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Synthesis of a Polymerizable Fluorosurfactant for the Construction of Stable Nanostructured Proton-Conducting Membranes

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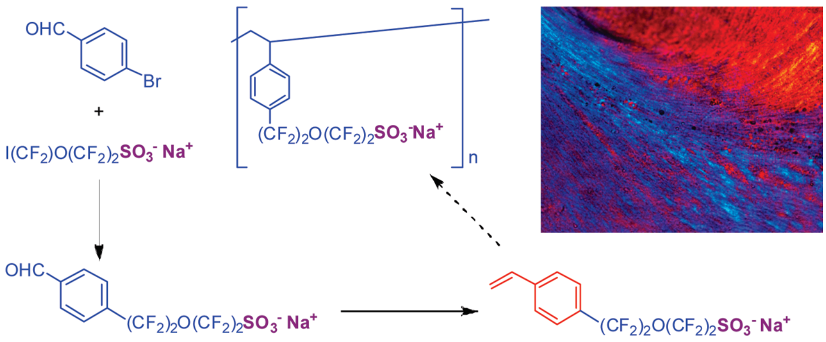

The synthesis of the polymerizable fluorinated surfactant sodium 1,1,2,2-tetrafluoro-2-(1,1,2,2-tetrafluoro-2-(4-vinylphenyl)ethoxy)ethanesulfonate (**1**) and a number of related fluorocarbon compounds is described. Compound **1** is synthesized using a copper-mediated cross-coupling reaction of 4-bromobenzaldehyde and sodium 5-iodooctafluoro-3-oxapentanesulfonate. The resulting benzaldehyde is converted to a styrene unit using a Wittig reaction with methyltriphenylphosphonium bromide in acetonitrile, using DBU as a base. This strategy for converting an iodo-functionalized fluorosurfactant to a styrene-containing fluorosurfactant is highly efficient because both reactions are performed in polar solvents and are compatible with the sulfonate moiety. In addition, the copper-mediated cross-coupling reaction is most efficient with electron-poor aryl bromides like 4-bromobenzaldehyde. We wish to employ **1** for the construction of nanostructured membranes by polymerization of **1** in a microemulsion or in lyotropic liquid crystalline phases.

Introduction

Nanostructured polymer membranes, composed of polymers with a well-defined morphology and consisting of at least two phases, find application in many areas.[1] Well known are membranes for filtration that are composed of cross-linked polymers, which contain mesoscale pores. We are interested in developing proton-conducting membranes for polymer electrolyte membrane fuel cells (PEMFC). For this application, apolar polymers decorated with anionic hydrophilic proton-conducting moieties, usually $-SO_3$, are employed.[2] The apolar polymer phase provides structural integrity, and the anionic moieties form proton-conducting hydrophilic channels in the membrane.[2] Ideally, the proton conducting polymer must possess long-term chemical stability, notably against negative pH, high temperatures, and aggressive radicals like $OH^\bullet$ and $OOH^\bullet$, which are present in operating fuel cells.[3] In practice, (partially) fluorinated and aromatic polymers have[4] the appropriate properties, and thus, they are suitable for making proton conducting membranes. In the present generation PEMFCs, the sulfonated fluoropolymer Nafion, a statistical copolymer of tetrafluoroethylene

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and a sulfonate containing fluorinated comonomer, is the most commonly used proton-conducting material.[2] From an emulsion of this polymer, proton-exchange membranes are produced by various pressing, stamping, and ink deposition techniques. These membranes are cocontinuous and highly proton conducting with channel sizes in the order of 1−4 nm.

For membranes prepared from the statistical copolymers like Nafion, little control over the microstructure is obtained because of the low mobility of the polymer during membrane preparation. In addition, the statistical nature of the polymer does not facilitate a discrete phase separation and the formation of regular and well-developed morphologies. Another drawback associated with the use of polymers is that the degree of sulfonation is limited to fairly low values because highly sulfonated polymers are water-soluble. It is a known fact that the proton conductivity, water uptake, and subsequent swelling are strongly influenced by chemical structure, morphology, and the percentage of proton-carrying groups in the polymer.[5,6] Thus, it is a challenge to enhance the conductivity by increasing the degree of substitution with proton carrying groups without increasing the water uptake and swelling. This problem can partly be solved by synthesizing block or graft copolymers, in which one of the blocks is apolar in nature and the other is hydrophilic and carries anionic functionalities. These polymers can form phase-separated systems. For example, Chung and coworkers[6] have shown that the conductivity of phase separated membranes of poly(vinylidenefluoride)-*g*-sulfonated polystyrene (PVDF-*g*-SPS) graft copolymers is better than that of Nafion 112 due to a higher degree of sulfonation.[7] In this polymer, the water swelling was controlled by the graft copolymer morphology. However, the rate of membrane manufacturing is still limited by the slow dynamics of polymer chains.

