Ionic Liquids with Fluorine-Containing Cations

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Interest in ionic liquids with fluorine-containing cations has grown markedly in recent years. The syntheses, characterization and properties of quaternary fluoroalkyl-substituted ammonium, imidazolium, triazolium, pyridinium, pyrazinium, pyridazinium, pyrimidinium, piperazinium, pyrrolidinium, oxazolidinium, and morpholinium salts have been studied in detail. By modifying the anion or the fluorine-containing substituent on the cation, a wide range of properties of fluorine-containing ionic liquids can be tuned, including viscosity, melting point, density, conductivity, solubility, liquid range, thermal and hydrolytic stability. They are promising solvents for electrochemical, photovoltaic, surfactant and synthetic applications. In this Microreview, only the literature dealing with ionic liquids that involve fluorine-containing cations is presented.

1. Introduction

Ionic liquids are salts with low melting points (< 100 °C). Since ionic liquids exhibit extremely low vapor pressures, long liquid ranges, and are highly polar yet noncoordinating, they are good solvents for a wide range of organic and inorganic materials. These interesting compounds are achieved either by incorporating a bulky asymmetric cation into the structure in order to preclude good crystal packing and/or by selecting an anion in which there is considerable delocalization of the electron cloud over the molecular backbone that tends to decrease interionic interaction, e.g., bis(trifluoromethylsulfonyl)amide or polyfluoro-β-diketonate. Results described in current publications indicate that replacing an organic solvent by an ionic liquid may lead to remarkable improvement in well-known processes. A number of reviews that cover the history, properties, and uses of ionic liquids are available.[1–9] These amazing liquids have been utilized not only as clean solvents, but also as catalysts for green chemistry and electrolytes for batteries, photochemistry, and electrosynthesis, and even as advanced heat transfer fluids and lubricants. Many of these types of ionic liquids are available commercially,[10] see, for example, Acros, Aldrich, Cytec, Strem and Merck.

Hong Xue was born in 1969 in Changchun, China, and received his Ph. D. in polymer chemistry from Dalian University of Technology (China) in 1999. He held a postdoctoral position for two years at Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, and worked on living polymerization and chiral polymer materials. In 2002, he joined the group of Professor Jean'ne M. Shreeve as a postdoctoral fellow. His current research focuses on the syntheses and application of organofluorine compounds, ionic liquids and energetic materials.

Jean'ne M. Shreeve is a Montana native. She received a BA in chemistry from the University of Montana, MS in analytical chemistry from the University of Minnesota, and Ph. D. in inorganic chemistry from the University of Washington, Seattle. She joined the University of Idaho faculty in 1961, became department head in 1973, and, in 1987, assumed the role of Vice-President for Research and Graduate Studies. In January 2000, she returned to full time research. She was privileged to have worked with three of the finest gentlemen of fluorine chemistry – Professors George H. Cady, Harry J. Emeléus, and Oskar Glemser. Her research interests include the syntheses, characterization and reactions of new fluorine-containing compounds as exemplified by more than 370 refereed publications. In July 2004, she became Jean'ne M. Shreeve Chemistry Professor.

MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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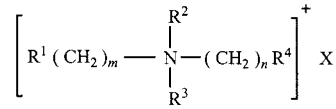
Earlier generations of ionic liquids were extremely water-sensitive – most often due to the presence of polychlorometallates as the anions. However, recently developed ionic liquids without halometallates, are water- and air-insensitive and possess remarkably high thermal stability. Typically, they are composed of bulky 1,3-dialkylimidazolium, alkylammonium, alkylphosphonium, or alkylpyridinium organic cations and inorganic/organic anions, such as NO_3^-, ClO_4^-, $CF_3SO_3^-$, PF_6^-, BF_4^-, $(CF_3SO_2)_2N^-$, $CF_3CO_2^-$.[1–9] Until now, the ionic liquid field has been extensively dominated by imidazolium salts with anions most frequently being fluorine-containing. Somenew fluoroanions, such as fluorohydrogenates,[11] tetrakis{*p*-[dimethyl(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)silyl]phenyl}borate,[12] perfluoroalkyl-β-diketonates,[13] tris(perfluoroalkyl) trifluorophosphates,[14] and perfluoroalkyl trifluoroborates,[15] have been reported as useful in the synthesis of new low melting salts.

