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Quaternary Salts Containing the Pentafluorosulfanyl (SF_5) Group

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The first quaternary salts of pyridine (**2**), *N*-methyl imidazole (**3**), *N*-propyl triazole (**4**), and pyridazine (**5**) that contain the pentafluorosulfanyl (SF_5) group were prepared and characterized. Neat reactions of the aromatic nitrogen compounds with $SF_5(CF_2)_n(CH_2)_mI$ (n = 2 or 4, m = 2 or 4) gave quaternary iodides **6a**–**c**, **7a**–**c**, **8a**, and **9a**,**b**, which were metathesized with $LiN(SO_2CF_3)_2$ to form the bis(trifluoromethylsulfonyl)amides **10a**–**c, 11a**–**c, 12a,** and **13a**,**b**, in high yields. With the exception of the pyridine bis(trifluoromethylsulfonyl)amide salts, the compounds melted or exhibited a T_g at <0 °C. The methylimidazolium, pyridinium, and pyridazinium salts exhibited densities of ∼2 g/cm^3. Particularly striking was the density of $CF_3(CF_2)_5(CH_2)_2$-pyridazinium $N(CF_3SO_2)_2$ measured at 2.13 g/cm^3; however, an atypically high density for the 1-$CF_3(CF_2)_5(CH_2)_2$-3-methyl imidazolium amide (**14**) was also observed at 1.77 g/cm^3. All quaternary salts were characterized via IR, ^{19}F, ^{1}H, and ^{13}C NMR spectra and elemental analyses.

Introduction

Pyridinium, pyridazinium, imidazolium, and triazolium quaternary salts with alkyl[1] and, to a lesser extent, polyfluoroalkyl substituents[2] continue to be of broad interest. However, despite the continuing work with pentafluorosulfanyl-containing (SF_5) compounds, for example, in liquid crystal applications particularly where highly polar terminal groups are desired,[3] the introduction of this group via quaternization methodologies has not been examined. Therefore, the properties of such salts are unknown. Derivatives of sulfur hexafluoride (SF_6) often reflect the high thermal, radiative, and chemical stability of the parent compound and thus offer many opportunities for further exploration.[4]

While many low-melting salts have been reported that have sulfur-containing anions, such as $N(SO_2CF_3)_2^-$ and $R_fSO_3^-$ ($R_f = CF_3, C_4F_9$),[2a] the number of sulfur-containing cationic species in such salts is relatively small.[5] Trimethylsulfonium bromide readily forms low-melting, albeit viscous, salts with aluminum halides; however, with $N(SO_2CF_3)_2^-$, the triethylsulfonium salt (mp = −35 °C) is among the least viscous of the low-melting salts known (30 mP s at 25 °C) and its

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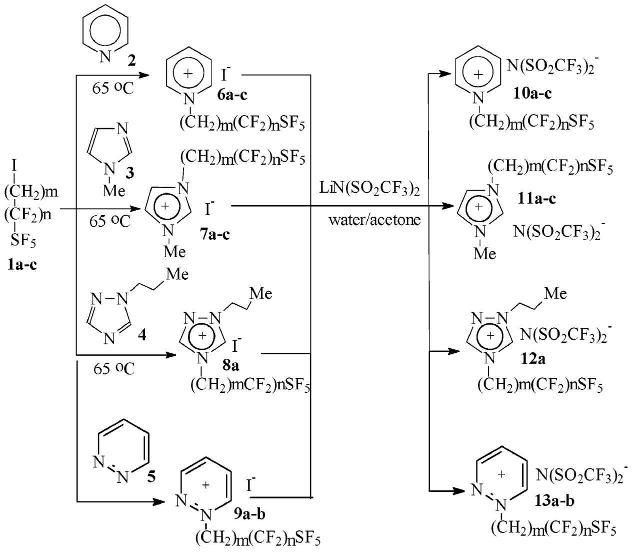
conductivity compares favorably with the analogous 1-ethyl-3-methylimidazolium salt. 3-Butyl-4/5-methylthiazolium tetrafluoroborate salts are reported as stable, yellow-orange liquids.[6] Additionally, a quaternary ammonium chloride that contains a sulfur substituent at nitrogen melts at 80 °C.[7]

