall yield approximately 19%) inhibits its widespread application.

In this work, we report a new fluorophilic phosphonium salt bearing six fluorous ponytails, i.e., tris{3,5-bis[(perfluorooctyl)-propyl]phenyl}methylphosphonium methyl sulfate, **10**. The salt has a high solubility (at least 14 mM) in the fluorous solvents

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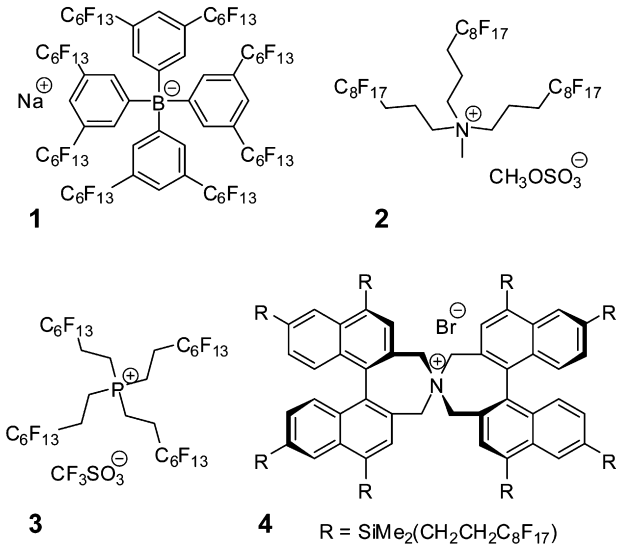


Fig. 1. Fluorophilic ions described in the literature.

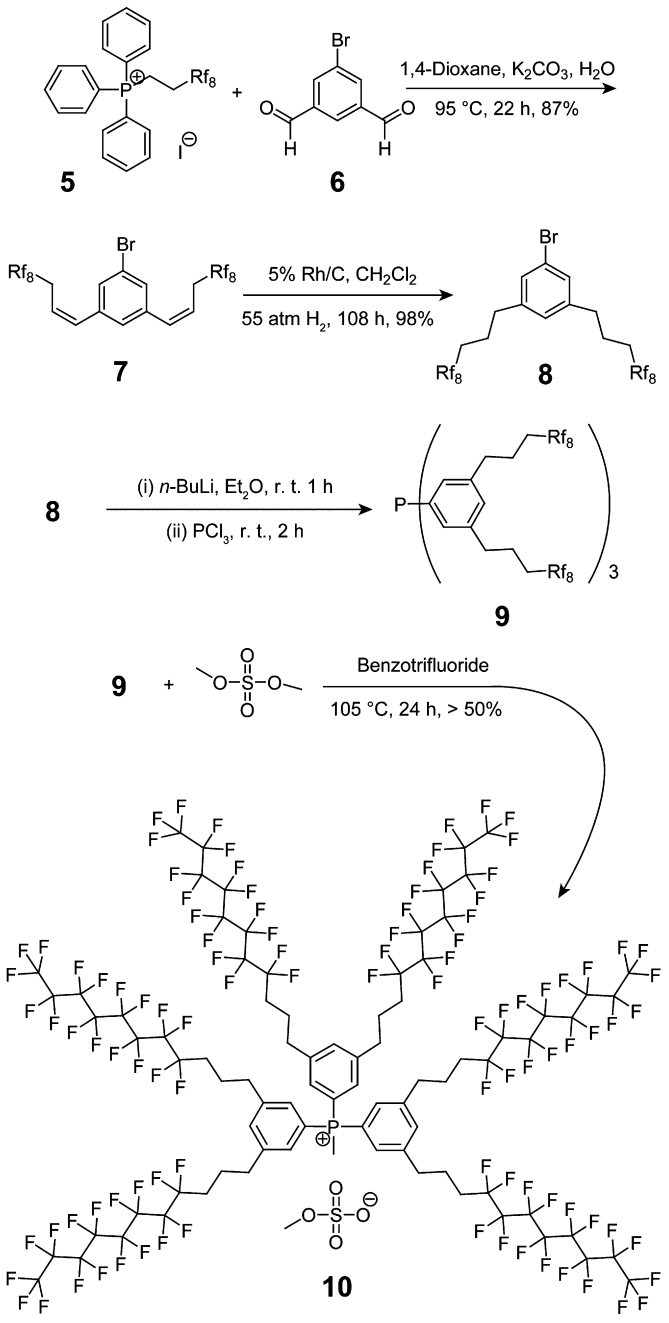
perfluoro(methylcyclohexane), perfluorohexanes, and perfluoro(perhydrophenanthrene), and requires only a relatively small synthetic effort to prepare. We describe here its use as a cationic site in the first reported fluorous anion-exchanger membrane electrode, focusing on membrane selectivities relative to conventional membranes made of the lipophilic matrixes *o*-nitrophenyl octyl ether (*o*NPOE) and chloroparaffin. Also, a new fluorophilic electrolyte salt, **11** – the tetrakis[3,5-bis(perfluorooctyl)phenyl]-borate salt of this fluorophilic phosphonium cation – was synthesized and used to lower the electrical resistance of the sensing membranes. Finally, we present our observations of the very slow spontaneous dearylation of the phosphonium cation when paired with weakly basic anions in the presence of water, resulting in the formation of a phosphine oxide.

