Journal of Fluorine Chemistry 129 (2008) 1029–1035

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

New aryl-containing fluorinated sulfonic acids and their ammonium salts, useful as electrolytes for fuel cells or ionic liquids

R. Arvai [a,b,c,d,e,f], F. Toulgoat [a,b,c,d,e,f], M. Médebielle [a,b,c,d,e,f], B. Langlois [a,b,c,d,e,f,*], F. Alloin [g], C. Iojoiu [g], J.Y. Sanchez [g]

[a] *ICBMS, Institut de Chimie et Biochimie Moléculaires et Supramoléculaires, Equipe SERCOF, 43 boulevard du 11 novembre 1918, Villeurbanne F-69622, France*
[b] *CNRS, UMR5246, Villeurbanne F-69622, France*
[c] *Université de Lyon, Lyon F-69622, France*
[d] *Uuniversité Lyon 1, Lyon F-69622, France*
[e] *INSA-Lyon, Villeurbanne F-69622, France*
[f] *CPE Lyon, Villeurbanne F-69616, France*
[g] *Laboratoire d'Electrochimie et de Physico-chimie des Matériaux et des Interfaces, UMR 5631 CNRS-INPG-UJF, BP.75, 38402 Saint-Martin-d'Hères, France*

ARTICLE INFO

Article history:
Received 29 March 2008
Accepted 4 June 2008
Available online 20 June 2008

Keywords:
Fluoroalkanesulfonic acids
Fluoroalkanesulfonates
Electrolytes
Batteries
Fuel cells
Ionic liquids

ABSTRACT

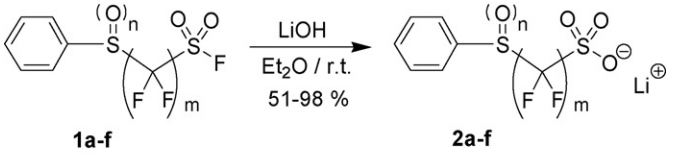
Several aryl-containing ammonium sulfonates have been prepared either by cationic metathesis from the corresponding lithium sulfonates or from the corresponding sulfonic acids. The latter have been obtained by elution of an Amberlite resin with alcoholic solutions of the lithium sulfonates. These ammonium sulfonates exhibit interesting conductivities and thermal properties which allow them to be promising candidates as electrolytes for electricity storage.

1. Introduction

Several decades have already passed from the first appearance of the Nafion® perfluorinated ionomeric membrane, originally developed by E.I. Dupont de Nemours Co. [1]. Yet, it became probably the most used and studied proton-conducting membrane for Proton Exchange Membrane Fuel Cells (PEMFC). It has been demonstrated that Nafion ionomers exhibit long-term stability, high ionic conductivity, gas permeability and good mechanical properties [2,3]. However, their high conductivity is tributary to their water uptake (two to five molecules of H_2O per H^+) and dramatically decreases at temperatures higher than 80 °C. Moreover, low working temperature fuel cells (below 80 °C) can suffer from Pt-catalyst inhibition by fuel impurities. This problem was attempted to be overcome mostly by synthesising novel polymer electrolyte membranes, by doping functional polymers with room temperature ionic liquids [3,4] or acid proton carriers with low vapour pressure (e.g. phosphoric acid [5], phosphotungstic acid [6] or zirconium phosphate [2]) or by combination of both ionic liquid and acid proton carriers [7,8]. An innovative approach was proposed by Watanabe quite recently using protic ionic liquids [9–12]. The physical and electrochemical properties of protic ionic liquids were also deeply studied by Angell and co-workers [13]. While Watanabe mostly studied salts from bis-(trifluoromethanesulfonyl) amide and organic nitrogen bases, Angell and co-workers examined ammonium salts from trifluoromethanesulfonic acid, trifluoroacetic acid or formic acid. The highest conductivities were obtained with trifluoromethanesulfonates and the influence of vapour pressure, viscosity, conductivity and ΔpK_a (between the acid and the base) was reported by Angell and co-workers.

* Corresponding author.
E-mail address: Bernard.Langlois@univ-lyon1.fr (B. Langlois).

0022-1139/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2008.06.009



Scheme 1. Phenyl-containing fluorinated sulfonyl fluorides and sulfonates.

In a recent work [14], we reported the synthesis of new phenyl-containing fluorinated sulfonyl fluorides **1a–f** and their saponification into the corresponding lithium sulfonates **2a–f** (Scheme 1), which are under evaluation as promising salts in solid polymer electrolytes for lithium batteries, having in mind the possibility to prepare analogues bearing a reactive substituent on the phenyl ring. Such moieties could allow the sulfonate incorporation (by copolymerization or grafting) in a polymer, in order to decrease the mobility of the anion and to increase the cationic conductivity of Li^+. This modification is under study and will be published soon.

In this context, despite the presence of the aromatic ring, the resulting salts exhibit improved cationic conductivity as compared to triflates. Indeed, the presence of the sulfanyl linker ($n = 0$) is important to increase the flexibility of the anions whereas the presence of the sulfonyl linker decreases the pK_a of the conjugated superacid and, consequently, the basicity, the nucleophilicity and the oxidability of the sulfonate.

2. Discussion

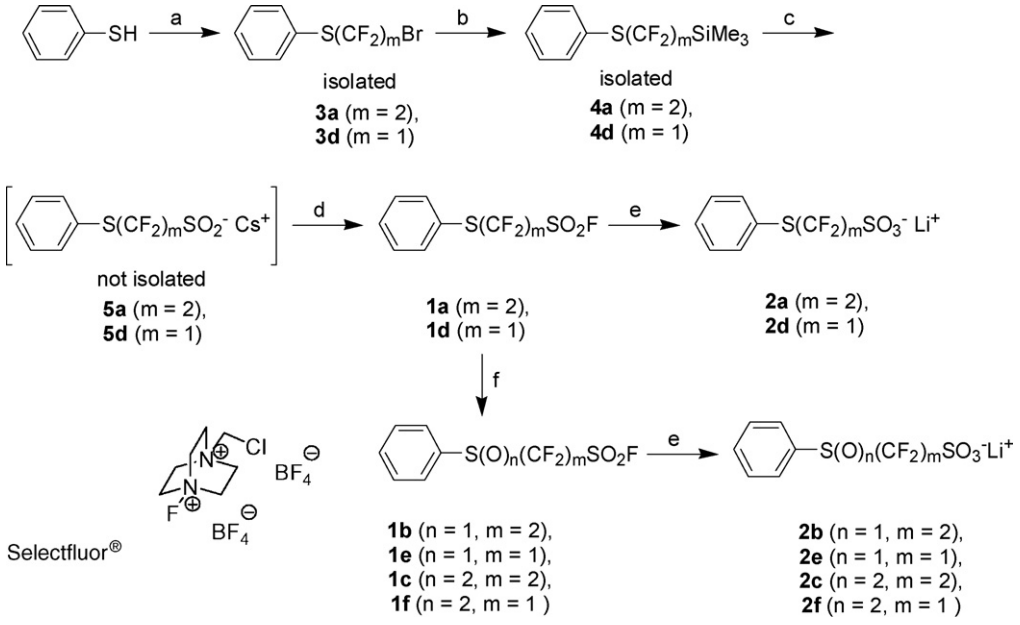
As we previously described [14], perfluoroalkylsulfonyl fluorides **1a,d**, the key compounds in the synthesis of sulfonates, are accessible in a good overall yield after condensation of benzenethiolate with, respectively, 1,2-dibromo-1,1,2,2-tetrafluoroethane or dibromodifluoromethane, according to the protocol of Suda and Hino [15], then transformation of resulted bromides **3a,d** into the corresponding silanes **4a,d**. The latter are further converted to sulfinates **5a,d** which are oxidized into sulfonyl fluorides **1a,d** by electrophilic fluorination with Selectfluor®. Oxidation of **1a,d** by *m*CPBA delivers either **1b,e** or **1c,f**, depending on the excess of *m*CPBA. Finally, saponification of **1a–f** with lithium hydroxide offers **2a–f** in good to excellent overall yield (Scheme 2).