With an electronegativity of ~3.62[8a] (fluorine = ~4.00), the pentafluorosulfanyl group as a substitutent on a carbon chain should be suitable as a replacement for its counterparts that contain a trifluoromethyl group (~3.35). In an excellent study, the electronic effects of the SF_5 and the CF_3 group on an aromatic ring were determined. The ionization constants of a number of benzoic acids, anilinium ions, and phenol derivatives containing NO_2, SF_5, and CF_3 groups showed that the SF_5 group is more strongly electron withdrawing than a CF_3 group and approaches a nitro group in inductive power. Also, from polarographic reduction measurements with substituted nitrobenzenes, the following series in order of decreasing electron withdrawing power was $NO_2 > SF_5 > CO_2H > CF_3 > H > CH_3$.[8b]

However, because of the greater molecular mass and greater polarity of the SF_5 group, the physical properties of these compounds may differ from CF_3 analogues. On the basis of its chemical robustness and lipophilic character, the SF_5 group has considerable potential as a structural component in polymeric, fuel-cell electrolyte, surface, and dielectric applications.[9]

Recently we have reported some low-melting polyfluoroalkyl-substituted quaternary imidazolium and triazolium salts that have wide liquid ranges and high thermal stabilities.[2b−e] Additionally, the *N*-mono- and *N*,*N*′-dibipyridinium quaternary polyfluoroalkyl salts that are water stable and decompose at >340 °C have been synthesized.[10] Most of these materials melt below 100 °C, and all become liquid at <150 °C. In the present work, we have carried out quaternization reactions of pyridine, pyridazine, *N*-methyl imidazole, and *N*-propyl triazole with $SF_5(CF_2)_n(CH_2)_mI$ ($n = 2$ or 4, $m = 2$ or 4)[11] and metathesized the resulting salts with $Li(NSO_2CF_3)_2$ in order to obtain low-melting, dense liquids. The properties of these stable salts are compared with their CF_3 and CH_3 analogues. Some of the former are also reported here for the first time.

Scheme 1



	m	n
1a, 6a, 7a, 8a, 9a, 10a, 11a, 12a:	4	2
1b, 6b, 7b, 9b, 10b, 11b, 13b:	2	2
1c, 6c, 7c, 10c, 11c:	2	4

Results and Discussion

Initially pyridine (**2**), *N*-methyl imidazole (**3**), *N*-propyl triazole (**4**), or pyridazine (**5**) was mixed with $SF_5CH_2CH_2Br$[12] at 25 °C for several days with essentially no reaction. Heating the mixture at 65 °C for several hours did give quaternary compounds, but major decomposition of the pentafluorosulfanyl-containing compound occurred. This may be due to intrinsic instability of the SF_5 functionality in this compound. However, in sharp contrast, $SF_5CF_2CF_2CH_2CH_2CH_2CH_2I$ (**1a**) gave excellent yields. For example, reaction of **1a** with pyridine (**2**) in 1:1.1 molar ratio without solvent at 65 °C for 12 h led to the formation of the quaternary salt (**6a**) in 90% isolated yield (Scheme 1). Under similar conditions, reactions of **1a** with *N*-methyl imidazole (**3**), *N*-propyl triazole (**4**), and pyridazine (**5**) gave the monoquaternary salts (**7a, 8a, 9a**) in >85% isolated yields. Next we examined the reactions of $SF_5CF_2CF_2CH_2CH_2I$ (**1b**) and $SF_5CF_2CF_2CF_2CF_2CH_2CH_2I$ (**1c**) with **2** and **3** and **1b** with **5** at