2. Results and discussion

2.1. Synthesis

Because fluorous phases are the most nonpolar, nonpolarizable liquids known and ions are inherently polar, a fluorophilic ion must bear several perfluoroalkyl chains ("ponytails") to facilitate a significant solubility in fluorous solvents. In order to incorporate these ponytails and to partially delocalize the positive charge, our original intention was to prepare a tetraphenylphosphonium derivative with two fluorous ponytails per aryl group, giving a cation with a total of eight ponytails. In the corresponding case of a fluorophilic anion, such as the fluorophilic borate **1**, the strong electron-withdrawing properties of the fluorous ponytails assist in the delocalization of the negative charge. However, in the case of a fluorophilic cation, the perfluoroalkyl groups destabilize the positive charge center. In order to mitigate the electron-withdrawing effect of the perfluoroalkyl groups on the already electron-deficient center, propylene spacers were therefore inserted between the aryl groups and the fluorous ponytails [18].

As shown in Scheme 1, the synthesis of the fluorophilic phosphonium methyl sulfate salt, **10**, was started with a Wittig reaction to prepare the unsaturated, polyfluoroalkylated bromobenzene **7**. Initial attempts to hydrogenate the olefinic bonds of **7** with H_2 and a Pd/C catalyst were successful but, as observed elsewhere [19,20], the Pd/C catalyst was not sufficiently selective, resulting in reductive debromination. However, use of a Rh/C catalyst [19] under 55 atm of H_2 afforded the desired product, **8**, in



Scheme 1. Synthesis of a methyl sulfate salt of the fluorophilic phosphonium cation.

high yield. Due to the low solubility of the aryllithium reagent of **8** in most organic solvents, arylation of PCl_3 had to be carried out at room temperature, forming the fluorophilic triarylphosphine precursor **9**.

Attempts to synthesize a symmetrical tetraarylphosphonium salt by arylation of **9** with another fluorophilic aryl group using $NiBr_2$ or $CoCl_2$ catalyst, following procedures reported for the synthesis of the unsubstituted tetraphenylphosphonium ion [21,22], were unsuccessful. Moreover, the reaction of a Grignard reagent of bromobenzene with **9** in the presence of oxygen according to another known procedure for tetraphenylphosphonium synthesis [23] gave the phenylated product albeit in small amounts, while a similar reaction of a Grignard reagent of **8** with **9** yielded no detectable tetraarylphosphonium product. This is probably in part due to the fact that even the propyl spacers are

not able to completely shield the phosphorus from the electron-withdrawing effect of the fluorous ponytails [18]. Besides this electronic effect, there may be also steric hindrance in the fluorophilic phosphine **9**, preventing quaternization with another bulky fluorophilic aryl group. However, quaternization of the phosphine **9** was successfully achieved by methylation with dimethyl sulfate. Fortuitously, six fluorous ponytails suffice to make the fluorophilic phosphonium methyl sulfate salt, **10**, highly soluble (greater than 14 mM) in perfluorohexanes, perfluoro(perhydrophenanthrene) (**12**), and perfluoro(methylcyclohexane).

2.2. Fluorous anion-exchanger membranes

When ion-selective electrodes are placed in real-life samples such as body fluids, food, or environmental samples, they exhibit drift and loss of selectivity that interfere with accurate measurements [24,25]. This sort of sensor biofouling is partly caused by the extraction of electrically neutral, lipophilic compounds that partition from the sample into the sensing membrane [26]. Once there, the interferents act as non-specific receptors, competing with the ionophore to determine the selectivity of the sensor. In order to reduce sensor fouling in the presence of these naturally occurring interferents, our laboratory is exploring the use of sensor membranes made with fluorous matrixes, which exhibit a low solubility for naturally occurring hydrophobic lipids. For example, at 37 °C, stearic acid has a solubility in hexane of 430 mM, whereas in the fluorous solvent *trans*-1,2-bis(perfluorohexyl)ethylene it has a solubility of only 0.026 mM—over four orders of magnitude lower [27].

While we previously reported on fluorous cation-selective membranes, this work describes the first fluorous anion-selective electrode membranes. Perfluoro(perhydrophenanthrene), **12**, was used as the fluorous liquid matrix (Fig. 2), the new fluorophilic cationic site, **10**, as ion-exchanger salt (2 mM), and the new fluorophilic salt, **11**, as electrolyte salt (10 mM) to reduce the membrane resistance.

A perfluorooctanesulfonate ($PFOS^-$) calibration curve measured with an electrode comprising a fluorous anion-selective membrane is shown in Fig. 3. In the linear region between 10^{-4} and 10^{-7} M, the electrode responds in the expected "Nernstian" fashion, i.e., a 59 mV decrease in potential for every ten-fold increase in the $PFOS^-$ activity is observed. Below 10^{-7} M, the potential remains relatively constant and thus indifferent of the $PFOS^-$ activity, indicating that the detection limit of the sensor has been reached.