Following the syntheses of the first fluorine-containing ionic liquids, 3-methyl-1-(2,2,2-trifluoroethyl)imidazolium salts, which were characterized as hydrophobic, highly conductive ambient-temperature molten materials,[16] the interest in ionic liquids with fluoroalkyl-substituted cations has grown markedly.[17–36] By modifying the anion or the fluorine-containing substituent on the cation, a wide range of properties of fluorine-containing ionic liquids can be tuned, including, for example, viscosity, melting point, density, conductivity, solubility, liquid range, thermal and hydrolytic stability, and heat of formation. The influence of inter-ion hydrogen bonding can be diminished by introducing fluorine-containing groups into the cation and especially when employing anions such as bis(trifluorosulfonyl)amide and perfluoroalkyldiketonate.[13,37] Excellent reviews of room-temperature ionic liquids with alkylimidazolium cations and fluoroanions are available.[38,39] A U.S. patent issued in 1998 claims a vast number of "hydrophobic ionic liquids," many of which have fluorine-containing cations.[22] In summarizing the inventions described in the patent, the authors conclude that when the cation and/or the anion is fluorinated, the hydrophobic ionic liquids of the invention have certain additional special properties, including 1) inertness to organic solvents and oxidizing agents; 2) resistance to corrosive acids and bases; and 3) resistance to extremes of temperature and pressure. The applications for the perfluorinated hydrophobic ionic liquids claimed in the patent encompass superior hydraulic, inert liquid diluents for highly reactive chemicals and solvents with a high capacity for dissolved gases such as oxygen, and useful for catalysis and for oil and gas separations where the desired product is partitioned between an aqueous and hydrophobic perfluorinated ionic liquid phase. These applications are, of course, in addition to all of those suggested for conventional ionic liquids. These points provide the raison d'être for further syntheses, characterization and study of new ionic liquids that contain the element fluorine. In this paper, only the literature dealing with ionic liquids that involve fluorine-containing cations is reviewed.

2. Syntheses and Properties of Quaternary (Fluoroalkyl)ammonium Salts

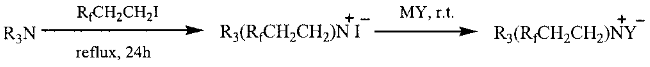
Since the report of a liquid ammonium salt, $EtNH_3^+NO_3^-$, early in the last century,[40] many additional quaternary ammonium salts have been synthesized and studied. Typically, introduction of greater asymmetry into the ionic species by decreasing the symmetry of the cation results in lowering of the melting point.[41] Until very recently only a very few (fluoroalkyl)ammonium salts, such as $(CH_3)_3(CH_2F)N^+X^-$ (X = Br, I), had been reported.[42] Selected quaternary ammonium salts containing polyfluoroalkyl groups (Figure 1), such as dimethylbis(4,4,5,5,6,6,7,7,7-nonafluoroheptyl)ammonium chloride (m.p. 70–72 °C), were claimed in a patent.[43] However, the characterization was limited.



R^1, R^4 = fluoroalkyl; R^2 = alkyl; R^3 = alkyl or $R^1(CH_2)_m$-; X = anion

Figure 1. Quaternary ammonium salts containing polyfluoroalkyl groups.

Now a series of water- and thermally stable low-melting salts based on quaternary trialkyl(polyfluoroalkyl)ammonium cations has been synthesized and characterized. Metathetical reactions of the iodide salts with fluorine-containing anions resulted in new liquid salts (Scheme 1). The marked variations in melting points appear to be a function of the anion primarily and is essentially independent of the substituents on the cation. In this series, iodide salts of the triisooctyl(polyfluoroalkyl)amines are also liquids at 25 °C.[18] In some cases, the viscosities of these salts are remarkably low. Another novel iodide, diallyl(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)(methyl)ammonium iodide (m.p. 65–68 °C) has been described as an effective antimicrobial agent.[19]



$$R_3N \xrightarrow[\text{reflux, 24h}]{R_fCH_2CH_2I} R_3(R_fCH_2CH_2)\overset{+}{N}\overset{-}{I} \xrightarrow{\text{MY, r.t.}} R_3(R_fCH_2CH_2)\overset{+}{N}\overset{-}{Y}$$

R = n-C_3H_7, n-C_4H_9, i-C_8H_{17}

$R_f = (CF_2)_xCF_3$, x = 3, 7, 9

M = Ag, Li; Y = $N(CF_3SO_2)_2$, CF_3SO_3, $C_3F_7CO_2$

R	R_f	Y	Yield[a]	d[b]	T_m (T_g)[c]	T_d[d]
n-C_4H_9	$CF_3(CF_2)_3$	I	80	–	82	252
n-C_4H_9	$CF_3(CF_2)_7$	I	85	–	91	260
i-C_8H_{17}	$CF_3(CF_2)_3$	I	83	1.1	22.5	270
i-C_8H_{17}	$CF_3(CF_2)_7$	I	80	1.0	20.1	265
i-C_8H_{17}	$CF_3(CF_2)_9$	I	78	1.0	18.2	279
n-C_4H_9	$CF_3(CF_2)_7$	Bu_fCO_2[e]	80	1.4	(–48)	345
n-C_4H_9	$CF_3(CF_2)_3$	NTf_2[f]	90	1.2	15.5	374
n-C_4H_9	$CF_3(CF_2)_7$	NTf_2	90	1.3	22.1	290
i-C_8H_{17}	$CF_3(CF_2)_7$	NTf_2	90	1.0	(–62.6)	358