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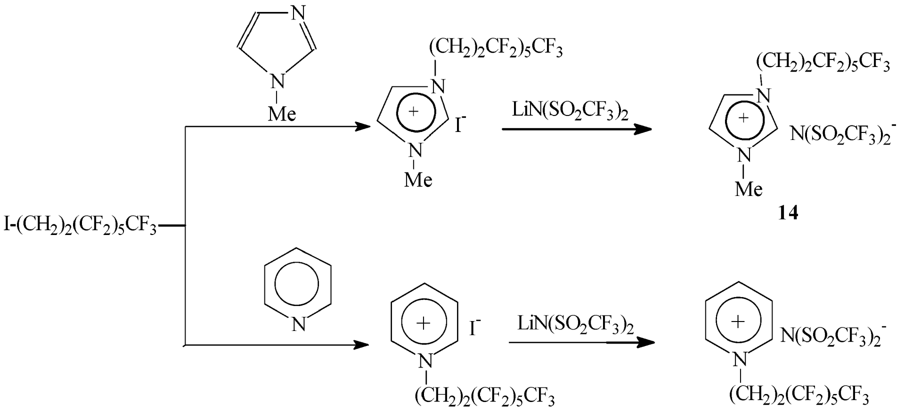
Table 1. Melting Point (phase transition) and Density Data for Bis(trifluoromethane-sulfonyl)amides

	pyridinium		pyridazinium		MeIm		PrTriazolium	
R	T_m (T_g)[a]	d[b]	T_m (T_g)	d	T_m (T_g)	d	T_m (T_g)	d
$SF_5(CF_2)_2(CH_2)_4$	18	2.02	(−41.7)	1.87	−56.7	2.01	−54.8	1.89
$SF_5CF_2)_2(CH_2)_2$	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[c]	−74	1.44[d]	(−67)[e]	1.60
$CF_3(CF_2)_5(CH_2)_2$	38.4		−13	2.13[c]	(−50)	1.77	28[e]	
$CH_3(CH_2)_2$					(−87)	1.48[f]		
$CH_3(CH_2)_6$					7(−85)	1.34[f]		
$CH_3(CH_2)_7$					(−84)	1.32[f]		

[a] Melting point (°C), phase transition (°C). [b] Density, pycnometer. [c] Reference 13. [d] Reference 2b,c. [e] Reference 2d,e; butyl. [f] Reference 14.

Scheme 2



14

15

65 °C without solvent. The iodides, **6b, 6c, 7b, 7c**, and **9b** were obtained in good yields (Scheme 1).

Reactions of **1b** and **1c** with **3** were found to be sluggish on heating, but lower temperatures were necessary because when the reaction was carried out at >65 °C, some decomposition occurred. All of the iodide salts (**6a−c, 7a−c, 8a**, **9a−b**) were stable to water and air and were solids at 25 °C. With the exception of the pyridazinium iodides (**9a**,**b**), which displayed only partial miscibility with all solvents tried, **6a−c, 7a−c**, and **8a** were soluble in acetone and ethyl acetate. Water solubility was a function of the number of fluorine atoms in the SF_5 chain, i.e., **6a, 6b, 7a, 7b,** and **8a** were soluble while **6c** and **7c** were only slightly miscible.

Each of the iodides was metathesized with $LiN(SO_2CF_3)_2$ at 25 °C in water or in a water/acetone mixture (1:1) to form, with the exception of the SF_5-pyridiniuim amides, **10b** (mp = 33 °C) and **10c** (mp = 36.1 °C), new salts that melted or showed a phase transition below 25 °C. Compound **10a** melts at 18 °C. The remaining room-temperature liquids exhibit T_m or T_g at −50 °C or below (Table 1).