In an alternative approach, nanostructured membranes can be assembled by polymerizable surfactants or surfmers in microemulsions[8] or lyotropic liquid crystalline (LLC) phases.[9] Now the mobility of the surfactant molecules is no longer a limiting factor, and equilibrium states with well-defined morphologies may be obtained quickly. Mechanically stable membranes are obtained by a subsequent polymerization of the polymerizable surfactants. By employing multifunctional monomers in these systems, cross-linked polymer membranes are obtained. For such membranes the degree of sulfonation, and therefore the conductivity, can be increased, since the cross-linking prevents the polymer from becoming water-soluble and will also control the degree of swelling.

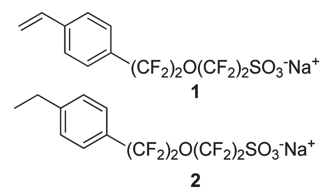

FIGURE 1. Polymerizable fluorosurfactant **1** and nonpolymerizable fluorosurfactant **2**.

The approach of using surfmers was pioneered by Luzzati and co-workers.[10] The preparation of proton-conducting membranes by polymerization of a bicontinuous microemulsion of a zwitterionic surfmer, 3-((11-acryloyloxyundecyl)-imidazoyl)propyl sulfonate, has been reported.[11] However, the chemical stability of this polymer is expected to be low due to the presence of an easily hydrolyzable acrylate group.

Polymerizable surfactants with hydrocarbon backbones[12] and (semi)fluorinated backbones[13] have been synthesized and studied for various objectives like micellar polymerization, drug delivery systems, and applications in paints. Most polymerizable fluorosurfactants are cationic and nonionic in nature. In one report,[14] an anionic ($-\mathrm{CO\bar{O}}$-based) fluorinated surfmer, monofluoroalkyl maleate, has been used by Pich et al. as a stabilizer in the miniemulsion polymerization of styrene and *n*-butyl methacrylate.

Here, we report on the synthesis of the polymerizable fluorosurfactant **1** and its nonpolymerizable analogue **2** (Figure 1). In the design of **1**, we chose the sulfonate group as the proton- conducting moiety because of its high stability and high proton conductivity. In addition, many fluorocarbons containing fluorosulfonyl groups, from which the sulfonate group is readily obtained by basic hydrolysis, are available.[13] The styryl functionality was selected because aromatic moieties can directly be attached to fluorocarbon chains by a copper-mediated coupling reaction.[15] In this fashion, hydrolyzable ester and amide functionalities, that are present in acrylates and acrylamides, are avoided. Although polymerizable surfactants have been synthesized by direct coupling of styryl moieties using methods like esterification[16] or etherification,[17,18] the harsh conditions of the copper-mediated coupling prevented such a direct approach. Therefore, 4-bromobenzaldehyde was coupled to the fluorosurfactant molecule and subsequently converted into a functional styrene group.

It is expected that the styrene moiety in **1**, in contrast to most fully fluorinated monomers,[19,20] is readily polymerized

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[7] The degree of sulfonation is best represented by the equivalent weight (EW), which represents the mass of the polymer per SO_3^- unit. The equivalent weights for Nafion 112 and the (PVDF-g-SPS) graft copolymer reported by Chung are 1100 and 454, respectively.