[a] %. [b] g/cm^3, pycnometer; 25°C. [c] Melting point (phase transition) [°C]. [d] Thermal decomposition [°C]. [e] Heptafluorobutyrate. [f] Bis(trifluoromethanesulfonyl)amide.

Scheme 1.

3. Syntheses and Properties of Quaternary Fluoroalkyl-Substituted Imidazolium Salts

An ionic liquid in which the cation is a polyfluoroalkyl-substituted imidazolium species derived from the antifungal drug miconazole becomes a soft yellow wax over a period of hours but is readily reliquified by heating to 92–96 °C (Scheme 2[20] It is stable in air to ≥ 150 °C. It also exhibits lyotropic liquid-crystalline behavior while inducing the gelation of benzene. 1-Alkyl-3-(polyfluoroalkyl)imidazolium hexafluorophosphates were employed as surfactants to promote the formation and stabilization of dispersions of perfluorocarbons in a conventional ionic liquid, such as 1-hexyl-3-methylimidazolium hexafluorophosphate [(6-mim)-PF_6] (Figure 2).[21]

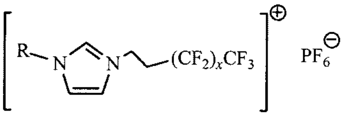
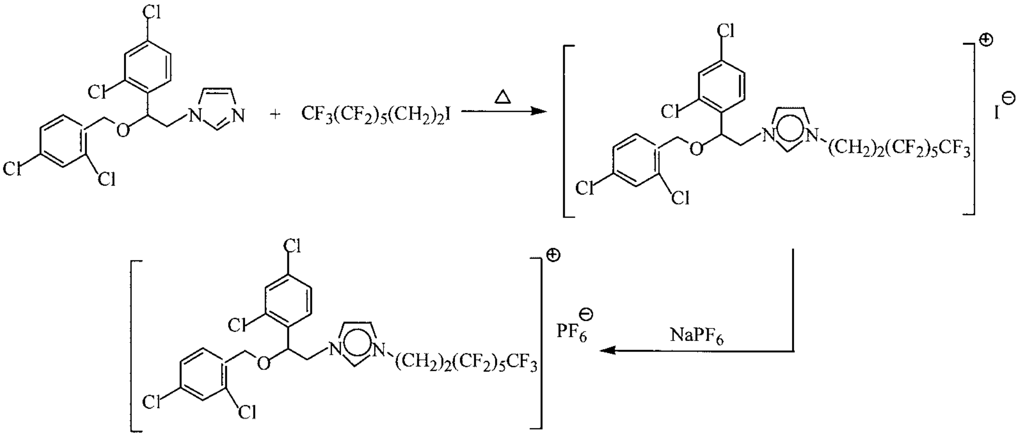

R = Me, *n*Bu; *x* = 5, 7

Figure 2. 1-Alkyl-3-(polyfluoroalkyl)imidazolium hexafluorophosphates.

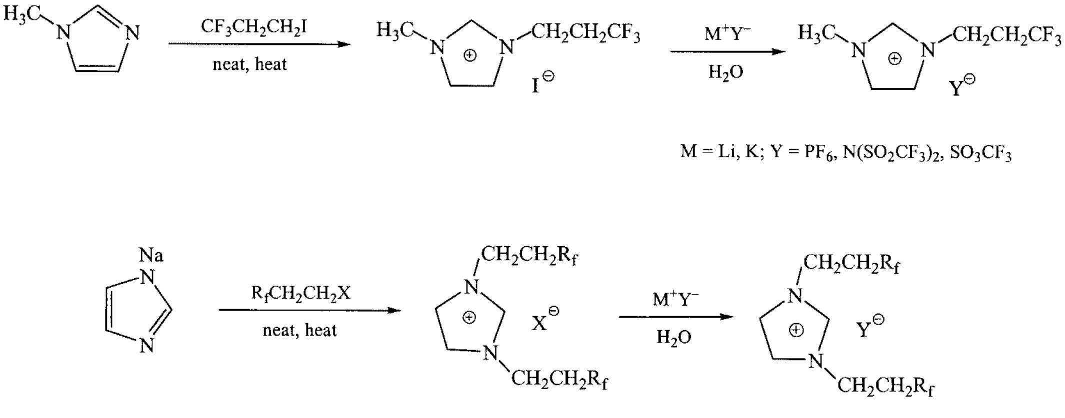
The presence of fluorine markedly increases the density of fluoroalkyl-substituted imidazolium ionic liquids and, in some cases, may cause increases in the melting points even in the presence of a constant anion (Scheme 3).[23] Some of the bis(polyfluoroalkyl)imidazolium salts are liquids with higher densities, e. g., the density of *N*,*N′*-bis(3,3,3-trifluoropropyl)imidazolium bis(trifluoromethylsulfonyl)amide (m.p. –62 °C) is 1.85 g cm^{-3}.