However, if lithium sulfonates **2a–f** are potentially valuable salts for lithium batteries, they are not adapted for fuel cells and must be turned into proton conductors. Thus, we searched for new routes to tertiary ammonium cations associated with the same sulfonate anions as in **2a,c**, potentially useful as proton-conducting ionic liquids, and also to analogous quaternary ammonium salts behaving as aprotic ionic liquids, which could be used as ionic solvents valuable additives in batteries and fuel cells.

For this purpose, cation metathesis between lithium sulfonates **2a,d** and ammonium halides was first examined. In a typical experiment, an aqueous solution of the ammonium chloride was added to a solution of **2a,d** in acetone. After stirring at room temperature, evaporation to dryness, dissolution in water, extraction with dichloromethane and evaporation of the organic phase, some organic sulfonates have been isolated. Such a process was successful for different sulfonates, gathered in Table 1, which were obtained in a pure state (no chloride anion was detected by cyclic voltammetry).

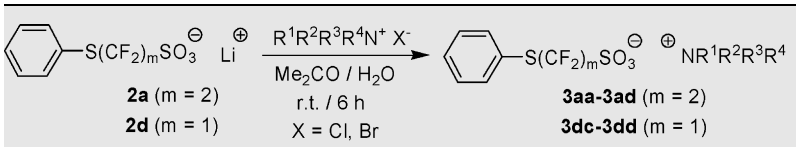
However, this method failed with *N*-methylimidazolium 2-(phenylsulfanyl)-1,1,2,2-tetrafluoroethanesulfonate which was not hydrophobic enough to be extracted by dichloromethane. So, we turned to the synthesis of the sulfonic acids corresponding to **2a** and **2c** which, in principle would be very strong and could be neutralized by a large variety of organic or inorganic bases. Only few references were found in the literature for the preparation of free aryl-containing perfluoroalkyl sulfonic acids by acidification of the corresponding sulfonate [16,17] (Fig. 1).

Obviously, these acids, as those we plan to prepare, are not volatile enough to be distilled from a suspension of the corresponding alkaline sulfonate in pure sulfuric acid, as it is done for triflic acid [18]. So, Prakash et al. prepared **4a,b** in a dynamic process, by



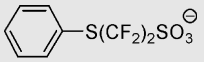
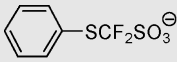
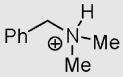
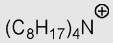
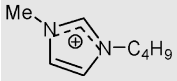
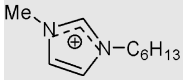
Scheme 2. Overall synthesis of lithium sulfonates **2a–f**. (a) NaH, dry DMF, $BrCF_2CF_2Br$ ($m = 2$) or CF_2Br_2 ($m = 1$); (b) Me_3SiCl, Mg, THF, −78 °C to rt overnight; (c) SO_2, CsF, dry MeCN, rt, overnight; (d) Selectfluor® (1 eq.), MeCN, −40 °C to rt; (e) $LiOH{\cdot}H_2O$, Et_2O; (f) *m*CPBA (2 eq., $n = 1$; 8 eq., $n = 2$), CH_2Cl_2 3 days.

Table 1
Preparation of ammonium sulfonates **3ac–d** and **3dc–d** by cationic metathesis

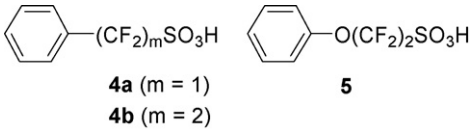


2a (m = 2)
2d (m = 1)

3aa-3ad (m = 2)
3dc-3dd (m = 1)

	 (Isolated yield)[a] (Isolated yield)[a]	 (Isolated yield)[a] (Isolated yield)[a]
	**3aa** (74%)	Not prepared
	**3ab** (89%)	Not prepared
	**3ac** (62%)	**3dc** (79%)
	**3ad** (81%)	**3dd** (69%)

[a] Overall yields vs. R_fSO_2F.



4a (m = 1)
4b (m = 2)

5

Fig. 1. Exemples of perfluoroalkyl sulfonic acids with a pendant aromatic ring [16,17].

elution of an acidic resin with an aqueous solution of the corresponding sulfonates. Consequently, they obtained the sulfonic acids as aqueous solutions, from which **4a,b** could not be isolated by evaporation since they decomposed under heating [16]. On the other hand, as far as **5** is concerned, no experimental data are available.

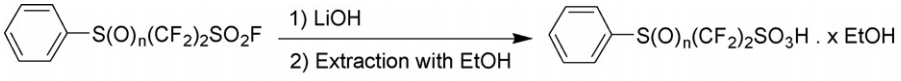
Thus, we carried out a similar technique but we eluted the Amberlite resin with a solution of **2a** or **2c** in pure ethanol. In such a way, we anticipated that ethanol could be evaporated under vacuum without heating and, consequently, without decomposition of the resulting sulfonic acids **6a,c**. It must be noticed that, in order to avoid any introduction of moisture, **2a,c** were prepared from **1a,c** but not isolated. Indeed, it worked, though isolated **6a,c** were obtained as solvates with ethanol (about 1.5 EtOH/R_fSO_3H, Scheme 3).

Such a solvation is not surprising since it can be thought that ethanol is, at least, tightly associated by hydrogen bonds with such strong acids or, acting as a base, could be even neutralized to provide an oxonium sulfonate. However, this is not a drawback since these sulfonic acids were further neutralized to provide different salts. This latter step was simply done by adding, at room temperature, an inorganic hydroxide as well as a secondary or tertiary amine to a solution of **6a,c** in dichloromethane (Table 2).