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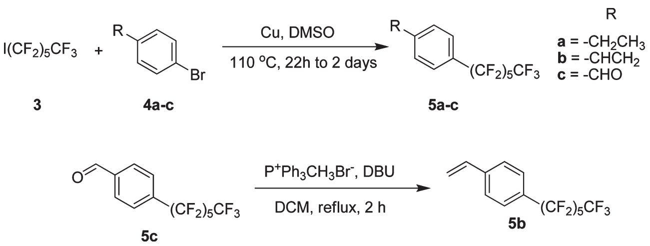
with a wide variety of comonomers under anionic, cationic, coordination, and controlled radical conditions.[21] It is also expected that the partial fluorination of **1**, by the attachment of a fluorocarbon tail, increases the stability of Poly-**1**.[22] To the best of our knowledge, compound **1** is the only fluorinated surfactant that contains a sulfonate and a readily polymerizable styrene that can be synthesized using standard synthetic tools. Special equipment for handling volatile and highly toxic halogenated compounds is not required. We wish to employ **1** for the construction of nanostructured membranes by polymerization of **1** in a microemulsion or in an LLC phase. Compound **2** is expected to be very similar to **1** regarding its physical properties but without the ability to be polymerized. Therefore, **2** is regarded as a nonpolymerizable model surfactant that is well suited for investigating the morphology formation in microemulsions and LLC phases.

Results and Discussion

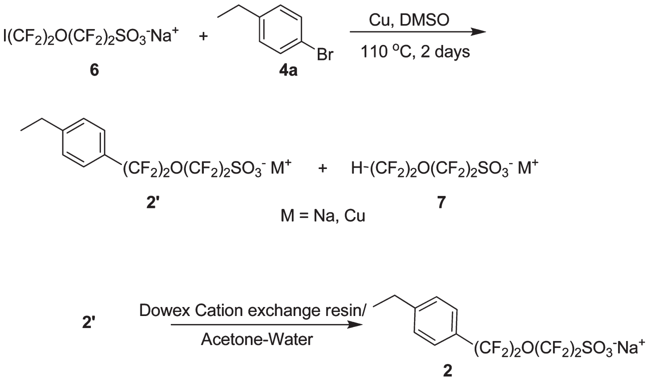
The synthesis of compounds **1** and **2** is based upon sodium 5-iodooctafluoro-3-oxapentanesulfonate (**6**), which contains an iodo and a sulfonate group at opposite ends of a fluorocarbon chain.[13] For the substitution of the iodo moiety by an aromatic substituent, a copper-mediated cross-coupling is employed. In this reaction, an iodine to copper exchange takes place that forms a copper(I) fluoroalkyl adduct, which subsequently reacts with an aromatic iodide or bromide.[15a,b] This reaction has been described using a wide range of aromatic iodides and bromides and appears to be tolerant to the presence of functional groups like esters, carboxylic acids, nitro groups, and amines.[15a]

We decided to investigate the copper-mediated cross-coupling reactions in the synthesis of model compounds **5**, which did not contain sulfonate groups (Scheme 1). In this manner, potential interference of the sulfonate with the reaction and tedious surfactant purifications are avoided. The reaction of 1-iodofluorohexane (**3**) with bromo-4-ethylbenzene (**4a**) yielded 1-ethyl-4-(perfluorohexyl)benzene (**5a**) in a moderate 60% yield. A direct coupling of 4-bromostyrene (**4b**) with **3** was attempted, but instead of the desired 1-(perfluorohexyl)-4-vinylbenzene (**5b**), a highly viscous polymeric mass was obtained. Clearly, the reaction conditions were too harsh for the styryl moiety, and premature styrene polymerization had taken place. In order to obtain **5b**, we decided to couple 4-bromobenzaldehyde (**4c**) to the fluorocarbon iodide **3**, and 4-(perfluorohexyl)benzaldehyde (**5c**)[23] was obtained in 88% yield. Compound **5c** appeared to be very sensitive to oxidation by air (even in the solid state) and had to be handled under an argon atmosphere to avoid oxidation to carboxylic acid. A subsequent Wittig reaction with methyl triphenylphosphonium bromide in DCM,[24a] using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a base, yielded the desired styrene compound **5b** in 77% yield; see Scheme 1. The introduction of a styryl functionality by various methods, like dehydration of an alcohol,[25] dehydrohalogenation,[26] or a Wittig reaction with an aldehyde,[24a,b] has been reported. We have chosen for the attachment an aldehyde followed by a Wittig olefination, because this method is efficient, is performed under mild conditions, and can be employed in polar solvents in which fluorosulfonate compounds are soluble.[24a]