Among several highly halogenated, low-melting imidazolium salts which exhibit densities ranging from 1.95 to 2.80 g cm^{-3} are two highly brominated (polyfluoroalkyl)-imidazolium bis(trifluoromethylsulfonyl)amides with densities of 2.11 and 2.35 g cm^{-3} (Scheme 4). These dense, viscous liquids are thermally and hydrolytically remarkably stable.[24]

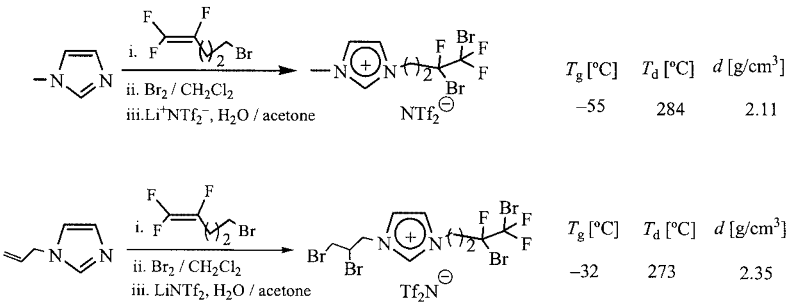
Quaternization of 1-(tetrafluoroethyl)imidazole with electrophiles such as RI (R = Me, Et, *n*Pr, *i*Pr, *n*Bu) followed by metathesis with $LiNTf_2$ or $AgBF_4$ gives rise to the first examples of ionic liquids with substituents at the nitrogen atom bonded through $–CF_2–$, i.e., CF_2CF_2H.[25]



Scheme 2.



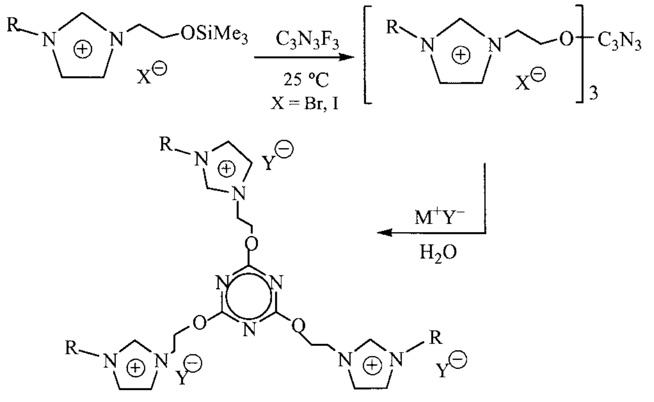
Scheme 3.



Scheme 4.

Bis[(4,4,4-trifluorobutyl)imidazolium] quaternary salts based on *p-tert*-butylcalix[4]arenes have melting points >100 °C.[26]

A number of structurally different trimethylsilylated and tris[(oxyethyl)imidazolium] and tris[(oxyethyl)ammonium] ionic liquids built on the triazine ring, including polyfluorinated ones, were prepared and characterized (Scheme 5).[27] The physical and thermal properties were studied in this work, and the densities of the polyfluorinated triquaternary salts on the triazine frame were shown to lie between 1.69 and 1.88 g cm^{-3}.

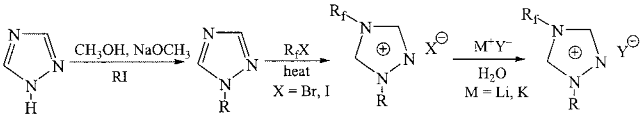


R	Y	T_g [°C]	T_d [°C]	d [g/cm³]
$CH_2CH_2CH_2F$	NTf_2	–35	300	1.72

Scheme 5.