One of the most important properties of ion-selective electrodes is that they exhibit selectivity for particular types of ions over

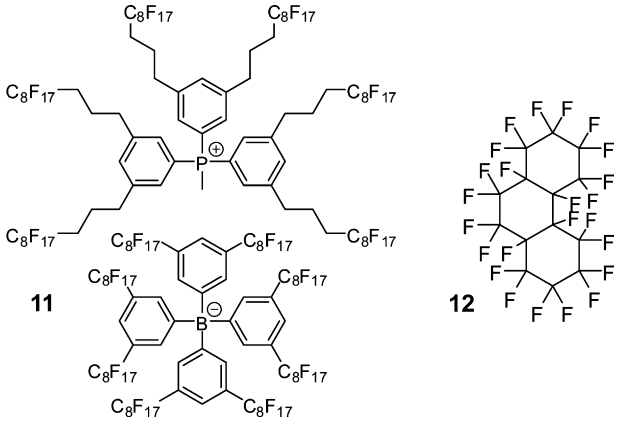


Fig. 2. Fluorophilic electrolyte salt and fluorous liquid matrix.

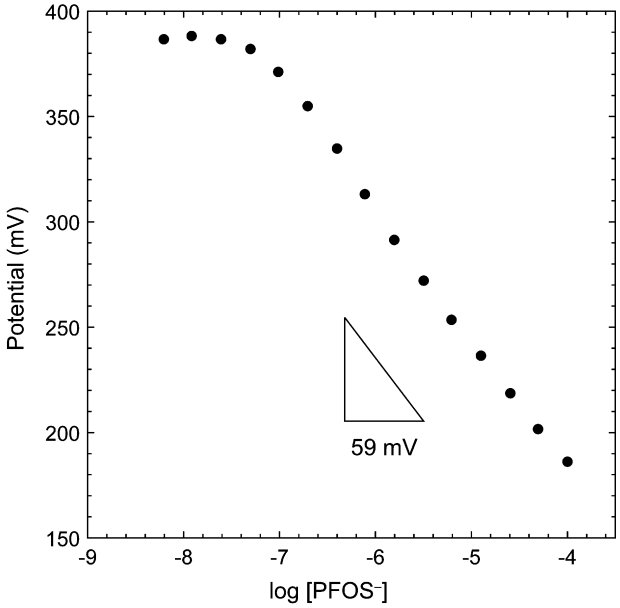


Fig. 3. $PFOS^-$ calibration curve measured with a fluorous-membrane anion-exchanger electrode (outer filling solution: 0.1 mM KPFOS, 10 μM KCl). The sample solution contained a constant 10 μM KCl background at all $PFOS^-$ concentrations.

others. Selectivity coefficients are used to quantify the degree of selectivity displayed by a sensor towards a certain type of ion over another. For ions of equal charge, the selectivity coefficient for ion I over ion J ($K^{pot}_{I,J}$) is the ratio of the individual ion activities that each produce the same potential [28].

Fig. 4 shows anion selectivities of the fluorous anion-exchanger, along with the selectivities of a PVC/*o*NPOE and a PVC/chloroparaffin anion-exchanger for comparison. In our previous work, an analogous fluorous cation-exchanger membrane composed of perfluoro(perhydrophenanthrene), **12**, and the fluorophilic borate, **1**, exhibited a selectivity range nearly 8 orders of magnitude wider than a comparable lipophilic sensor membrane [12]. The selectivity increase was attributed to the use of a fluorous sensor matrix, which offers very little stabilization to ions dissolved in the membrane. However, the anion-exchanger selectivities of the fluorous membranes are not as significantly different from those of non-fluorous membranes, except in the cases of perfluorooctanoate (PFO^-) and perfluorooctanesulfonate ($PFOS^-$). It may be that selectivities are only affected by the fluorous matrix to a relatively small degree because the phosphonium cation coordinates some of the smaller, more hydrophilic ions—an effect that would be amplified by the highly inert fluorous matrix. Indeed, such coordination has been reported for phosphonium ions with F^- [29,30], NO_2^- [31], and alkanolates [32].

Interestingly, the fluorous membranes exhibit very high selectivities for the fluorinated anions $PFOS^-$ and PFO^- ($\log K^{pot}_{Cl^-,PFOS^-} = 10.6$, $\log K^{pot}_{Cl^-,PFO^-} = 7.4$). Also, the selectivity of the fluorous membrane for PFO^- is 1.4 orders of magnitude better than the PVC/chloroparaffin membrane. While it would be desirable to also compare to the $PFOS^-$ selectivity of the PVC/chloroparaffin membrane and the PFO^- and $PFOS^-$ selectivities of the PVC/*o*NPOE membranes, the poor detection limits of those electrodes prevented the determination of those values. In those cases, the solubility of the potassium salt of $PFOS^-$ or PFO^- in water seems to be lower than the detection limits of the non-fluorous-membrane sensors, which were caused by strong fluxes of PFO^- or $PFOS^-$ from the sample to the inner filling solution through the sensor membrane [7–9].