SCHEME 1. Synthesis of Compounds 5a−c



SCHEME 2. Synthesis of Non-polymerizable Fluorosurfactant 2



The synthesis of the model surfactant **2** is outlined in Scheme 2. After the cross-coupling of sodium 5-iodoocta-fluoro-3-oxapentanesulfonate (**6**) and **4a**, a mixture of **2′**, which may contain Cu$^+$ or Na$^+$ as the counterion, and the hydrogen-substituted byproduct **7** was obtained.[27] The crude yield of this reaction, based on ^{1}H NMR spectra, was typically 70%. For standard reactions, in which the ratio between the reactants **6** and **4a** was 1:1, the **2′**:**7** ratio was typically 8:1. The substitution of iodide by hydrogen in this cross-coupling has been reported and is ascribed to reaction of the Cu(I)−fluorocarbon adduct with water during workup.[15a]

Isolation of **2** from this reaction mixture turned out to be difficult and very sensitive to the exact workup procedure. It turned out that only if the starting material contains DMSO can **2** and **7** be separated by column chromatography. Based on these findings, we performed the synthesis of **2** using

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[23] The synthesis of **5c** via ethyl 4-bromobenzoate has been reported previously, but a reaction step using LiAlH$_4$ in this synthetic scheme, which may reduce the sulfonate group, made this procedure unsuitable for our work; see: Reichardt, C.; Eschner, M.; Schafer, G. *J. Phys. Org. Chem.* **2001**, *14* (11), 737–751.

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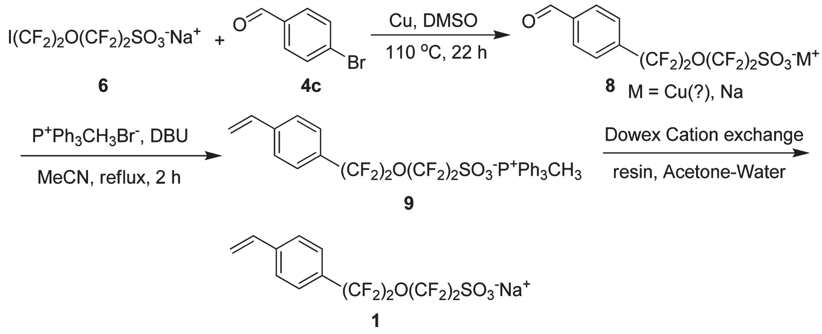
[27] It is noteworthy that we did not find a similar hydrogenated product while preparing **5a**. Presumably, this product has been formed, but since it is highly volatile, it has not been isolated.

SCHEME 3. **Synthesis of the Polymerizable Fluorosurfactant 1**



2 equiv of **4a**, which reduces the contents of **7** in the crude product to a mere 4%. For the removal of copper salts from the reaction, an ethyl acetate−brine extraction was used. After addition of DMSO to the mixture of **2′** and **7** a single column chromatography separation followed by cation exchange using an ion-exchange column was sufficient to obtain **2** in pure form.[28] The isolated yield after purification was 60%.[29]

The synthesis of the polymerizable surfactant **1** is depicted in Scheme 3. The cross-coupling of **4c** and **6** produced compound **8**. After ethyl acetate and brine extraction, a procedure by which ionic contaminants and DMSO are removed and eventual Cu$^+$ ions are exchanged by Na$^+$ ions, the yield of **8** was 85%. Despite precautions to exclude air, traces of the carboxylic acid were observed in the NMR spectra of **8**.[30] Remarkably, the hydrogenated product **7**, a compound that would be easily identified by ^{1}H and ^{19}F NMR, was not detected. The subsequent Wittig reaction, performed with 2−3 equiv of Wittig reagent, yielded the styrene **9**, in which the triphenylmethylphosphonium ion acts as the counterion. After ion exchange using a sodium-loaded Dowex column, followed by chromatography on a silica column, **1** was obtained. Recrystallization from toluene gave crystalline **1** in 50% yield.