4. Syntheses and Properties of Quaternary Fluoroalkyl-Substituted Triazolium Salts

Until recently, there were very few triazolium quaternary salts with melting points < 100 °C, especially polyfluoroalkylated or perfluoroalkylated triazolium compounds. Considerable attention has been devoted to changes in the properties of polyfluoroalkyl-1,2,4-triazolium ionic liquids as a function of the chain length and extent of fluorination of the chain, as well as the impact of a variety of anions (Scheme 6).[28] As the number of carbon atoms in the alkyl and polyfluoroalkyl substituent chains on the cation increases resulting in concomitantly less efficient packing in the solid, the melting points are observed to decrease. The density increases with elongation of the fluoroalkyl substituent and the degree of fluorination of the chain and decreases as the alkyl group becomes bulkier. The liquid ranges and the thermal stabilities of these ionic liquids are impressive covering, in many cases, over 400 °C and frequently decomposing at > 400 °C.



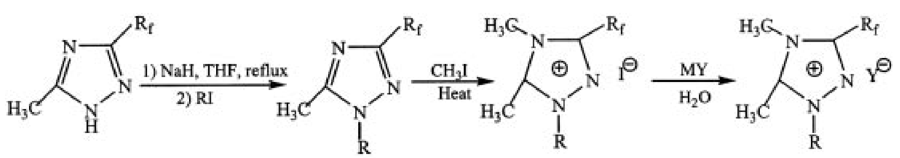
R	R_f	Y	T_m (T_g)[a]	T_d[b]
CH_3	$(CH_2)_2CF_3$	NTf_2	(–58)	376
$CH_3(CH_2)_3$	$(CH_2)_2CF_3$	NTf_2	(–67)	395
$CH_3(CH_2)_6$	$(CH_2)_2CF_3$	NTf_2	(–67)	402
$CH_3(CH_2)_9$	$(CH_2)_2CF_3$	NTf_2	(–68)	400
$CH_3(CH_2)_3$	$(CH_2)_2(CF_2)_3CF_3$	NTf_2	69	394
$CH_3(CH_2)_6$	$(CH_2)_2(CF_2)_3CF_3$	NTf_2	55	396
$CH_3(CH_2)_9$	$(CH_2)_2(CF_2)_3CF_3$	NTf_2	53	396
CH_3	$(CH_2)_2(CF_2)_5CF_3$	NTf_2	62	381
$CH_3(CH_2)_3$	$(CH_2)_2(CF_2)_5CF_3$	NTf_2	28	368
$CH_3(CH_2)_6$	$(CH_2)_2(CF_2)_5CF_3$	NTf_2	22	405
$CH_3(CH_2)_6$	$(CH_2)_2F$	NTf_2	(–70)	359
$CH_3(CH_2)_9$	$(CH_2)_2F$	NTf_2	(–62)	425
$CH_3(CH_2)_9$	$(CH_2)_2F$	OTf	46	362
$CH_3(CH_2)_6$	$(CH_2)_2F$	BF_4	52	336
$CH_3(CH_2)_3$	$(CH_2)_2CF_3$	OTf	33	379

[a] Melting point/phase transition temperature [°C]. [b] Thermal degradation [°C].

Scheme 6.

An efficient procedure for the syntheses of a family of perfluoroalkyl-containing triazolium quaternary salts, 1-alkyl-4,5-dimethyl-3-(perfluoroalkyl)-1,2,4-triazolium salts was developed (Scheme 7).[29] Although the molecular weight of the cation of 1-alkyl-4,5-dimethyl-3-(perfluorooctyl)-1,2,4-triazolium tetrafluoroborate is threefold greater than that of the 3-(trifluoromethyl) derivative, its melting point is 32 °C lower (98 °C vs. 130 °C) (Figure 3). In general, these ionic salts are not miscible with nonpolar organic liquids such as hexane but miscible with acetone and water.

4-Functionalized 1-alkyl- or 1-(polyfluoroalkyl)-1,2,4-triazolium salts were synthesized to give a series of triazolium cations that contain covalently bound anionic sites, such as sulfonate, fluorohomoallylic, fluorocarboxy, and fluoroalkanol groups, and were converted by metathesis with fluorine-containing salts to a wide range of low-melting salts (Scheme 8).[30] These functionalized triazolium salts possess many characteristics of excellent ionic liquids with respect to air, water, and thermal stability. Most of them exhibit phase-transition temperatures between –22 and ca. –68 °C,



R_f	R	MY	T_m[a]	T_d[b]
CF_3	CH_3	$LiNTf_2$	70	368
CF_3	$CH_2CH_2CH_2F$	$LiNTf_2$	49	323
C_8F_{17}	CH_3	$LiNTf_2$	81	313
C_8F_{17}	CH_3	$AgClO_4$	90	294
C_8F_{17}	CH_3	$AgBF_4$	98	306

[a] Melting point [°C]. [b] Thermal degradation [°C].

Scheme 7.