In order to have a first evaluation of the interest, as electrolytes, of most of these ammonium sulfonates, their conductivities (in the pure state at 85–100 °C) and their thermal characteristics (glass transition temperature, T_g, melting point, mp) have been measured. Melting points have been determined either by differential scanning calorimetry (DSC, indicating the beginning of melting) or in capillary tubes (indicating the end of melting) and T_g have been measured by DSC. T_g and mp are gathered in Table 3.

It has been also noticed that some ammonium sulfonates crystallize at a much lower temperature than they melt, after heating them above their melting point. For example, **3ac** crystallizes at −30 °C (melting point: 38 °C), **3dc** at 41 °C (melting point: 77 °C) and **3dd** does not solidify at all. This phenomenon has been often reported for ionic liquids.

As it appears from Table 3, a number of ammonium sulfonates exhibit a conductivity higher than 10^{-3} S cm^{-1}, a very low glass transition point and a moderate melting point. Such properties allow them to be good candidates as proton-conducting electrolytes for PEMFCs operating above 100 °C. Deeper investigations, such as the transference numbers, are under study to precise their interest in such applications.

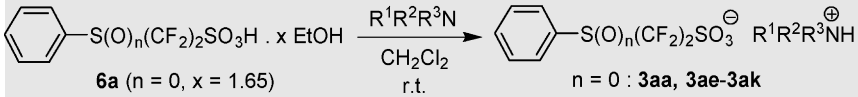


1a (n = 0)
1c (n = 2)

6a (n = 0) 86 %, x = 1.65
6c (n = 2) 90 %, x = 1.50

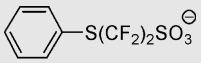
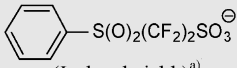
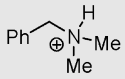
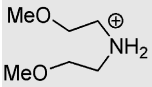
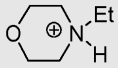
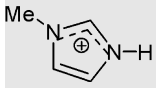
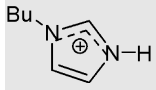
Scheme 3. Preparation of sulfonic acids **6a,c**.

Table 2
Preparation of ammonium sulfonates **3aa**, **3ae–3ak**, **3ca**, **3ce–3cg**, **3ci**, **3cj**



6a (n = 0, x = 1.65)
6c (n = 2, x = 1.50)

n = 0 : **3aa, 3ae-3ak**
n = 2 : **3ca, 3ce-3cg, 3ci, 3cj**

	 (Isolated yield)[a]	 (Isolated yield)[a]
	**3aa** (80%)	**3ca** (94%)
	**3ae** (98%)	**3ce** (96%)
	**3af** (95%)	**3cf** (97%)
	**3ag** (99%)	**3cg** (94%)
	**3ah** (90%)	Not prepared
	**3ai** (89%)	**3ci** (88%)
	**3aj** (96%)	**3cj** (95%)
	**3ak** (65%)	Not prepared

[a] Overall yields vs. R_fSO_2F.

Table 3
Conductivities and thermal properties of different ammonium sulfonates.

Sulfonate	Conductivity σ (S cm^{-1}) (at t °C)	Differential scanning calorimetry (5 °C min^{-1})	
		T_g (°C)	mp (°C)
3aa	N.D.	−43 °C	43 °C[a]
3ca	N.D.	−36 °C	112 °C
3ac	4.9×10^{-3} (90 °C)	N.D.	38 °C[b]
3dc	5.9×10^{-3} (90 °C)	N.D.	77 °C[b]
3ad	3.8×10^{-4} (85 °C)	−54 °C[b]	Oil
3dd	6.5×10^{-4} (90 °C)	N.D.	40 °C[b]
3ae	4.0×10^{-3} (100 °C)	−60 °C	Oil
3ce	1.3×10^{-3} (100 °C)	−60 °C	30 °C
3af	2.6×10^{-3} (100 °C)	−50 °C	Oil
3cf	N.D.	N.D.	Oil
3ag	3.3×10^{-3} (90 °C)	−40 °C	Oil
3cg	7.8×10^{-4} (100 °C)	−56 °C	36 °C
3ah	2.1×10^{-3} (100 °C)	N.D.	Oil
3ai	4.0×10^{-3} (100 °C)	−60 °C	12 °C
3ci	1.5×10^{-3} (100 °C)	−36 °C	48 °C
3aj	4.0×10^{-3} (100 °C)	N.D.	65 °C
3cj	2.2×10^{-3} (100 °C)	N.D.	85 °C[c]
3ak	1.1×10^{-3} (100 °C)	N.D.	Oil

N.D.: Not determined.
[a] mp: 76 °C in capillary tubes.
[b] DSC at 10 °C min^{-1}.
[c] Recrystallized compound. Before recrystallization, mp: 72 °C (capillary tube).

3. Conclusion

In conclusion, several tertiary or quaternary ammonium aryl-containing sulfonates, useful as aprotic ionic liquids or proton-conducting ones, have been prepared by cationic metathesis between the corresponding lithium sulfonates and ammonium halides. In order to broaden the availability of such salts, the corresponding sulfonic acids were synthesised by eluting Amberlite resin with an alcoholic solution of lithium sulfonates. In such a way, these acids were easily isolated as solvates with ethanol, then neutralized with a variety of secondary or tertiary amines in dichloromethane, that allowed the resulting ammonium sulfonates to be quickly isolated. Some of these ammonium sulfonates exhibit good conductivities and rather low melting points, so that they will be evaluated as proton-conducting electrolytes for fuel cells. Their syntheses and properties have been recently patented [19].

4. Experimental

Prior to use, solvents were distilled and stored over 3 Å molecular sieves under N_2. Commercially available reagents were used as received. Sulfonyl fluorides **1a,c** and lithium sulfonates

2a,d were obtained according to ref. [14]. Amberlite (IR-120, H^+-form, Fluka, mesh 28–35 Å) was activated (elution with 6 M HCl, then with deionized water, absolute ethanol and finally diethyl ether) and dried *in vacuo* prior use. All reactions were carried out under nitrogen atmosphere. TLC analyses were carried out on silica gel (Merck Kieselgel $60F_{254}$) deposited on aluminum plates, detection being done by UV (254 nm). Flash-chromatographies were performed on silica gel Merck Geduran SI 60 (230–400 mesh). Unless stated otherwise, NMR spectra were recorded in $CDCl_3$. ^1H NMR were recorded at 300 MHz and ^{13}C NMR spectra at 75 MHz. ^{19}F NMR spectra were recorded at 282 MHz. Chemical shifts (δ) are given in ppm vs. TMS (^1H, ^{13}C) or $CFCl_3$ (^{19}F), used as internal references. Coupling constants are given in hertz. The substitution pattern of the different carbons were determined by a "DEPT 135" sequence. Mass spectrometry was carried out on a Thermo Finnigan Mat 95xL apparatus (mode of ionization: electrospray, chemical ionization or electron impact). Melting points were determined either in capillary tubes on a Büchi apparatus (uncorrected) or by differential scanning calorimetry (DSC).