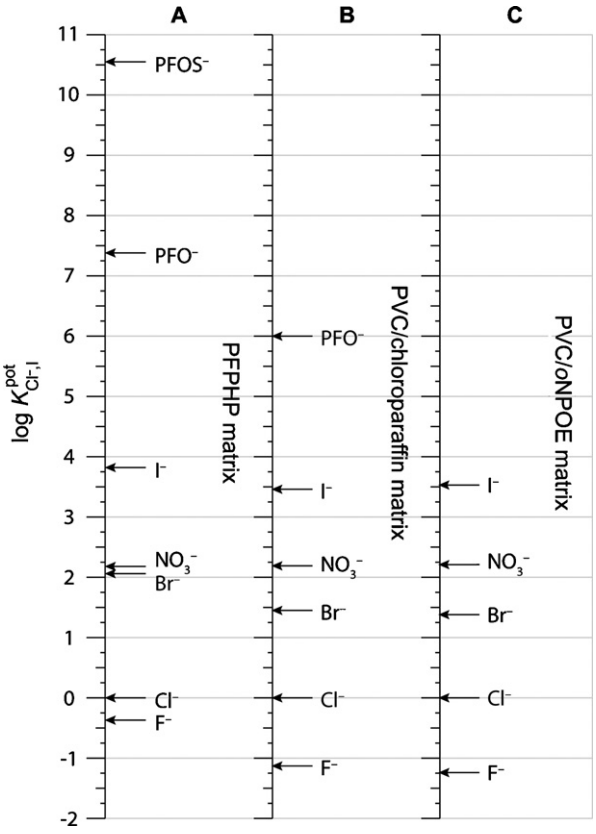


Fig. 4. Logarithmic representation of the selectivities of (A) the fluorous anion-exchanger membrane (2 mM **10** and 10 mM **11** in perfluoro(perhydrophenanthrene)) and two lipophilic anion-exchanger membranes for reference, i.e., (B) a PVC/chloroparaffin membrane containing 5% (w/w) tridodecylmethylammonium chloride, and (C) a PVC/*o*NPOE membrane also containing 5% (w/w) tridodecylmethylammonium chloride.

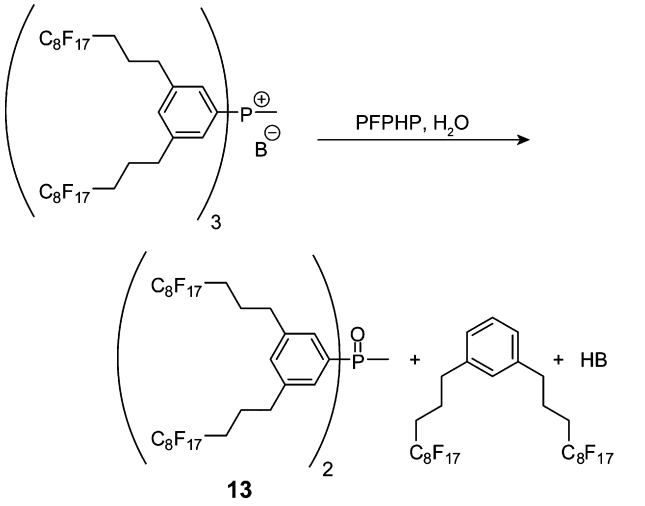


Fig. 6. Oxidation of fluorophilic phosphonium cation in a perfluoro-(perhydrophenanthrene) (PFPHP) matrix when paired with a weakly basic anion (B^-) in the presence of water.

2.3. Phosphonium oxidation

The anion-selective fluorous-membrane sensors exhibited Nernstian responses and fast response times (less than 1 min) when measuring NO_3^-, I^-, and Br^-. Response times were somewhat slower (between 1 and 5 min) for $PFOS^-$, PFO^-, and Cl^-. However, when measuring the ions F^-, OAc^-, NO_2^-, OH^-, and HCO_3^-, the fluorous electrodes exhibited very noisy responses, and in some cases response times increased to over 30 min. For these ions, the response was strongly dependent on the rate of stirring of the sample, as shown in Fig. 5 for the response of a fluorous anion-exchanger exposed to different sample KF concentrations. A stir rate dependence is often observed when significant fluxes of ions between the sample and the electrode inner filling solution occur. In Fig. 5, the solution in contact with the backside of the sensor membrane contained 1 mM KF while the concentration of KF in the sample solution was lowered from 100 to 0.1 mM. If ion fluxes were the cause of the stir rate dependence, the response to stirring would reverse as the ion concentration gradients reverse [33]. However, at sample concentrations above and below the inner filling solution concentration, the stir rate response remained the same.