For the synthesis of compounds **1**, **2**, **5a**, and **5b**, the cross-coupling reactions between an aromatic moiety ArBr **4** and the fluorocarbon iodides **3** and **6** were employed. We found that this reaction performed much better with 4-bromobenzaldehyde than with 1-bromo-4-ethylbenzene. With 4-bromobenzaldehyde both the yields were higher and hydrogenated side-products were absent. These observations are best explained by assuming that the reactivity of the aromatic bromide in this reaction is enhanced by electron-withdrawing substituents at the aromatic core. This conclusion is consistent with reported yields for this reaction.[15a] For the synthesis of fluoroalkyl-substituted styrenes a direct coupling of 4-bromostyrene was not possible. We have found that the coupling of benzaldehyde followed by a Wittig reaction was an efficient method for the synthesis of these compounds. Both the copper-mediated cross coupling and the Wittig reactions were not affected by the presence of a sulfonate moiety. The isolated yields of the sulfonate containing surfactants **1** and **2**, however, were markedly lower than those of **5a** and **5b**, but this was due to losses during purification of the surfactants. For the surfactant purification, ion-exchange and column chromatography were required. In particular, the isolation of **2** from mixtures with the side product **7** was very challenging. Attempts to avoid the formation of sulfonate containing surfactants by reversing the sequence of reaction steps, and making sulfonyl fluorides instead, were not successful. We have found that sulfonyl fluorides are not compatible with the copper-mediated cross-coupling conditions.

The physical properties of **1** and **2**, with regard to their phase behavior in aqueous systems and the polymerization of **1** are currently under investigation. In view of the envisaged application of **1**, however, it is appropriate to show the most important results here. Compound **1** is readily polymerized under standard free-radical polymerization conditions[31] in polar solvents like water and DMF, and ^{1}H and ^{19}F NMR spectra of the resulting polymer are shown in Figures S36 and S37 (Supporting Information). The phase behavior of **1** and **2** is very similar, and various lyotropic phases have been identified by cross-polarized optical microscopy pictures of binary mixtures of **2** in water, as illustrated in Figure S38 (Supporting Information). These findings imply that compound **1** is capable of forming various nanostructured phases in water and can be readily polymerized in this solvent. On the basis of these observations, it is reasonable to assume that the polymerizable fluorosurfactant **1** is well suited for the construction of nanostructured proton-conducting membranes.

Conclusions

Compounds **1** and **2** were synthesized using the readily accessible sodium 5-iodooctafluoro-3-oxapentanesulfonate **6** as a starting compound. Coupling of aromatic molecules ArBr (**4**) to **6** was achieved by a copper-mediated cross-coupling. The presence of a sulfonate moiety did not interfere with this reaction. The reaction of **6** with 1-bromo-4-ethylbenzene **4a** was slow and produced the hydrogenated side product **7**. The formation of **7** during the synthesis of **2** resulted in a challenging purification procedure. Attachment of a styryl functionality to **6** was achieved in two steps. The attachment of 4-fluorobenzaldehyde to **8** was a fast, efficient, and clean reaction. The conversion of the aldehyde **8** to the polymerizable surfactant by a Wittig reaction proceeded

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[28] After two columns, traces of **7** could be detected by ^{1}H and ^{19}F NMR. The percentage of **7** in the product was below 1%.

[29] Compound **2** can be recrystallized from toluene, but this procedure does not improve the purity of **2**.

[30] The coupled product **8** is very prone to oxidation. Fortunately, the carboxylic acid that is formed is removed in the ethyl acetate and brine extraction.

[31] For an example, see: Jager, W. F.; Sarker, A. M.; Neckers, D. C. *Macromolecules* **1999**, *32*, 8791–8799.

smoothly. Extensive purification of this surfactant, including column chromatography and ion-exchange, however, seriously reduced the isolated yields. Along with **1** and **2**, the monomer **5b** was synthesized by the cross-coupling of 4-bromobenzaldehyde and 1-iodofluorohexane followed by a Wittig reaction with methyltriphenylphosphonium bromide.

In our current research, the phase behavior of the surfactants **1** and **2** in water are being investigated along with the polymerization of **1** and **5b**.