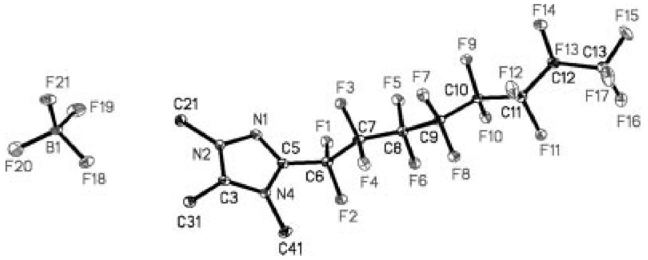
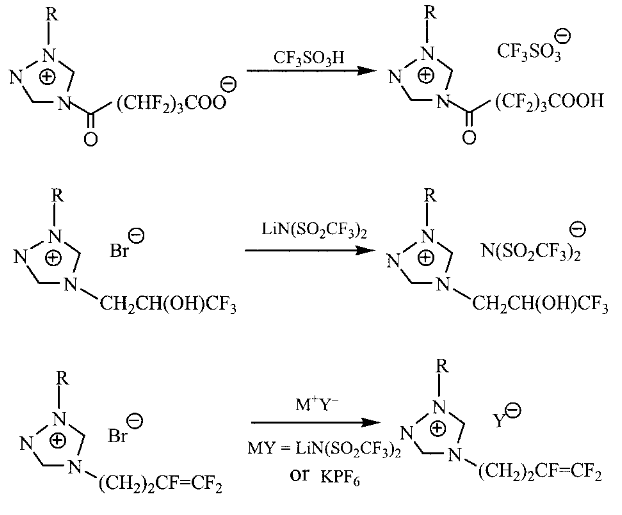


Figure 3. 1,4,5-Trimethyl-3-perfluorooctyl-1,2,4-triazolium tetrafluoroborate.

have decomposition temperatures between 254 and 408 °C, and densities between 1.45 and 1.61 g cm^{-3}.

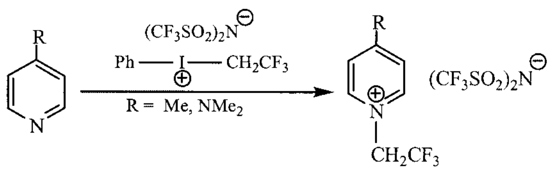


R = butyl, heptyl, decyl

Scheme 8.

5. Syntheses and Properties of Quaternary Fluoroalkyl-Substituted Pyridinium and Bipyridinium Salts

(Fluoroalkyl)pyridinium salts that melt at > 100 °C have been studied for more than 20 years.[44] However, in a one-step method using the powerful alkylating reagent, phenyl(trifluoroethyl)iodonium bis(trifluoromethylsulfonyl)amide, direct trifluoroethylation of pyridine derivatives gave the 4-methyl-*N*-(trifluoroethyl)pyridinium salts, whose melting points are lower than 100 °C (Scheme 9).[31]



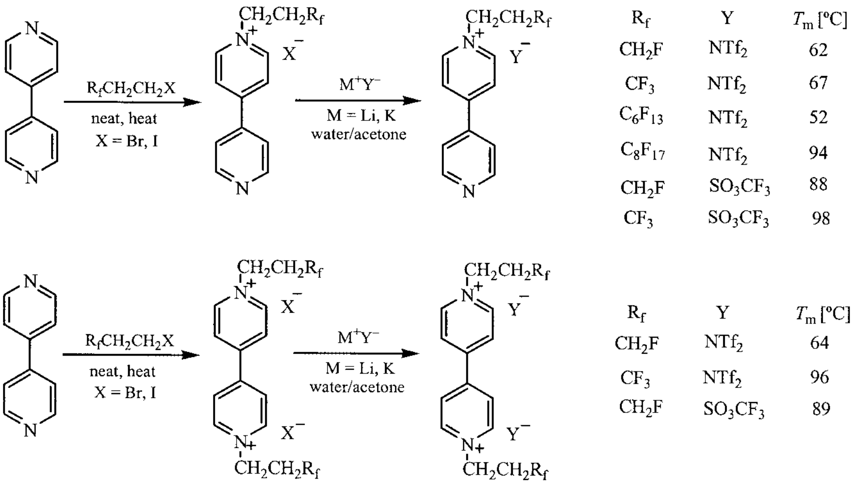
Scheme 9.

In addition, several bridged tetraquaternary salts derived from *N*,*N*′-bis(polyfluoroalkyl)-4,4′-bipyridine were found to meet the melting point criterion for ionic liquids (Scheme 10).[32]

All of the 4,4′-bipyridinium salts are stable in water and air and are thermally stable up to 340 °C as determined by DSC. They are generally soluble in acetone, ethyl acetate, DMF, and DMSO. The polyfluoroalkylated mono-, di-, and tetraquaternary 4,4′-bipyridinium salts are likely to have a considerable practical chemistry.