These pentafluorosulfanyl polyfluoroalkyl quaternary salts exhibit densities around 2 g/cm^3, making them the most dense of any of the non-chloroaluminate salts reported to date. This is not surprising since the SF_5 moiety adds considerable mass to the cation. Interestingly, comparison of the melting points or glass transition points of the methyl imidazolium salts showed that they all occur at ≤−50 °C with the latter for the non-fluoroalkyl-substituted salts being around −85 °C. The densities of these salts decrease drastically from the SF_5 polyfluoroalkyl derivatives at ∼2.0 g/cm^3 to $CF_3CH_2CH_2-$[2b,c] ≈ $CH_3CH_2CH_2-$[14] at 1.44−1.48 g/cm^{-3}. Surprisingly, the methyl imidazolium salt with an eight-carbon polyfluoroalkyl substituent, $CF_3(CF_{2)5}(CH_2)_2-$ (**14**), with a density at 1.77 g/cm^3 greatly exceeds the salts with seven- and eight-carbon alkyl groups, $CH_3(CH_2)_6-$ and $CH_3(CH_2)_7-$, at 1.32 g/cm^3.[14]While it is expected that the fluorine-containing analogue should be somewhat more dense, such a marked difference was not anticipated. In keeping with the greater density arising when the substituent is $CF_3(CF_2)_5(CH_2)_2-$, note that the pyridazinium salt[13] is the most dense yet at 2.13 g/cm^3, even exceeding the SF_5 polyfluoroalkyl derivatives. However, as with the SF_5 polyfluoroalkyl pyridinium amides, the $CF_3(CF_2)_5(CH_2)_2$-substituted pyridinium salt (**15**) melts at 38.4 °C. Typical of polyfluoroalkyl triazolium salts, the SF_5 polyfluoroalkyl propyl triazolium compound has a density at ∼1.90 g/cm^3 whereas the butyl $CF_3(CF_2)_5(CH_2)_2$ triazolium amide is a solid that melts at 28 °C.[2d,e] With the exception of the SF_5 polyfluoroalkyl salts that are thermally stable in the vicinity of >300 °C, all of the others (non-SF_5-containing) are stable to >375 °C and higher. This lower thermal stability likely results from instability of the SF_5 moiety itself.

Conclusion

In conclusion, new thermally stable, pentafluorosulfanyl polyfluoroalkyl pyridinium, pyridazinium, methyl imidazolium, and propyl tetrazolium quaternary salts have been synthesized and characterized. Melting points (or T_g) are

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lower than 0 °C. The presence of the pentafluorosulfanyl group markedly increases the densities of the bis(trifluorosulfonyl)amide salts. However, $CF_3(CF_2)_5(CH_2)_2^-$ as a substitutent on the ring also plays a major role in causing an increase in the liquid densities relative to the C8 alkyl or to shorter polyfluoroalkyl substitutents and, in some cases, to the pentafluorosulfanyl polyfluoroalkyl substitutents.

Experimental Section

General. All the reagents used were analytical reagents purchased from commercial sources and used as received. The SF_5 compounds were synthesized by the Gard group at Portland State University.[11] ^1H, ^{19}F, and ^{13}C NMR spectra were recorded in acetone-d_6 on a spectrometer operating at 300, 282, and 75 MHz, respectively. Chemical shifts are reported in ppm relative to the appropriate standard, $CFCl_3$ for ^{19}F and TMS for ^1H and ^{13}C NMR spectra. IR spectra were recorded using NaCl plates for neat liquids and KBr pellets for solids. Differential scanning calorimetry (DSC) data were recorded in the range of −85 to 400 °C. Elemental analyses were carried out at the Shanghai Institute for Organic Chemistry.

General procedure. Pyridine (**2**), *N*-methyl imidazole (**3**), N-propyltriazole (**4**), or pyradizine (**5**) (5 mmol) and $I(CH_2)_m(CH_2)_n$-SF_5 (**1a**−**c**) were sealed in a Pyrex glass tube in vacuo by cooling to liquid nitrogen temperature and then heated at 65 °C for ∼12 h. After cooling at room temperature, the tube was opened and the volatile material was removed at reduced pressure. Washing crude products with an acetone/pentane mixture (1:3) gave **6a**−**c**, **7a**−**c**, **8a**, and **9a**−**b** in good yields. Reaction of these iodides with $LiN(SO_2CF_3)_2$ in a water/acetone mixture (2:1) in 1:1.2 molar ratio was carried out at room temperature for 5 h. After the acetone was removed, the water-insoluble oily liquid was separated and washed with a small amount of water to give **10a**−**c**, **11a**−**c**, **12a**, and **13a**−**b** in high yields.