A better explanation for the unusual stir rate dependence is that the phosphonium salt is unstable and degrades in the presence of those anions that cause the noisy, stir rate dependent responses. When a PFPHP solution of the fluorophilic phosphonium salt was stirred at room temperature for 24 h in the presence of an aqueous 1 M NaOH solution, we observed by ^{31}P NMR spectroscopy that the fluorophilic phosphonium cation decomposed to form a phosphine oxide. This type of oxidative cleavage is known and has even been used for the preparation of certain fluorous phosphines [34] (Fig. 6).

Mass spectrometry measurements revealed that the decomposition of the phosphonium cation is accompanied by loss of an aryl group, and results in formation of the phosphine oxide **13**, which is insoluble in perfluoro(perhydrophenanthrene). Evidently, the stir rate dependence and noisy electrode response is caused by oxidation of the phosphonium cationic site in the presence of weakly basic anions. Specifically, ions such as NO_3^-, I^-, and Br^-, which have only an extremely weak affinity for protons (pK_a values of the conjugate acids are −1.5, −10, and −9, respectively) show no stir rate dependence, while the more basic ions F^-, NO_2^-, and OAc^- (pK_a values of conjugate acids are 3.2, 3.3, and 4.8, respectively) show a strong stir rate dependence. It appears likely that the

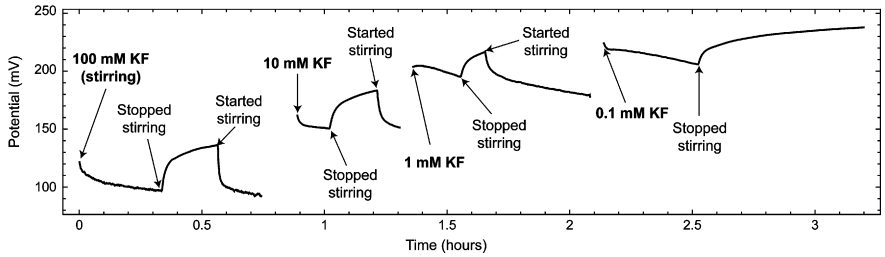


Fig. 5. Stir test with fluorous anion-exchanger electrodes in KF solutions of different concentrations. The electrode outer filling solution was 1 mM KF while the inner filling solution was 1 mM KCl.

anions play the role of general base catalysts, promoting the decomposition of the phosphonium ion the better the higher their base strength is.

3. Conclusions

The highly fluorophilic character of the phosphonium salt **10** allowed its use as a cationic site in the first fluorous anion-selective electrode. While the limited stability of the fluorophilic phosphonium salt in the presence of certain anions with appreciable basicity necessitates the development of a new, more stable fluorophilic cationic site, the fluorous anion-exchanger showed exceptionally high selectivity for $PFOS^-$ and PFO^-. In recent years, perfluorooctanesulfonic acid and perfluorooctanoic acid (the conjugate acids of $PFOS^-$ and PFO^-), along with several other perfluorinated acids, have received increasing attention as they were shown to be persistent and bioaccumulative in humans and wildlife, and are potentially toxic [35–38]. In future work, we will implement methods [7–9,39] to lower the detection limit of the fluorous anion-selective electrode, which should make it an attractive sensor for routine measurement of perfluorinated acids. The fluorophilic phosphonium salt presented here could also find other application. The uniquely high solubility of the salt in fluorous solvents and its relatively uncomplicated synthesis could make it an attractive phase-transfer catalyst for fluorous biphasic catalysis [40,41]. It could also find uses as an electrolyte salt in the new field of fluorous voltammetry [42] and in battery and fuel cell technology.

4. Experimental

4.1. General experimental procedures

All reagents were of the highest commercially available purity and were used as received. Sample solutions were prepared using deionized and charcoal-treated water (0.182 MΩ m specific resistance) obtained with a Milli-Q PLUS reagent-grade water system (Millipore, Bedford, MA, USA). Perfluoro(perhydrophenanthrene) (**12**), 1,4-dioxane, and 5% Rh/C catalyst were purchased from Alfa Aesar (Ward Hill, MA, USA). 1.0 M BCl_3 in hexane, 2.5 M *n*-butyllithium in hexanes, 1.7 M *t*-butyllithium in pentane, PCl_3, and dimethyl sulfate were purchased from Aldrich or Fluka (Milwaukee, WI, USA). Perfluorohexanes (FC-72) was purchased from 3M (St. Paul, MN, USA) and benzotrifluoride from Oakwood products (West Columbia, SC, USA). Et_2O was distilled from $LiAlH_4$ prior to use.