4.1. Cationic metathesis between lithium sulfonates 2a,d and ammonium halides

4.1.1. Benzyldimethylammonium 2-(phenylsulfanyl)-1,1,2,2-tetrafluoroethanesulfonate 3aa

Benzyldimethylammonium chloride (125 mg, 0.74 mmol), dissolved in water (2 mL), was added, under inert atmosphere, to a solution of **2a** (290 mg, 0.96 mmol) in acetone (5 mL). The mixture was stirred at room temperature for 6 h then evaporated to dryness. Water was added to the residue and the aqueous phase was extracted with CH_2Cl_2 (6×10 mL). The gathered organic phases were washed with water (3×15 mL) then dried over $MgSO_4$ and evaporated. **3aa** was obtained as a white solid (0.32 g, 0.86 mmol, 74% from 1 mmol of $PhSCF_2CF_2SO_2F$ [14]). mp: 43–76 °C. ^{19}F NMR: δ −85.14 (t, 2 F, $^3J_{F-F}$ = 5.7 Hz), −112.24 (t, 2F, $^3J_{F-F}$ = 5.7 Hz). ^1H NMR: δ 7.64 (m, 2H), 7.36–7.46 (m, 8H), 6.85 (broad s, 1H), 4.15 (s, 2H), 2.78 (s, 6H). ^{13}C NMR: δ 137.2 (s), 130.8 (s), 130.6 (s), 130.2 (s), 129.4 (s), 129.2 (s), 128.9 (s), 124.2 (t, $^3J_{F-C}$ = 2.5 Hz), 124.2 (tt, $^1J_{F-C}$ = 289.8 Hz, $^2J_{F-C}$ = 32.7 Hz), 115.1 (tt, $^1J_{F-C}$ = 288.7 Hz, $^2J_{F-C}$ = 34 Hz), 61.5 (s), 42.7 (s).

4.1.2. Tetra-n-octylammonium 2-(phenylsulfanyl)-1,1,2,2-tetrafluoroethanesulfonate 3ab

2a (455 mg, 1.54 mmol) and tetra-*n*-octylammonium bromide (842 mg, 1.54 mmol) were dissolved in acetone (10 mL) and stirred at room temperature for 5 min. Then, the solvent was evaporated and the residue was dispersed in CH_2Cl_2. After stirring, the insoluble lithium bromide was filtered on Celite and washed with dichloromethane. After evaporation, **3ab** was obtained as an oil (1.04 g, 1.37 mmol, 89% from $PhSCF_2CF_2SO_2F$). ^{19}F NMR (acetone): δ −85.1 (t, 2F, $^3J_{F-F}$ = 8 Hz), −113.9 (t, 2F, $^3J_{F-F}$ = 8 Hz). ^1H NMR (acetone): δ 7.61–7.64 (m, 2H), 7.40–7.54 (m, 3H), 3.38–3.43 (m, 8H), 1.66–1.83 (m, 8H), 1.27–1.83 (m, 40H), 0.84–0.88 (m, 12H). ^{13}C NMR (acetone): δ 137.4 (s), 130.9 (s), 129.8 (s), 126.2 (s), 124.9 (tt, $^1J_{F-C}$ = 290 Hz, $^2J_{F-C}$ = 32 Hz), 115.6 (tt, $^1J_{F-C}$ = 290 Hz, $^2J_{F-C}$ = 32 Hz), 59.1 (s), 32.3 (s), 29.7 (s), 29.5 (s), 26.8 (s), 23.2 (s), 22.4 (s), 14.4 (s).

4.1.3. 1-n-Butyl-3-methylimidazolium 2-(phenylsulfanyl)-1,1,2,2-tetrafluoroethanesulfonate 3ac

3ac was prepared in the same way as **3aa**, starting from **2a** (200 mg, 0.68 mmol), dissolved in acetone (8 mL), and 1-*n*-butyl-3-methylimidazolium chloride (105 mg, 0.6 mmol), dissolved in water (5 mL). Yield: 62% (180 mg) from $PhSCF_2CF_2SO_2F$. Beige solid. mp: 38 °C. ^{19}F NMR: δ −85.0 (t, 2F, $^3J_{F-F}$ = 5.7 Hz), −113.0 (t, 2F, $^3J_{F-F}$ = 5.7 Hz). ^1H NMR: δ = 9.16 (s, 1H), 7.60–7.65 (m, 2H), 7.26–7.42 (m, 5H), 4.13 (t, 2H, ^3J = 7 Hz), 3.91 (s, 3H), 1.75 (m, 2H), 1.25 (m, 2H), 0.89 (t, 3H, ^3J = 7 Hz). ^{13}C NMR: δ 137.1 (s), 136.5 (s), 130.3 (s), 129.0 (s), 124.5 (t, $^3J_{F-C}$ = 2.5 Hz), 124.2 (tt, $^1J_{F-C}$ = 289.8 Hz, $^2J_{F-C}$ = 32.7 Hz), 123.6 (s), 122.1 (s), 115.1 (tt, $^1J_{F-C}$ = 288.7 Hz, $^2J_{F-C}$ = 34 Hz), 49.7 (s), 36.3 (s), 31.9 (s), 19.2 (s), 13.3 (s).

4.1.4. 1-n-Hexyl-3-methylimidazolium 2-(phenylsulfanyl)-1,1,2,2-tetrafluoroethanesulfonate 3ad

3ad was prepared in the same way as **3aa**, starting from **2a** (202 mg, 0.68 mmol), dissolved in acetone (8 mL), and 1-*n*-hexyl-3-methylimidazolium chloride (132 mg, 0.65 mmol), dissolved in water (5 mL). Yield: 81% (252 mg) from $PhSCF_2CF_2SO_2F$. Oil. ^{19}F NMR: δ −85.2 (t, 2F, $^3J_{F-F}$ = 5.7 Hz), −113.0 (t, 2F, $^3J_{F-F}$ = 5.7 Hz). ^1H NMR: δ 9.12 (s, 1H), 7.62–7.63 (m, 2H), 7.29–7.42 (m, 5H), 4.11 (t, 2H, ^3J = 7.3 Hz), 3.89 (s, 3H), 1.79 (m, 2H), 1.24 (m, 6H), 0.80 (t, 3H, ^3J = 7 Hz). ^{13}C NMR: δ 137.1 (s), 136.8 (s), 130.3 (s), 129.0 (s), 124.5 (t, $^3J_{F-C}$ = 2.5 Hz), 124.2 (tt, $^1J_{F-C}$ = 289.8 Hz, $^2J_{F-C}$ = 32.7 Hz), 123.7 (s), 122.0 (s), 115.1 (tt, $^1J_{F-C}$ = 288.7 Hz, $^2J_{F-C}$ = 34 Hz), 50.0 (s), 36.2 (s), 30.9 (s), 30.0 (s), 25.7 (s), 22.3 (s), 13.9 (s).