Experimental Section

Instrumentation. TLC analysis was performed on silica gel, and ^{1}H, ^{19}F, and ^{13}C NMR spectra were measured in $CDCl_3$ or CD_3OD at 300 or 400 MHz and 282.3 and 75.4 MHz, respectively. Chemical shifts are given in ppm (δ). Tetramethylsilane (TMS) was used as internal standard for ^{1}H and ^{13}C NMR, whereas for ^{19}F NMR we used trifluoroacetic acid as the standard. LC−MS data were collected with a liquid chromatograph mass spectrometer, with a diode-array detector. The column used was the Xbridge Shield RP 18.5 mm (4.6 × 150 mm) on MeOH. Fast atom bombardment (FAB) mass spectrometry was carried out with a four sector mass spectrometer, coupled to a system program. Samples were loaded in a matrix solution (3-nitrobenzyl alcohol) onto a stainless steel probe and bombarded with Xenon atoms with energy of 3 keV. During the high-resolution FAB-MS measurements a resolving power of 10000 (10% valley definition) was used. IR spectra were from KBr pellets with an FTIR spectrophotometer.

1-Ethyl-4-(perfluorohexyl)benzene (5a). A 25 mL round-bottom flask was charged with copper powder (33 mmol, 3.07 g) and heated above 150 °C under an argon flow using a hot gun. The flask was cooled to ambient temperature, and perfluorohexyl iodide (6.73 mmol, 3.00 g), 4-bromoethylbenzene (6.74 mmol, 1.27 g), and DMSO (6 mL) were added to the flask and heated to 110 °C for 2 days using an oil bath. The reaction mixture was cooled, 20 mL of water was added, and then the mixture was filtered. The filtrate was further extracted with (3 × 20 mL) DCM. All of the DCM layers were collected, washed with 20 mL of water two times, and dried over anhydrous Na_2SO_4. Column chromatography with pentane gave **5a** as a colorless liquid (1.75 g, 61%): ^{1}H NMR (400 MHz, $CDCl_3$), 7.49 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.16 Hz, 2H), 2.72 (q, J = 7.56 Hz, 2H), 1.27 (t, J = 7.6 Hz, H); ^{19}F NMR (282.3 MHz, $CDCl_3$), −81.12 (t, J =9.03 Hz, 3F), −110.64 (t, J = 13.55 Hz, 2F), −121.76 (s, 2F), −122.173 (s, 2F), −123.08 (s, 2F), −126.41 (s, 2F); ^{13}C NMR (75.4 MHz, $CDCl_3$), 148.73, 128.28, 127.02, 126.5 (aromatic-C), 120.00−105.00 (CF_2 and CF_3), 28.90, 15.25 (ethyl-C); IR ν cm^{-1} 3045, 2974, 2941, 2881, 1517, 1464, 1420, 1363, 1239, 1091, 1040, 1015. Anal. Calcd for $C_{14}H_9F_{13}$: C, 39.64; H, 2.14; F, 58.22. Found: C, 39.44; H, 2.13; F, 58.1.

4-(Perfluorohexyl)benzaldehyde (5c). Reaction conditions and purification procedures were similar to those for **5a**, except the purification was done under an argon atmosphere. The reaction was performed with copper powder (50 mmol, 3.15 g), perfluorohexyl iodide (11.2 mmol, 5.00 g), and 4-bromobenzaldehyde (10.0 mmol, 2.07 g) in DMSO (9 mL). The reaction was performed for 22 h. Column chromatography (pentane/DCM = 0.7:0.3) gave a white solid 5c (4.5 g, 94%). ^{1}H NMR, ^{19}F NMR, and IR data were consistent with those reported in ref 23.

1-(Perfluorohexyl)-4-vinylbenzene (5b). Methyltriphenylphosphonium bromide (18.7 mmol, 6.69 g) and DBU (19 mmol, 2.89 g) were dissolved in freshly distilled DCM (65 mL). The solution was refluxed for 30 min, and **5c** (6.25 mmol, 2.65 g) dissolved in 15 mL of freshly distilled DCM was added to the refluxing solution at once. The mixture was refluxed for 2 h and subsequently washed with water (3 × 20 mL) and dried over Na_2SO_4. The solvent was removed using vacuum at 40 °C, and purification was done by column chromatography (pentane/DCM = 0.9:0.1). Compound **5b** was obtained as a colorless liquid (2.05 g, 77%). ^{1}H NMR, ^{19}F NMR, and IR data were consistent with those reported in ref 24a.