6. Syntheses and Properties of Quaternary Fluoroalkyl-Substituted Pyrazinium, Pyridazinium, Pyrimidinium, Piperazinium and Pyrrolidinium Salts

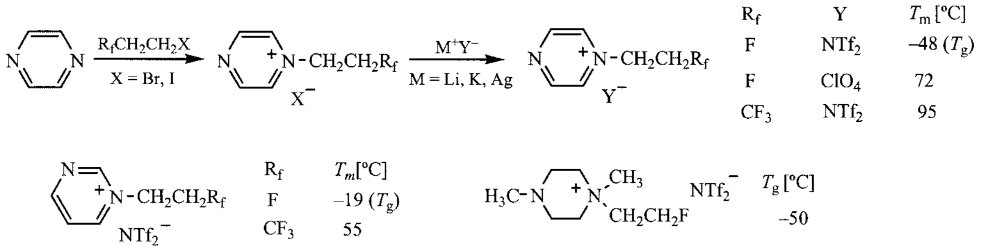
A variety of new quaternized salts of pyridazine, pyrazine, pyrimidine and 1,4-dimethylpiperazine that contain polyfluoroalkyl and alkyl substituents were synthesized and characterized (Scheme 11).[33] Many of these quaternary salts melt below 100 °C and therefore fall into the ionic liquid class. The thermal stability is largely a function of the cation with the pyridazinium compounds being the most stable. These salts also have the lowest melting points, and were prepared under the mildest reaction conditions. The pyridazinium bis(trifluoromethylsulfonyl)amide salts exhibit relatively high densities between 1.81 and 2.13 g/cm^3. The latter is one of the most dense ionic liquids excluding the hydrolytically unstable metal salts. Pyrazinium and pyridazinium salts are much less susceptible to hydrogen/deute-



R_f	Y	T_m [°C]
CH_2F	NTf_2	62
CF_3	NTf_2	67
C_6F_{13}	NTf_2	52
C_8F_{17}	NTf_2	94
CH_2F	SO_3CF_3	88
CF_3	SO_3CF_3	98

R_f	Y	T_m [°C]
CH_2F	NTf_2	64
CF_3	NTf_2	96
CH_2F	SO_3CF_3	89

Scheme 10.



R_f	Y	T_m [°C]
F	NTf_2	–48 (T_g)
F	ClO_4	72
CF_3	NTf_2	95

R_f	T_m[°C]
F	–19 (T_g)
CF_3	55

	T_g [°C]
NTf_2^-	–50

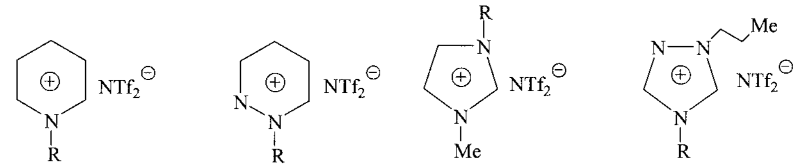
Scheme 11.

rium exchange than the analogous imidazolium compounds which may allow for applications of the former liquid salts where the latter may not be suitable.

N-Alkylpyrrolidines are also readily quaternized with fluoroalkyl bromides and iodides to give ionic liquids when metathesized with lithium bis(trifluoromethylsulfonyl)-amide.[34]

7. Syntheses and Properties of Quaternary Salts Containing the Pentafluorosulfanyl (SF_5) Group

The first quaternary salts of pyridine, *N*-methylimidazole, *N*-propyltriazole, and pyridazine that contain the pentafluorosulfanyl (SF_5) group were found to be low melting (Scheme 12).[35] The presence of the pentafluorosul-



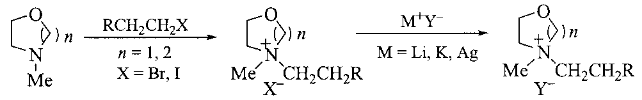
R	T_m (T_g) [°C]	d [g/cm^3]	T_g [°C]	d [g/cm^3]	T_g [°C]	d [g/cm^3]	T_g [°C]	d [g/cm^3]
$SF_5(CF_2)_2(CH_2)_4$	18	2.02	–41.7	1.87	–56.7	2.01	–54.8	1.89
$SF_5(CF_2)_2(CH_2)_2$	33	1.96	–14	1.93	–55.5	2.00		
$SF_5(CF_2)_4(CH_2)_2$	36.1 (–39.7)	1.97			–50	1.97		
$CF_3CH_2CH_2$			–64	1.85	–74	1.44	–67	1.60
$CF_3(CF_2)_5(CH_2)_2$	38.4		–13	2.13	–50	1.77	28	