4.1.5. 1-n-Butyl-3-methylimidazolium 2-(phenylsulfanyl)difluoromethanesulfonate 3dc

3dc was prepared in the same way as **3aa**, starting from **2d** (200 mg, 0.81 mmol), dissolved in acetone (8 mL), and 1-*n*-butyl-3-methylimidazolium chloride (140 mg, 0.80 mmol), dissolved in water (5 mL). Yield: 79% (252 mg) from $PhSCF_2SO_2F$. White solid. mp: 77 °C. ^{19}F NMR: δ −79.0 (s). ^1H NMR: δ 9.22 (s, 1H), 7.60–7.64 (m, 2H), 7.32–7.40 (m, 5H), 4.16 (t, 2H, ^2J = 7 Hz), 3.93 (s, 3H), 1.80 (m, 2H), 1.25 (m, 2H), 0.88 (t, 3H, ^2J = 7 Hz). ^{13}C NMR: δ 137.0 (s), 136.5 (s), 129.8 (s), 129.0 (s), 126.0 (t, $^1J_{F-C}$ = 289.8 Hz), 124.5 (t, $^3J_{F-C}$ = 2.5 Hz), 123.7 (s), 122.1 (s), 49.7 (s), 36.4 (s), 32.0 (s), 19.4 (s), 13.3 (s).

4.1.6. 1-n-Hexyl-3-methylimidazolium 2-(phenylsulfanyl)difluoromethanesulfonate 3dd.

3dd was prepared in the same way as **3aa**, starting from **2d** (192 mg, 0.78 mmol), dissolved in acetone (8 mL), and 1-*n*-hexyl-3-methylimidazolium chloride (152 mg, 0.75 mmol), dissolved in water (5 mL). Yield: 69% (220 mg) from $PhSCF_2SO_2F$. Beige solid. mp: 40 °C. ^{19}F NMR: δ −79.1 (s). ^1H NMR: δ 9.12 (s, 1H), 7.62–7.63 (m, 2H), 7.29–7.41 (m, 5H), 4.11 (t, 2H, ^2J = 7 Hz), 3.89 (s, 3H), 1.78 (m, 2H), 1.24 (m, 6H), 0.80 (t, 3H, ^2J = 7 Hz),. ^{13}C NMR: δ 137.1 (s), 136.8 (s), 130.3 (s), 129.0 (s), 126.1 (t, $^1J_{F-C}$ = 289.8 Hz), 124.5 (t, $^3J_{F-C}$ = 2.5 Hz), 123.7 (s), 122.0 (s), 50.0 (s), 36.2 (s), 30.9 (s), 30.0 (s), 25.7 (s), 22.3 (s), 13.9 (s).

4.2. Synthesis of sulfonic acids 6a and 6c

4.2.1. 2-(phenylsulfanyl)-1,1,2,2-tetrafluoroethanesulfonic acid 6a

Solid $LiOH{\cdot}H_2O$ (0.09 g, 2.18 mmol) was added, at room temperature, to a stirred solution of $PhSCF_2CF_2SO_2F$ (0.27 g, 1 mmol), in Et_2O (15 mL). Stirring was held for 24 h. The reaction was followed by TLC (SiO_2/pentane) and ^{19}F NMR. After removal of the solvent under vacuum, the solid residue was dissolved in absolute ethanol (3 mL) and the solution was dropped slowly, over 10 min, through a column (15 cm) of Amberlite IR 120 (H^+ form), previously washed with absolute ethanol. Volatiles compounds were removed for 24 h *in vacuo*. The residue was pure enough to be used in the next step without further purification. Brown-red oil (0.32 g, 0.86 mmol, 86%). ^1H NMR: δ 10.38 (s, 4H), 7.64 (d, $^3J_{H-H}$ = 7.0 Hz, 2H), 7.48–7.33 (m, 3H), 3.89 (q, $^3J_{H-H}$ = 7.1 Hz, 3.3H), 1.27 (t, $^3J_{H-H}$ = 7.1 Hz, 5H). ^{19}F NMR: δ −85.64 (t, $^3J_{F-F}$ = 5.1 Hz, 2F), −112.21 (t, $^3J_{F-F}$ = 5.1 Hz, 2F). ^{13}C NMR: δ 137.28 (s), 130.70 (s),

129.28 (s), 123.82 (t, $^3J_{F-C}$ = 2.5 Hz), 123.41 (tt, $^1J_{F-C}$ = 290.3 Hz, $^2J_{F-C}$ = 32.7 Hz), 114.53 (tt, $^1J_{F-C}$ = 289.3 Hz, $^2J_{F-C}$ = 35.2 Hz), 60.12 (s), 16.02 (s).

4.2.2. 2-Benzenesulfonyl-1,1,2,2-tetrafluoroethanesulfonic acid **6c**

Brown-red oil (90% yield). ^{1}H NMR: δ 10.40 (s, 2.5H), 8.00 (d, $^3J_{H-H}$ = 7.0 Hz, 2H), 7.84–7.75 (m, 1H), 7.69–7.60 (m, 2H), 3.96 (q, $^3J_{H-H}$ = 7.1 Hz, 3H), 1.30 (t, $^3J_{H-H}$ = 7.1 Hz, 4,5H). ^{19}F NMR: δ −110.51 (t, $^3J_{F-F}$ = 18.9 Hz, 2F), −112.67 (t, $^3J_{F-F}$ = 18.9 Hz, 2F). ^{13}C NMR: δ 136.38 (s), 132.59 (s), 130.83 (s), 129.68 (m), 115.13 (tt, $^1J_{F-C}$ = 299.7 Hz, $^2J_{F-C}$ = 35.9 Hz), 114.27 (tt, $^1J_{F-C}$ = 290.2 Hz, $^2J_{F-C}$ = 33.5 Hz), 59.61 (s), 16.17 (s). UV (0.2 mM in CH_2Cl_2): λ_{max} = 268.4–229.8.

4.3. Neutralization of sulfonic acids **6a** and **6c** with amines

4.3.1. Benzyldimethylammonium 2-(phenylsulfanyl)-1,1,2,2-tetrafluoroethanesulfonate **3aa**

Benzyldimethylamine (637 mg, 4.71 mmol) was dropped at 0 °C, under argon, into a solution of **6a** (1.5 g, 4.71 mmol) in freshly distilled CH_2Cl_2 (30 mL). The solution was stirred at room temperature for 1 h, then evaporated to dryness. The residue was dried under vacuum ($P < 0.02$ mbar) to offer **3aa** (1.63 g, 80%), the characteristics of which are given in Section 4.1.1.