$SF_5CF_2CF_2CH_2CH_2CH_2CH_2$-$NC_5H_5^+I^-$ (6a). Yield, 90%. IR (KBr pellet): 3034, 1633, 1491, 1463, 1392, 1319, 1288, 1178, 1112, 1037, 870, 821, 737 cm^{-1}. ^{19}F NMR: δ 70.74 (m, 1F), 48.50 (d, m, 4F), −95.55 (m, 2F), −116.50 (m, 2F) cm$^-$. ^1H NMR: δ 1.83 (m, 2H), 2.22 (m, 4H), 5.05 (m, 2H), 8.16 (t, 2H, J = 6.9 Hz), 8.58 (t, 1H, J = 7.8 Hz), 9.58 (d, 2H, J = 5. 5 Hz). ^{13}C NMR: δ 18.1, 31.7 (t, J = 22.1 Hz), 31.9, 114.0−127.0 (m), 129.4, 145.8, 146.4. Anal. Calcd for $C_{11}H_{13}F_9INS$: C, 26.99; H, 2.66; N, 2.86. Found: C, 27.06; H, 2.88; N, 2.82.

$SF_5CF_2CF_2CH_2CH_2$-$NC_5H_5^+I^-$ (6b). Yield, 87%. IR (KBr pellet): 3041, 1633, 1580, 1487, 1429, 1363, 1229, 1195, 1119, 1003, 960, 869, 816, 729 cm^{-1}. ^{19}F NMR: δ 64.41 (m, 1F), 43.47 (d, m, 4F), 96.43 (m, 2F), −115.28 (m, 2F) cm^{-1}. ^1H NMR: δ 2.66 (m, 2H), 4.47 (m, 2H), 7.67 (t, 2H, J = 6.7 Hz), 8.17 (t, 1H, J = 7.8 Hz), 8.93 (d, 2H, J = 5. 5 Hz). ^{13}C NMR: δ 33.0 (t, J = 21.2 Hz), 56.5, 114.0−127.0 (m), 128.7, 145.9, 147.1. Anal. Calcd for $C_9H_9F_9INS$: C, 23.43; H, 1.95; N, 3.04. Found: C, 24.20; H, 2.28; N, 3.19.

$SF_5CF_2CF_2CF_2CF_2CH_2CH_2$-$NC_5H_5^+I^-$ (6c). Yield, 85%. IR (neat): 3042, 1635, 1580, 1528, 1480, 1295, 1188, 1122, 1013, 928, 867, 828, 736 cm^{-1}. ^{19}F NMR: δ 63.36 (m, 1F), 43.62 (d, m, 4F), −94.55 (m, 2F), −113.78 (m, 2F) 122.86 (m, 4F). ^1H NMR: δ 2.84 (m, 2H), 4.82 (m, 2H), 7.80 (t, 2H, J = 6.7 Hz), 8.41 (t, 1H, J = 7.8 Hz), 8.85 (d, 2H, J = 5. 5 Hz). ^{13}C NMR: δ 32.3 (t, J = 21.3 Hz), 54.4, 114.0−127.0 (m), 129.5, 145.7, 147.4. Anal. Calcd for $C_{11}H_9F_{13}INS$: C, 23.50; H, 1.6; N, 2.50. Found: C, 23.57; H, 1.84; N, 2.48.

$SF_5CF_2CF_2CH_2CH_2CH_2CH_2$-$NC_5H_5^+N(SO_2CF_3)_2^-$ (10a). Liquid (mp = 18 °C, DSC). Yield, 92%. IR (neat): 3093, 1635, 1633, 1490, 1354, 1180, 1137, 1060, 875, 828, 738, cm^{-1}. ^{19}F NMR: δ 66.09 (m, 1F), 44.40 (d, m, 4F), −75.22 (s, 6F), −90.54 (m, 2F), −110.94 (m, 2F). ^1H NMR: δ 1.84 (m, 2H), 2.2−2.4 (m, 4H), 4.95 (m, 2H), 8.29 (t, 2H, J = 6.9 Hz), 8.74 (t, 1H, J = 7.8 Hz), 9.19 (d, 2H, J = 5. 5 Hz). ^{13}C NMR: δ 18.0, 31.1, 31.5 (t, J = 22.5 Hz), 31.9, 114.0−127.0 (overlapped quartet with multiplets), 129.6, 145.7, 146.8. Anal. Calcd for $C_{13}H_{13}F_{15}N_2O_4S_3$: C, 24.30; H, 2.02; N, 4.45. Found: C, 24.49; H, 2.18; N, 4.65.