4.1.1. Membranes

Supported liquid-phase membranes with polytetrafluoroethylene (PTFE) filter disks were used as an inert support for the fluorous liquid sensing membranes [11–13]. Fluoropore membrane filters (pure PTFE, 47 mm diameter, 0.45 μm pore size, 50 μm thick, 85% porosity) were obtained from Millipore. A hole punch was used to cut 13 mm diameter disks out of the larger, commercial Fluoropore membrane filters. Supported liquid-phase membranes were made from two of these disks stacked on top of each other. To impregnate the filter disks with the liquid sensing phase, a perfluoro(perhydrophenanthrene) solution containing 2 mM of the fluorophilic cationic site **10** and 10 mM of the fluorophilic electrolyte salt **11** was applied to the surface of the porous filter disks, into which the fluorous solution permeated spontaneously. Solution was added to the filter disks until they went from opaque white to translucent with a glossy surface, which required about 24–32 μL of the fluorous phase.

4.1.2. Electrodes

The fluorous membranes prepared in this way were mounted into custom-machined electrode bodies made from poly(chlorotrifluoroethylene) [13]. A screw cap with an 8.3 mm diameter hole in the middle was screwed onto the membranes, mechanically sealing the perimeter while leaving the center exposed. The solution inside each electrode was divided into two parts by a small glass wool plug: an outer filling solution (in contact with the backside of the sensing membrane) and an inner filling solution (in contact with the outer filling solution through the glass wool plug and in contact with an AgCl-coated Ag wire). The inner filling solution was always aqueous 1 mM KCl. For selectivity measurements, the outer filling solution was composed of an aqueous 1 mM solution of the potassium salt of the anion of interest. An electrochemical cell was obtained by immersion of the thus fabricated electrode and a double-junction type external reference electrode (DX200, Mettler Toledo, Switzerland; saturated KCl as inner solution and 3 M KCl or 1 M LiOAc as bridge electrolyte) into the sample solution. Prior to measurements, the electrodes were conditioned for 2–3 h in a solution of the same composition as the outer filling solution.

4.1.3. Potentiometric measurements

EMF Suite 1.03 (Fluorous Innovations, Arden Hills, MN) was used to control an EMF 16 potentiometer (Lawson Labs, Malvern, PA, US). Selectivity coefficients were determined by the fixed interference and separate solution methods [28], and Nernstian responses were confirmed for all ions in the concentration range where selectivities were tested. Selectivity values were obtained from two or three measurements. The error in the selectivity measurements was ±0.2. Ion activities were calculated according to a two parameter Debye–Hückel approximation [43].

4.1.4. Oxidation of $[3,5\text{-}(CH_2CH_2CH_2C_8F_{17})_2C_6H_3]_3CH_3P^+$ $CH_3OSO_3^-$ (10)

50 mg of **10** was dissolved in 3 mL of **12**, and added to 30 mL of 1 M NaOH/H_2O solution. Stirring of the two phase-system at room temperature led to the formation of a precipitate, which was collected after 24 h by filtration and identified as **13**. ^1H NMR (499.9 MHz, $CDCl_3$): δ 7.58 (4H, d, *o*-C_6H_3), δ 7.39 (2H, s, *p*-C_6H_3), δ 2.95–2.85 (m), δ 2.30–2.18 (m), δ 2.10–1.90 (m). ^{31}P NMR (121.4 MHz, acetone-d_6): δ 26.47 (1P, s). MS *m*/*z* (relative intensity, ion): 2080.51 (13.5%, M^+), 2079.52 (55.7%, M^+), 2078.52 (100%, M^+), 2060.52 (5.7%, M^+-HF), 2059.53 (14.2%, M^+-HF), 2058.52 (24.5%, M^+-HF).

4.2. Synthesis

4.2.1. Synthesis of 1-Br-3,5-$(CH{=}CHCH_2C_8F_{17})_2C_6H_3$ (7)

The Wittig reagent **5** and 1-Br-3,5-$(CHO)_2C_6H_3$, **6**, were synthesized by previously reported procedures [44,45]. The Wittig reaction for the synthesis of **7** is similar to a previously reported procedure [45]. 39 g (0.0466 mol) of **5**, 4.52 g (0.0212 mol) of **6**, 8.54 g (0.0466 mol) of K_2CO_3, 0.26 mL H_2O, and 156 mL of 1,4-dioxane were added to a round-bottom flask fitted with a condenser that was open to the atmosphere. After the mixture was stirred for 22 h at 95 °C, all volatiles were removed by rotary evaporation. The residue was taken up in CH_2Cl_2, washed with H_2O, dried with $MgSO_4$, filtered, and the CH_2Cl_2 was removed by rotary evaporation. The residue was then taken up in a small amount of hexanes and filtered through a column of silica gel with hexanes. The volatiles were removed by rotary evaporation and then under vacuum for 16 h to give the product, **7** (a mixture of isomers), as a light yellow oil with a yield of 87%. Characterization of most prominent isomer: ^1H NMR (499.9 MHz, $CDCl_3$): δ 7.27

(2H, s, *o*-C_6H_3), δ 7.00 (1H, s, *p*-C_6H_3), δ 6.77 (2H, d, *J* = 11.5 Hz, C*H*CHCH$_2$C$_8$F$_{17}$), δ 5.83 (2H, dt, $J_{CH,CH}$ = 11.5 Hz, J_{CH,CH_2} = 7.5 Hz, C*H*CH$_2$C$_8$F$_{17}$), δ 3.03 (4H, dt, $J_{CH_2,CH}$ = 7.5 Hz, J_{CH_2,CF_2} = 18.0 Hz, C*H*$_2$C$_8$F$_{17}$). Anal. cald. for $C_{28}H_{11}BrF_{34}$: C, 31.34; H, 1.03; F, 60.19. Found: C, 31.79; H, 1.13; F, 59.77.