4.3.2. Benzyldimethylammonium 2-(benzenesulfonyl)-1,1,2,2-tetrafluoroethanesulfonate **3ca**

3ca was obtained in the same way as **3aa**, starting from benzyldimethylamine (537 mg, 3.97 mmol) and **6c** (1.5 g, 3.97 mmol) in CH_2Cl_2 (30 mL). Beige solid (1.70 g, 94%). mp: 112 °C. ^{1}H NMR: δ 9.00 (broad s, 1H), 8.00–7.99 (m, 2H), 7.80–7.56 (m, 3H), 7.40 (m, 5H), 4.19 (d, $^3J_{H-H}$ = 13.7 Hz, 2H), 2.79 (d, $^3J_{H-H}$ = 7.8 Hz, 6H). ^{19}F NMR: δ −110.2 (t, $^3J_{F-F}$ = 6.9 Hz, 2F), −112.4 (t, $^3J_{F-F}$ = 6.9 Hz, 2F). ^{13}C NMR: δ 136.01 (s), 130.65 (s), 130.52 (s), 130.08 (s), 129.41 (s), 129.18 (s), 116.73 (tt, $^1J_{F-C}$ = 289.3 Hz, $^2J_{F-C}$ = 32.4 Hz), 115.71 (tt, $^1J_{F-C}$ = 289.3 Hz, $^2J_{F-C}$ = 32.4 Hz), 61.39 (s), 42.47 (s).

4.3.3. Triethylammonium 2-(phenylsulfanyl)-1,1,2,2-tetrafluoroethanesulfonate **3ae**

Yellow oil (0.43 g, 1.10 mmol, 98%). ^{1}H NMR (acetone-d_6): δ 7.68 (m, 2H), 7.44–7.56 (m, 3H), 3.32 (q, $^3J_{H-H}$ = 7.3 Hz, 6H), 1.36 (t, $^3J_{H-H}$ = 7.3 Hz, 9H). ^{19}F NMR (acetone-d_6): δ −85.44 (t, $^3J_{F-F}$ = 6.9 Hz, 2F), −113.72 (t, $^3J_{F-F}$ = 6.9 Hz, 2F). ^{13}C NMR (acetone-d_6): δ 137.84 (s), 131.33 (s), 130.15 (s), 125.72 (t, $^3J_{F-C}$ = 2.5 Hz), 124.91 (tt, $^1J_{F-C}$ = 289.7 Hz, $^2J_{F-C}$ = 32.2 Hz), 115.69 (tt, $^1J_{F-C}$ = 288.9 Hz, $^2J_{F-C}$ = 31.2 Hz), 47.54 (s), 9.04 (s).

4.3.4. Triethylammonium 2-(benzenesulfonyl)-1,1,2,2-tetrafluoroethanesulfonate **3ce**

White solid (0.39 g, 0.92 mmol, 96%). mp: 30 °C. ^{1}H NMR (acetone-d_6): δ 8.06 (m, 2H), 7.96 (m, 1H), 7.81 (m, 2H), 4.16 (s, 1H), 3.18 (q, $^3J_{H-H}$ = 7.4 Hz, 6H), 1.28 (t, $^3J_{H-H}$ = 7.4 Hz, 9H). ^{19}F NMR (acetone-d_6): δ −110.67 (m, 2F), −113.44 (m, 2F). ^{13}C NMR (acetone-d_6): δ 137.05 (s), 134.62 (s), 131.55 (s), 130.65 (s), 116.72 (tt, $^1J_{F-C}$ = 295.2 Hz, $^2J_{F-C}$ = 37.4 Hz), 115.71 (tt, $^1J_{F-C}$ = 286.6 Hz, $^2J_{F-C}$ = 37.4 Hz), 47.48 (s), 9.03 (s).

4.3.5. Bis-(2-methoxyethyl)ammonium 2-(phenylsulfanyl)-1,1,2,2-tetrafluoroethanesulfonate **3af**

Yellow oil (0.40 g, 0.95 mmol, 95%). ^{1}H NMR (acetone-d_6): δ 7.69–7.66 (m, 2H), 7.56–7.45 (m, 3H), 6.25 (s, 1H), 3.69 (t, $^3J_{H-H}$ = 5.1 Hz, 4H), 3.34 (s, 6H), 3.28 (t, $^3J_{H-H}$ = 5.1 Hz, 4H). ^{19}F NMR (acetone-d_6): δ −85.39 (t, $^3J_{F-F}$ = 6.7 Hz), −113.78 (t, $^3J_{F-F}$ = 6.7 Hz). ^{13}C NMR (acetone-d_6): δ 137.79 (s), 131.27 (s), 130.10 (s), 125.73 (t, $^3J_{F-C}$ = 2.5 Hz), 124.91 (tt, $^1J_{F-C}$ = 289.3 Hz, $^2J_{F-C}$ = 32.2 Hz), 115.65 (tt, $^1J_{F-C}$ = 288.5 Hz, $^2J_{F-C}$ = 31.7 Hz), 68.39 (s), 58.83 (s), 48.26 (s).

4.3.6. Bis-(2-methoxyethyl)ammonium 2-(benzenesulfonyl)-1,1,2,2-tetrafluoroethanesulfonate **3cf**

Yellowish oil (0.48 g, 1.06 mmol, 97%). ^{1}H NMR (acetone-d_6): δ 8.05 (d, $^3J_{H-H}$ = 7.9 Hz, 2H), 7.99–7.89 (m, 1H), 7.84–7.74 (m, 2H), 3.73 (t, $^3J_{H-H}$ = 5.0 Hz, 4H), 3.44 (t, $^3J_{H-H}$ = 5.0 Hz, 4H), 3.32 (s, 6H). ^{19}F NMR (acetone-d_6): δ −106.82 (s), −109.62 (s). ^{13}C NMR: δ 137.02 (s), 134.66 (s), 131.55 (s), 130.64 (s), 116.75 (tt, $^1J_{F-C}$ = 287.3 Hz, $^2J_{F-C}$ = 33.5 Hz), 115.72 (tt, $^1J_{F-C}$ = 287.3 Hz, $^2J_{F-C}$ = 33.5 Hz), 67.55 (s), 58.86 (s), 48.24 (s).

4.3.7. N-Ethylmorpholinium 2-(phenylsulfanyl)-1,1,2,2-tetrafluoroethanesulfonate **3ag**

Yellow oil (0.40 g, 0.99 mmol, 99%). ^{1}H NMR (acetone-d$_6$): δ 7.69–7.67 (m, 2H), 7.58–7.45 (m, 3H), 6.28 (s, 1H), 3.97 (t, $^3J_{H-H}$ = 4.7 Hz, 4H), 3.35–3.25 (m, 6H), 1.37 (t, $^3J_{H-H}$ = 4.7 Hz, 3H). ^{19}F NMR (acetone-d_6): δ −85.45 (t, $^3J_{F-F}$ = 6.9 Hz), −113.67 (t, $^3J_{F-F}$ = 6.9 Hz). ^{13}C NMR (acetone-d_6): δ 137.81 (s), 131.39 (s), 130.17 (s), 125.46 (t, $^3J_{F-C}$ = 1.9 Hz), 124.96 (tt, $^1J_{F-C}$ = 289.0 Hz, $^2J_{F-C}$ = 31.8 Hz), 115.74 (tt, $^1J_{F-C}$ = 288.6 Hz, $^2J_{F-C}$ = 31.1 Hz), 64.43 (s), 53.40 (s), 52.39 (s), 9.13 (s).