$SF_5CF_2CF_2CH_2CH_2$-$NC_5H_5^+N(SO_2CF_3)_2^-$ (10b). Liquid (mp = 33 °C, DSC). Yield, 90%. IR (neat): 3197, 1635, 1492, 1354, 1220, 1180, 1060, 963, 879, 820 cm^{-1}. ^{19}F NMR: δ 64.58 (m, 1F), 43.61 (d, m, 4F), −80.62 (s, 6F), −96.62 (m, 2F), −115.91 (m, 2F) cm$^-$. ^1H NMR: δ 2.65 (m, 2H), 4.45 (m, 2H), 7.68 (t, 2H, J = 6.6 Hz), 8.18 (t, 1H, J = 7.8 Hz), 8.92 (d, 2H, J = 5. 5 Hz). ^{13}C NMR: δ 33.1 (t, J = 21.5 Hz), 56.4, 114.0−127.0 (overlapped quartet with multiplets), 128.8, 145.8, 147.0. Anal. Calcd for $C_{11}H_9F_{15}N_2O_4S_3$: C, 21.50; H, 1.50; N, 4.56. Found: C, 21.70; H, 1.67; N, 4.66.

$SF_5CF_2CF_2CF_2CF_2CH_2CH_2$-$NC_5H_5^+N(SO_3CF_3)_2^-$ (10c). Liquid (T_g = −39.5 °C, mp = 36.1 °C, DSC). Yield, 90%. IR (neat): 3047, 1633, 1581, 1533, 1487, 1298, 1157, 1197, 1120, 1003, 962, 873, 822, 730 cm^{-1}. ^{19}F NMR: δ 63.45 (m, 1F), 43.51 (d, m, 4F), −79.96 (s, 6F), −94.64 (m, 2F), −113.92 (m, 2F) 122.97 (m, 4F). ^1H NMR: δ 2.79 (m, 2H), 4.79 (m, 2H), 7.83 (t, 2H, J = 6.7 Hz), 8.32 (t, 1H, J = 7.8 Hz), 8.84 (d, 2H, J = 5. 5 Hz). ^{13}C NMR: δ 32.2 (t, J = 21.3 Hz), 54.6, 114.0−127.0 (overlapped quartet with multiplets), 129.3, 145.8, 147.2. Anal. Calcd for $C_{13}H_9F_{19}N_2O_4$: C, 21.90; H, 1.32; N, 4.53. Found: C, 22.05; H,1.46; N, 4.40.

1-$SF_5CF_2CF_2CH_2CH_2CH_2CH_2$-3-methylimidazolium$^+I^-$ (7a). Yield, 91%. IR(neat): 3074, 1568, 1460, 1330, 1041, 1196, 1116, 874, 826, 732 cm^{-1}. ^{19}F NMR: δ 66.00 (m, 1F), 44.45 (d, m, 4F), −95.65 (m, 2F), −115.54 (m, 2F). ^1H NMR: δ 1.64 (m, 2H), 1.8−2.2 (m, 4H), 4.00 (s, 3H), 4.38 (m, 2H), 7.51 (d, 2H, J = 41.0 Hz), 9.86 (s, 1H). ^{13}C NMR: δ 18.2, 30.3, 31.9 (t, J = 22.3 Hz), 37.8, 50.3, 123.5, 124.5, 137.4, 114.0−122.0 (m). Anal. Calcd for $C_{10}H_{14}F_9IN_2S$: C, 24.39; H, 2.85; N, 5.69. Found: C, 24.52; H, 2.91; N, 5.88.

1-$SF_5CF_2CF_2CH_2CH_2$-3-methylimidazolium$^+I^-$ (7b). Yield, 88%. IR (neat): 3082, 1573, 1521, 1458, 1381, 1280, 1118, 1001, 877, 809, 750 cm^{-1}. ^{19}F NMR: δ 66.64 (m, 1F), 43.71 (d, m, 4F), −96.41 (m, 2F), −115.80 (m, 2F). ^1H NMR: δ 2.45 (m, 2H), 3.83 (s, 3H), 4.18 (m, 2H), 6.67 (d, 2H, J = 34.6 Hz), 9.60 (s, 1H). Anal. Calcd for $C_8H_{10}F_9IN_2S$: C, 20.69; H, 2.16; N, 6.03. Found: C, 20.62; H, 1.94; N, 6.68.