Sodium 2-(2-(4-Ethylphenyl)-1,1,2,2-tetrafluoroethoxy)-1,1,2,2-tetrafluoroethanesulfonate (2). Copper powder (19.9 mmol, 1.25 g) was heated above 150 °C under flow of argon in a 25 mL round-bottom flask. Sodium 5-iodooctafluoro-3-oxapentanesulfonate (4.31 mmol, 2.00 g) and 4-bromoethylbenzene (4.6 mmol, 0.85 g) were stirred in DMSO (3.6 mL) for 2 days at 110 °C under an argon atmosphere. The reaction mixture was cooled, and 2-propanol (10 mL) was added. The solution was filtered, and 2-propanol was removed by vacuum. The remaining mixture was extracted using ethyl acetate (3 × 20 mL), and all the ethyl acetate layers were washed using saturated brine to remove the DMSO and inorganic impurities. The ethyl acetate layer was dried using anhydrous Na_2SO_4. Around 50% DMSO (w/w) was added to the dry powder obtained after evaporation of ethyl acetate and column chromatography was performed (DCM/2-propanol = 0.85:0.15) to give white **2** (1.09 g, 60%): mp 241−245 °C; ^{1}H NMR (300 MHz, DMSO-d_6) 1.26 (t, J = 7.8 Hz, 3H), 2.71 (q, J = 7.5 Hz, 2H), 7.36 (d, J = 6.9 Hz, 2H), 7.56 (d, J = 6.9 Hz, 2H); ^{19}F NMR (282.3 MHz, DMSO-d_6), −82.09 (t, J = 14.1 Hz, 2F), −87.10 (t, J = 13.0 Hz, 2F), −113.37 (s, 2F), −117.53 (s, 2F); ^{13}C NMR (75.4 MHz, DMSO-d_6) 148.83, 128.73, 127.15, 125.64 (aromatic-C), 121.92−108.01 (CF_2), 28.43, 15.54 (ethyl-C); IR ν cm^{-1} 3044, 2968, 2929, 2874, 1517, 1421, 1254, 1027, 1155, 1093, 1078, 1008; HRMS calcd for $C_{12}H_9F_8Na_2O_4S^+$ [M + Na]$^+$ 446.9889, found 446.9889. Anal. Calcd for $C_{12}H_9F_8NaO_4S$: C, 33.97; H, 2.14; F, 35.83; Na, 5.42; S, 7.56. Found: C, 33.92; H, 2.27; F, 35.20; Na, 5.38; S, 7.45.

Sodium 1,1,2,2-Tetrafluoro-2-(1,1,2,2-tetrafluoro-2-(4-formylphenyl)ethoxy)ethanesulfonate (8). Copper powder (62.0 mmol, 3.84 g) was strongly heated above 150 °C in argon atmosphere and cooled to room temperature. Added to it were compounds **6** (12.9 mmol, 6.00 g) and **4c** (13.0 mmol, 2.40 g). DMSO (11 mL) was added, and the reaction mixture was stirred for 22 h at 110 °C in inert conditions. 2-Propanol (20 mL) was added to the reaction mixture, and it was filtered. The filtrate was evaporated to remove 2-propanol and extracted with ethyl acetate (3 × 20 mL), and ethyl acetate layers were washed with brine. The ethyl acetate layer was dried over Na_2SO_4 under argon. The solvent was removed to give white solid **8** (4.77 g, 87%) and stored under an inert atmosphere: ^{1}H NMR (300 MHz, DMSO-d_6) 7.95 (d, J = 8.1 Hz, 2H), 8.09 (d, J = 7.8 Hz, 2H), 10.12 (s, 1H); ^{19}F NMR (282.3 MHz, DMSO-d_6) −81.86 (t, J = 12.98 Hz, 2F), −86.49 (broad s, 2F), −113.21 (s, 2F), −117.51 (s, 2F); ^{13}C NMR (75.4 MHz, DMSO-d_6) 193.47, 139.38, 133.32, 130.32, 128.40 (aromatic-C and −CHO), 122.09−108.18, (CF_2); IR ν cm^{-1} 3063, 2865, 1710, 1587, 1513, 1400, 1287, 1178, 1024, 1005; HRMS calcd for $C_{11}H_5F_8Na_2O_5S^+$ [M + Na]$^+$ 446.9525, found 446.9521.