4.3.8. N-Ethylmorpholinium 2-(benzenesulfonyl)-1,1,2,2-tetrafluoroethanesulfonate **3cg**

Yellow solid (0.42 g, 0.96 mmol, 94%). mp: 36 °C. ^{1}H NMR (acetone-d_6): δ 8.06–8.04 (m, 2H), 7.96–7.91 (m, 1H), 7.84–7.79 (m, 2H), 4.19 (s, 1H), 6.26 (s, 1H), 3.96 (t, $^3J_{H-H}$ = 4.6 Hz, 4H), 3.32–3.21 (m, 6H), 1.34 (t, $^3J_{H-H}$ = 4.6 Hz, 3H). ^{19}F NMR (acetone-d_6): δ −113.53–113.37 (m), −110.72 to 110.57 (m). ^{13}C NMR (acetone-d_6): δ 137.12 (s), 134.28 (s), 131.50 (s), 130.64 (s), 116.73 (tt, $^1J_{F-C}$ = 290.6 Hz, $^2J_{F-C}$ = 34.8 Hz), 115.72 (tt, $^1J_{F-C}$ = 287.7 Hz, $^2J_{F-C}$ = 34.2 Hz), 64.89 (s), 53.33 (s), 52.66 (s), 9.57 (s).

4.3.9. N-Methylpyrrolidinium 2-(phenylsulfanyl)-1,1,2,2-tetrafluoroethanesulfonate **3ah**

Yellow oil (90%). ^{19}F NMR: δ −85.4 (t, $^3J_{F-F}$ = 6.9 Hz), −112.6 (t, $^3J_{F-F}$ = 6.9 Hz). ^{1}H NMR: δ 9.6 (s), 7.68–7.63 (m, 2H), 7.44–7.32 (m, 3H), 3.84–3.76 (m, 2H), 3.00–2.80 (m, 2H), 2.90 (s, 3H), 2.20–2.00 (m, 4H).

4.3.10. N-Butylpyrrolidinium 2-(phenylsulfanyl)-1,1,2,2-tetrafluoroethanesulfonate **3ai**

Orange-red oil at room temperature (89%). mp: 12 °C. ^{1}H NMR: δ 7.64–7.29 (2m, 5H), 7.11 (m, 1H), 3.30–3.15 (m, 4H), 3.00 (m, 2H), 2.00 (quint, 4H), 1.65 (m, 2H), 1.30 (sext, 2H), 0.85 (t, $^3J_{H-H}$ = 3.6 Hz, 3H). ^{19}F NMR: δ −85.4 (t, $^3J_{F-F}$ = 5.7 Hz), −112.7 (t, $^3J_{F-F}$ = 5.7 Hz). ^{13}C NMR: δ 137.10 (s), 132.40 (s), 130.40 (s), 129.06 (s), 124.24 (t, $^3J_{F-C}$ = 1.9 Hz), 123.96 (tt, $^1J_{F-C}$ = 289.0 Hz, $^2J_{F-C}$ = 31.8 Hz), 115.00 (tt, $^1J_{F-C}$ = 288.6 Hz, $^2J_{F-C}$ = 31.1 Hz), 55.42 (s), 54.18 (s), 22.84 (s), 19.74 (s), 13.42 (s).

4.3.11. N-Butylpyrrolidinium 2-(benzenesulfonyl)-1,1,2,2-tetrafluoroethanesulfonate **3ci**

Beige solid (88%). mp: 48 °C. ^{1}H NMR: δ 8.0 (d, 2H), 7.8–7.5 (m, 3H), 6.0 (broad s, 1H), 3.4–3.2 (m, 4H), 3.0 (m, 2H), 2.2–2.0 (m, 4H), 1.7 (m, 2H), 1.4 (sext, 2H), 0.9 (t, 3H). ^{19}F NMR: δ −112.6 (m), −110.3 (m). ^{13}C NMR: δ 135.9 (s), 133.2 (s), 130.9 (s), 129.4 (s), 116.8 (tt, $^1J_{F-C}$ = 287.3 Hz, $^2J_{F-C}$ = 33.5 Hz), 115.7 (tt, $^1J_{F-C}$ = 287.3 Hz, $^2J_{F-C}$ = 33.5 Hz), 55.7 (s), 54.3 (s), 27.7 (s), 22.9 (s), 19.7 (s), 13.4 (s).

*4.3.12. 3-Methyl-3H-imidazol-1-ium 2-(phenylsulfanyl)-1,1,2,2-tetrafluoroethanesulfonate **3aj***

Yellow solid (96%). mp: 65 °C. ^{1}H NMR: δ 11.15 (s, 1H), 8.68 (s, 1H), 7.66–7.01 (m, 7H), 3.87 (s, 3H). ^{19}F NMR: δ −85.24 (t, $^{3}J_{F-F}$ = 5.7 Hz), −112.67 (t, $^{3}J_{F-F}$ = 5.6 Hz). ^{13}C NMR (acetone-d_6): δ 137.81 (s), 131.27 (s), 130.11 (s), 127.97 (s), 125.83 (t, $^{3}J_{F-C}$ = 2.8 Hz), 125.00 (tt, $^{1}J_{F-C}$ = 288.2 Hz, $^{2}J_{F-C}$ = 30.9 Hz), 123.91 (s), 121.53 (s), 115.78 (tt, $^{1}J_{F-C}$ = 288.2 Hz, $^{2}J_{F-C}$ = 30.9 Hz), 36.31 (s).

*4.3.13. 3-Methyl-3H-imidazol-1-ium 2-(benzenesulfonyl)-1,1,2,2-tetrafluoroethanesulfonate **3cj***

Yellowish solid (95%). mp: 72 °C (85 °C after recrystallization in CH_2Cl_2/pentane). ^{1}H NMR: δ 8.62 (s, 1H), 8.02 (d, $^{3}J_{H-H}$ = 7.5 Hz, 2H), 7.81–7.74 (m, 1H), 7.67–7.59 (m, 2H), 4.41 (s, 3H), 3.90 (s, 3H). ^{19}F NMR: δ −110.14 (t, $^{3}J_{F-F}$ = 19.5 Hz), −112.67 (t, $^{3}J_{F-F}$ = 19.5 Hz). ^{13}C NMR (acetone-d_6): δ 137.07 (s), 134.48 (s), 131.51 (s), 130.65 (s), 126.60 (s), 124.28 (s), 120.81 (s), 116.73 (tt, $^{1}J_{F-C}$ = 289.3 Hz, $^{2}J_{F-C}$ = 32.4 Hz), 115.73 (tt, $^{1}J_{F-C}$ = 289.3 Hz, $^{2}J_{F-C}$ = 32.4 Hz), 36.35 (s). UV (0.2 mM in CH_2Cl_2): λ_{max} = 268.4 and 231.2 nm.