4.2.2. Synthesis of 1-Br-3,5-(CH$_2$CH$_2$CH$_2$C$_8$F$_{17}$)$_2$C$_6$H$_3$ (8)

The procedure used for selective hydrogenation of the double bonds in **7** to give **8** is similar to a previously reported procedure [19]. 9.72 g (9.06 mmol) of **7**, 767 mg 5% Rh/C catalyst, and 58.3 mL H_2-saturated CH_2Cl_2 were added to a high-pressure, stainless steel reactor vessel containing a magnetic stir bar. After the mixture was stirred at room temperature for 108 h under 55 atm H_2 pressure, the solvent was removed by rotary evaporation, the residue was taken up in Et_2O and filtered through a pad of diatomaceous earth, and the solvent was again removed by rotary evaporation. The crude product was recrystallized from CH_2Cl_2 to give the product as clear crystals with a yield of 98.1%.

^{1}H NMR (299.8 MHz, FC-72): δ 6.47 (2H, s, *o*-C_6H_3), δ 6.15 (1H, s, *p*-C_6H_3), δ 1.90 (4H, t, *J* = 6.9 Hz, C*H*$_2$CH$_2$CH$_2$C$_8$F$_{17}$), δ 1.35 (4H, m, CH$_2$C$_8$F$_{17}$), δ 1.24 (4H, m, CH$_2$CH$_2$C$_8$F$_{17}$). Anal. cald. for $C_{28}H_{15}BrF_{34}$: C, 31.22; H, 1.40; F, 59.96. Found: C, 31.49; H, 1.26; F, 60.23.

4.2.3. Synthesis of [3,5-(CH$_2$CH$_2$CH$_2$C$_8$F$_{17}$)$_2$C$_6$H$_3$]$_3$P (9)

Because of the low solubility of the aryllithium reagent of **8** in Et_2O, the reaction was carried out at room temperature. 6 g (5.57 mmol) of **8** and 120 mL of Et_2O were added to a 300 mL round-bottom flask fitted with a rubber septum. The solution was stirred under argon while 4.233 mL (10.58 mmol, 1.9 equiv.) of 2.5 M *n*-butyllithium in hexanes was added quickly through a needle. After one hour, 138 μL of PCl_3 was added, and the solution was allowed to stir for another 2 h. The solvent was then removed by rotary evaporation, giving the crude product, **9**, as a faint yellow solid. The product did not need to be purified before the next step of the reaction. ^{1}H NMR (299.8 MHz, acetone-d_6): δ 7.26 (1H, s, *p*-C_6H_3), δ 7.10 (2H, d, *J* = 7.8 Hz, *o*-C_6H_3), δ 2.79 (12H, t, *J* = 7.3 Hz, C*H*$_2$CH$_2$CH$_2$C$_8$F$_{17}$), δ 2.21 (12H, m, C*H*$_2$C$_8$F$_{17}$), δ 1.99 (12H, m, C*H*$_2$CH$_2$C$_8$F$_{17}$). ^{31}P NMR (121.4 MHz, acetone-d_6): δ −4.15 (s).