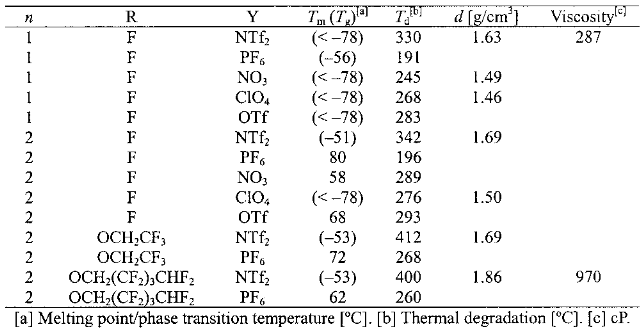
Scheme 12.

fanyl group markedly increases the densities of the bis(trifluoromethylsulfonyl)amide salts. The methylimidazolium, pyridinium, and pyridazinium salts exhibit densities of ca. 2 g cm^{-3}. However, $CF_3(CF_2)_5(CH_2)_2$– as a substituent on the ring also plays a major role in increasing the liquid densities relative to the C_8 alkyl or to shorter polyfluoroalkyl substitutents and, in some cases, to the polyfluoro(pentafluorosulfanyl)alkyl substitutents.

8. Syntheses and Properties of Fluoroalkyl-Substituted Oxazolidinium and Morpholinium Salts

A series of *N*-alkyl- and *N*-(fluoroalkyl)-substituted oxazolidinium- and morpholinium-based quaternary salts and their corresponding ionic liquids as well as ionic liquids obtained from quaternization of alkoxyethyl- and (fluoroalkoxy)ethyl-substituted morpholine compounds have been studied (Scheme 13).[36] All of the morpholinium bis(trifluoromethylsulfonyl)amide products are liquids at 25 °C and have interesting physical properties. They are stable thermally and have long liquid ranges. Overall, these ionic liquids with saturated core rings tend to exhibit greater thermal stabilities than those composed of unsaturated rings. This property plus the concomitant higher viscosities suggests higher temperature fluids applications.





n	R	Y	T_m (T_g)[a]	T_d[b]	*d* [g/cm^3]	Viscosity[c]
1	F	NTf_2	(< –78)	330	1.63	287
1	F	PF_6	(–56)	191		
1	F	NO_3	(< –78)	245	1.49	
1	F	ClO_4	(< –78)	268	1.46	
1	F	OTf	(< –78)	283		
2	F	NTf_2	(–51)	342	1.69	
2	F	PF_6	80	196		
2	F	NO_3	58	289		
2	F	ClO_4	(< –78)	276	1.50	
2	F	OTf	68	293		
2	OCH_2CF_3	NTf_2	(–53)	412	1.69	
2	OCH_2CF_3	PF_6	72	268		
2	$OCH_2(CF_2)_3CHF_2$	NTf_2	(–53)	400	1.86	970
2	$OCH_2(CF_2)_3CHF_2$	PF_6	62	260		

[a] Melting point/phase transition temperature [°C]. [b] Thermal degradation [°C]. [c] cP.

Scheme 13.

9. Applications of Fluorocationic Ionic Salts

The fluorocationic ionic liquids reviewed here are still being investigated in different research fields. Fluorinated quaternary ammonium salts are useful as phase-transfer reaction catalysts, especially in basic media,[43] as surfactants,[42] or as antimicrobials.[19] Fluoroalkyl-substituted imidazolium salts have also been reported as surfactants in conventional ionic liquids.[21] Triazine-based polyfluorinated triquaternary imidazolium liquid salts were used as solvents in the rhodium-catalyzed hydroformylation of 1-octene which resulted in a significant increase in selectivity with preference for 1-nonanal.[27] Highly hydrophobic ionic liquids, such as some imidazolium, pyrazolium, triazolium, thiazolium, oxazolium, pyridinium, pyridazinium, pyrimidinium and pyrazinium salts, have applications in non-aqueous batteries, electrochemical capacitors, electroplating, catalysis and chemical separations.[16,22] A recent review (> 350 references), which essentially ignores ionic liquids with fluorine-containing cations, reports adequately on the syntheses of non-fluorine-containing ionic liquids and chemical and biochemical transformations in them.[45]

10. Conclusion

In conclusion, ionic liquids with fluorine-containing cations have many special and valuable characteristics in comparison with their non-fluorine analogues. It has been shown that by changing the fluoroalkyl chain or fluorine-containing moiety on the cation or the inorganic and organic anion, a wide range of tunable properties of these novel ionic liquids can be obtained. They are promising solvents for electrochemical, photovoltaic, surfactant and synthetic applications.

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