*4.3.14. 3-n-Butyl-3H-imidazol-1-ium 2-(phenylsulfanyl)-1,1,2,2-tetrafluoroethanesulfonate **3ak***

Pale yellow oil (65 °C). ^{1}H NMR: δ 13.7 (broad s, 1H), 8.94 (s, 1H), 7.62–7.60 (m, 2H), 4.18 (m, 2H), 1.80 (m, 2H), 1.30 (qi, 2H), 0.80 (t, 3H). ^{19}F NMR: δ −85.3 (t, $^{3}J_{F-F}$ = 5.7 Hz), −112.8 (t, $^{3}J_{F-F}$ = 5.6 Hz). ^{13}C NMR: δ 134.77 (s), 136.97 (s), 130.24 (s), 128.93 (s), 125.6 (t, $^{3}J_{F-C}$ = 2.8 Hz), 124.9 (tt, $^{1}J_{F-C}$ = 288.2 Hz, $^{2}J_{F-C}$ = 30.9 Hz), 120.9 (s), 120.7 (s), 115.6 (tt, $^{1}J_{F-C}$ = 288.2 Hz, $^{2}J_{F-C}$ = 30.9 Hz), 49.0 (s), 31.9 (s), 13.8 (s), 13.1 (s).

5. Conductivity measurements

Conductivities were determined by electrochemical impedance spectroscopy using an HP 4192A Impedance Analyser in the frequency range 5 Hz–13 MHz. The samples were placed between two stainless steel electrodes under argon in a Swagelok cell with Teflon joints and spacers and measurements were performed from 100 to 20 °C. The temperature was equilibrated for 2 h before each measurement.

6. Thermal measurements

Glass transition temperatures (T_g) and melting temperatures (mp) were measured under nitrogen flow using a TA Instruments DSC 2920 modulated DSC. In a typical procedure, around 10 mg of compound were placed in a DSC aluminium crucible in glove box. After being maintained in a glove box for 1 month at least, the samples were cooled down to −100 °C then heated at 5 °C/min up to 100 °C. The oscillation period was 60 s and its amplitude was ±1 °C. T_g and mp were taken at the inflection point of, respectively, the specific heat increment at the glass–rubber transition and at the onset of the melting peak.

Acknowledgement

The authors gratefully acknowledge the Eras-Labo Co., especially Lionel Ogier, for synthetizing some of the described salts and preparing the larger quantities required for the conductivity measurements.

References

[1] H.H. Gibbs, R.N. Griffin, U.S. Patent 3,041,317 (1962) (to E.I. du Pont de Nemours & Co.).
[2] G. Alberti, M. Casciola, R. Palombari, J. Membrane Sci. 172 (2000) 233–239.
[3] (a) M. Doyle, S.K. Choi, G. Proulx, J. Electrochem. Soc. 147 (2000) 34–37;
(b) G. Pourcelly, C. Gavach, in: P. Colomban (Ed.), Proton Conductors, Solids, Membranes, and Gels-Materials and Devices, Cambridge University Press, Cambridge, 1992;
(c) C. Heitner-Wirguin, J. Membrane Sci. 120 (1996) 1.
[4] S.S. Sekhon, P. Krishnan, B. Singh, K. Yamada, C.S. Kim, Electrochim. Acta 52 (2006) 1639–1644.
[5] R. Savinell, E. Yeager, D. Tryk, U. Landau, J. Wainright, D. Weng, K. Lux, M. Litt, C. Rogers, J. Electrochem. Soc. 141 (1994) L46–L48.
[6] S. Malhotra, R. Datta, J. Electrochem. Soc. 144 (1997) L23–L26.
[7] Z. Li, Q. Zhang, H. Liu, P. He, X. Xu, J. Li, J. Power Sources 158 (2006) 103–109.
[8] Z. Li, H. Liu, Y. Liu, P. He, J. Li, J. Phys. Chem. B 108 (2004) 17512–17518.
[9] A. Noda, M.A.B.H. Susan, K. Kudo, S. Mitsushima, K. Hayamizu, M. Watanabe, J. Phys. Chem. B 107 (2003) 4024–4033.
[10] M.A.B.H. Susan, A. Noda, S. Mitsushima, M. Watanabe, Chem. Commun. (2003) 938–939.
[11] M.A.B.H. Susan, M. Yoo, H. Nakamoto, M. Watanabe, Chem. Lett. 32 (2003) 836–837.
[12] M. Watanabe, Mater. Integr. 16 (2003) 33–39.
[13] M. Yoshizawa, W. Xu, C.A. Angell, J. Am. Chem. Soc. 125 (2003) 15411–15419.
[14] (a) F. Toulgoat, B.R. Langlois, M. Médebielle, J.Y. Sanchez, J. Org. Chem. 72 (2007) 9046–9052;
(b) J.Y. Sanchez, B. Langlois, M. Médebielle, F. Toulgoat, WO Patent 2008/009816 A2 (2008) (to Institut National Polytechnique de Grenoble, Eras-Labo Co., Université Claude Bernard Lyon 1).
[15] M. Suda, C. Hino, Tetrahedron Lett. 22 (1981) 1997–2000.
[16] G.K.S. Prakash, J. Hu, J. Simon, D.R. Bellew, G.A. Olah, J. Fluorine Chem. 125 (2004) 595–601.
[17] (a) M.C. Doyle, A.E. Feiring, S.K. Choi, WO Patent 99 67304 (1999) (to DuPont de Nemours Co.), Chem. Abstr. 132, p. 5041.
(b) A.E. Feiring, W.R. Wonchoba, J. Fluorine Chem. 105 (2000) 129–135.
[18] (a) M. Tordeux, B. Langlois, C. Wakselman, Eur. Patent 278,822 (1988) (to Rhône-Poulenc Co.). Chem. Abstr. 110, p. 94514.;
(b) M. Tordeux, B. Langlois, C. Wakselman, French Patent 2,593,808 (1987) (to Rhône-Poulenc Co.). Chem. Abstr. 108, p. 166975.
[19] J.Y. Sanchez, B. Langlois, M. Médebielle, F. Toulgoat, E. Paillard, F. Alloin, C. Iojoiu, R. Arvai, WO Patent 2008/009815 A2 (2008) (to Institut National Polytechnique de Grenoble, Eras-Labo Co., Université Claude Bernard Lyon 1).