Sodium 1,1,2,2-Tetrafluoro-2-(1,1,2,2-tetrafluoro-2-(4-vinylphenyl)ethoxy)ethanesulfonate (1). Methyltriphenylphosphonium bromide (16.0 mmol, 5.71 g) and DBU (16.5 mmol, 2.51 g) were dissolved in 75 mL of freshly distilled acetonitrile. The solution was refluxed for 30 min. Compound **8** (8.0 mmol, 3.85 g), dissolved in acetonitrile (20 mL), was added to the refluxing solution at once, and the reaction mixture was refluxed for 2 h. After the mixture was cooled to room temperature, 10 mL of water was added and the mixture filtered. The solvent was removed using vacuum at 40 °C. The crude material was extracted with ethyl acetate (3 × 20 mL) and washed with 0.001 N HCl (3 × 20 mL). All of the ethyl acetate layers were collected and dried over Na_2SO_4. The solvent was removed, and the purification was done by column chromatography (DCM/2-propanol = 0.8:0.2) to give a waxy white material **9**. The yield was 3.9 g (70%) with ~75% purity:[32] ^{1}H NMR (400 MHz, $CDCl_3$) 2.92 (d, *J* = 13.6 Hz, 3H), 5.33 (d, *J* = 11.2 Hz, 1H), 5.81 (d, *J* = 17.6 Hz, 1H), 6.70 (double d, *J* = 11.1 and 8.0 Hz, 1H), 7.43−7.68 (m, 19H); ^{19}F NMR (282.3 MHz, $CDCl_3$) −82.62 (d, *J* = 12.70 Hz, 2F), −87.62 (s, 2F), −114.20 (s, 2F), −117.96 (s, 2F); LRMS calcd for $C_{12}H_7F_8O_4\bar{S}P^+Ph_3CH_3$ neg ion, $C_{12}H_7F_8O_4\bar{S}$ $[\bar{M}]$ 398.99, found 398.85; pos ion, $P^+Ph_3CH_3$ $[M']^+$ 277.11, found 276.95.

The solution of **9** in acetone/water mixture (1:1) was passed through a Dowex cation exchange column loaded with Na^+ ions. Column chromatography (DCM/2-propanol = 0.8:0.2) followed by recrystallization from toluene were performed to give **1**, a white crystalline solid 2 g (50%): mp 250 °C dec; ^{1}H NMR (300 MHz, MeOD) 5.3 (d, *J* = 11.1 Hz, 1H), 5.8 (d, *J* = 16.8 Hz, 1H), 6.67 (double d, *J* = 11.1 and 6.6 Hz, 1H), 7.42 (d, *J* = 8.9 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H); ^{19}F NMR (282.3 MHz, MeOD) −83.12 (t, *J* = 13.54 Hz, 2F), −87.76 (t, *J* = 12.98 Hz, 2F), −114.80 (s, 2F), −118.20 (s, 2F); ^{13}C NMR (75.4 MHz, DMSO-d_6) 141.49, 136.13, 127.71, 127.48, 127.13, 118.02 (Ar-C and vinyl-C), 127.00−113.00 (CF_2−C). IR ν cm^{-1} 3087, 3007, 1651, 1571, 1515, 1407, 1293, 1255, 1220, 1170, 1100, 1080, 1008, 915, 841; HRMS calcd for $C_{12}H_7F_8Na_2O_4S^+$ $[M + Na]^+$ 444.9727, found 444.9721. Anal. Calcd for $C_{12}H_7F_8NaO_4S$: C, 34.14; H, 1.67; F, 36.00; Na, 5.44; S, 7.59. Found: C, 33.87; H, 1.67; F, 35.00; Na, 5.44; S, 7.59.

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Supporting Information Available: ^{1}H NMR, ^{19}F NMR, and IR spectra of all synthesized compounds; ^{13}C NMR spectra for compounds **1**, **2**, **5a**, and **8**; HRMS for compounds **1**, **2**, and **8**; LRMS for **9**; elemental analysis of **5a**, **1**, and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[32] The remaining impurities were triphenylmethylphosphonium salts that were easily removed by the subsequent ion exchange.