4.2.4. Synthesis of [3,5-(CH$_2$CH$_2$CH$_2$C$_8$F$_{17}$)$_2$C$_6$H$_3$]$_3$CH$_3$P$^+$ CH$_3$OSO$_3^-$ (10)

Methylation of the fluorophilic phosphine **9** to give **10** was performed in analogy to a procedure reported previously [14]. To the crude product from the previous reaction (theoretically containing 4.8 g of **9**) was added 96 mL benzotrifluoride (BTF) and 3.03 mL (31.7 mmol) of dimethyl sulfate. The mixture was refluxed while stirring under argon, and ^{1}H NMR samples were periodically taken to check reaction progress. After 48 h, the reaction was determined to be complete, and the solvent was removed by rotary evaporation. The product was purified by running an Et_2O/BTF solvent mixture (1:1) through a deactivated silica gel column until all the color on the column eluted. The product was then collected by running an EtOH/BTF (1:1) solvent mixture through the column. The solvent was evaporated by rotary evaporation and the residue was taken up in 50 mL perfluorohexanes and washed with acetone (3 × 50 mL). The solvent was again removed by rotary evaporation and then under vacuum for 48 h to give the product as a clear, waxy solid in greater than 50% yield (over the course of the last two steps). ^{1}H NMR (299.8 MHz, acetone-d_6): δ 7.94 (6H, d, *J* = 13.5 Hz, *o*-C_6H_3), δ 7.82 (3H, s, *p*-C_6H_3), δ 3.38 (3H, s, $CH_3OSO_3^-$), δ 3.28 (3H, d, *J* = 14.1 Hz, CH_3P), δ 3.03 (12H, t, *J* = 7.6 Hz, C*H*$_2$CH$_2$CH$_2$C$_8$F$_{17}$), δ 2.36 (12H, m, C*H*$_2$C$_8$F$_{17}$) δ 2.10 (12H, m, C*H*$_2$CH$_2$C$_8$F$_{17}$). ^{31}P NMR (121.4 MHz, acetone-d_6): δ 22.62 (1P, s). MS *m*/*z* (relative intensity, ion): 3039.30 (4.7%, M$^+$), 3038.30 (25.3%, M$^+$), 3037.31 (87.0%, M$^+$), 3036.31 (100%, M$^+$), 3019.32 (2.6%, M$^+$−HF), 3018.31 (11.1%, M$^+$−HF), 3017.32 (35.8%, M$^+$−HF), 3016.32 (44.1%, M$^+$−HF), 2998.30 (1.3%, M$^+$−2 HF), 2997.30 (3.0%, M$^+$−2 HF), 2996.30 (4.4%, M$^+$−2 HF). Anal. cald. for $C_{86}H_{51}F_{102}O_4PS$: C, 32.80; H, 1.63. Found: C, 32.91; H, 1.69.

4.2.5. Synthesis of [3,5-(CH$_2$CH$_2$CH$_2$C$_8$F$_{17}$)$_2$C$_6$H$_3$]$_3$CH$_3$P$^+$ B[3,5-(C$_8$F$_{17}$)$_2$C$_6$H$_3$]$_4^-$ (11)

The fluorophilic electrolyte salt **11** was synthesized by a metathesis reaction between 0.928 g (0.336 mmol) Na$^+$ B[3,5-(C$_8$F$_{17}$)$_2$C$_6$H$_3$]$_4^-$ and 0.720 g (0.229 mmol) fluorophilic phosphonium salt, **10**, in 20 mL H_2O and 20 mL perfluorohexanes. After the fluorous layer was washed with H_2O (3 × 20 mL) and then with acetone (3 × 20 mL), the solvent was removed by rotary evaporation and then under vacuum for 48 h to give **11** as a clear, waxy solid in quantitative yield. ^{1}H NMR (299.8 MHz, FC-72): δ 7.76 (8H, s, *o*-C_6H_3B), δ 7.47 (4H, s, *p*-C_6H_3B), δ 7.40 (3H, s, *p*-C_6H_3P), δ 6.93 (6H, d, *J* = 13.8 Hz, *o*-C_6H_3P), δ 2.63 (12H, t, *J* = 6.3 Hz, C*H*$_2$CH$_2$CH$_2$C$_8$F$_{17}$), δ 2.08–1.74 (24H, m, CH$_2$CH$_2$C$_8$F$_{17}$), δ 1.58 (3H, t, *J* = 13.2 Hz, CH_3P), ^{31}P NMR (121.4 MHz, acetone-d_6): δ 22.44 (1P, s).

4.2.5.1. Synthesis of Na$^+$ B[3,5-(C$_8$F$_{17}$)$_2$C$_6$H$_3$]$_4^-$.

1-Bromo-3,5-(perfluorohexyl)benzene was synthesized according to a previously described procedure [46]. 5.00 g of a mixture of 1-bromo-3,5-bis(perfluorohexyl)benzene and 1,3,5-tris(perfluorohexyl)benzene (5.6:1, 4.06 mmol:0.726 mmol) and 250 mL Et_2O were added to a round-bottom flask. The solution was cooled to −78 °C before adding 4.89 mL (8.31 mmol) 1.7 M *t*-butyllithium in pentane followed by 0.914 mL (0.914 mmol) 1.0 M BCl_3 in hexane 60 min later. The solution was then allowed to warm to room temperature before 200 mL of H_2O was added and the water layer was saturated with NaCl. After extraction with Et_2O (3 × 100 mL), the solution was dried with $MgSO_4$, filtered, and the volatiles were removed by rotary evaporation. The residue was taken up in a small amount of BTF and purified by running BTF through a silica gel column until the impurities eluted. The product was then collected by running MeOH through the column. The solvent was evaporated by rotary evaporation, giving Na$^+$ B[3,5-(C$_8$F$_{17}$)$_2$C$_6$H$_3$]$_4^-$ (tetrahydrate) as clear crystals with 75% yield. ^{1}H NMR (299.8 MHz, acetone-d_6): δ 7.72 (8H, s, *o*-C_6H_3), δ 7.60 (4H, s, *p*-C_6H_3). MS *m*/*z* (relative intensity): 3667.22 (3.4%), 3666.22 (26.4%), 3665.23 (83.2%), 3664.23 (100%), 3663.21 (9.7%). Anal. cald. for $C_{88}H_{20}BF_{136}NaO_4$: C, 28.12; H, 0.54. Found: C, 28.20; H, 0.71.

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