1-$SF_5CF_2CF_2CF_2CF_2CH_2CH_2$-3-methylimidazolium$^+I^-$ (7c). Yield, 88%. IR (neat): 3131, 1565, 1470, 1428, 1358, 1175, 1142, 1055, 882, 773 cm^{-1}. ^{19}F NMR: δ −63.82 (m, 1F), 43.52 (d,m, 4F), −94.51 (m, 2F), −115.11 (m, 2F) 123.52 (m, 4F). ^1H NMR: δ 2.62 (m, 2H), 3.88 (s, 3H), 4.38 (m, 2H), 7.16 (s, 1H), 7.36 (s, 1H), 8.72 (s, 1H). ^{13}C NMR: δ 31.5 (t, J = 21.5 Hz), 36.8, 42.6, 54.3, 114.0−127.0 (m), 123.2, 124.5, 137.5. Anal. Calcd for $C_{10}H_{10}F_{13}IN_2S$: C, 21.20; H, 1.77; N, 4.96. Found: C, 21.63; H, 2.35; N, 5.30.

1-$SF_5CF_2CF_2CH_2CH_2CH_2CH_2$-3-methylimidazolium$^+$-$N(SO_2CF_3)_2^-$ (11a). Liquid (mp = −56.7 °C, DSC). Yield, 87%. IR (neat): 3157, 1572, 1464, 1432, 1352, 1192, 1136, 1059, 880, 828, 790 cm^{-1}. ^{19}F NMR: δ −65.51 (m, 1F), 43.76 (d,m, 4F), −80.32 (s, 6F), −96.09 (m, 2F), −116.24 (m, 2F). ^1H NMR: δ 1.47 (m, 2H), 1.8−2.0 (m, 4H), 3.56 (s, 3H), 4.03 (m, 2H), 7.25 (d, 2H, J = 28.9 Hz), 8.58 (s, 1H). ^{13}C NMR: δ 17.8, 29.7, 31.4 (t, J = 22.5 Hz), 36.6, 49.8, 114.0−127.0 (overlapped quartet with multiplets), 123.1, 124.4, 136.7. Anal. Calcd for

$C_{12}H_{14}F_{15}N_3O_4S_3$: C, 22.32; H, 2.17; N, 6.51. Found: C, 22.50; H, 2.20; N, 6.79.

1-$SF_5CF_2CF_2CH_2CH_2$-3-methylimidazolium$^+$N$(SO_2CF_3)_2^-$ (11b). Liquid (mp = −55.5 °C, DSC). Yield, 86%. IR (neat): 3160, 1568, 1463, 1432, 1352, 1189, 1136, 1058, 1058, 1002, 882, 741 cm^{-1}. ^{19}F NMR: δ 65.45 (m, 1F), 44.10 (d,m, 4F), −80.38 (s, 6F), −96.50 (m, 2F), −115.15 (m, 2F). ^{1}H NMR: δ 2.54 (m, 2H), 3.60 (s, 3H), 4.27(m, 2H), 7.25 (d, 2H, J = 42 Hz), 8.60 (s, 1H). ^{13}C NMR: δ 32.4 (t, J = 22.5 Hz), 36.5, 42.4, 114.0−127.0 (overlapped quartet with multiplets), 123.2, 124.5, 137.5. Anal. Calcd for $C_{10}H_{10}F_{15}N_3O_4S_3$: C, 19.44; H, 1.62; N, 6.80. Found: C, 19.67; H, 1.56; N, 6.65.

1-**$SF_5CF_2CF_2CF_2CF_2CH_2CH_2$-3-methylimidazolium$^+$-N$(SO_3CF_3)_2^-$ (11c).** Liquid (mp = −50.0 °C, DSC). Yield, 85%. IR (neat): 3125, 1568, 1465, 1432, 1402, 1352, 1188, 1143, 1059, 883, 788 cm^{-1}. ^{19}F NMR: δ −63.40 (m, 1F), 44.32 (d,m, 4F), −80.15 (s, 6F), −94.72 (m, 2F), −114.59 (m, 2F) 123.38 (m, 4F). ^{1}H NMR: δ 2.51 (m, 2H), 3.57 (s, 3H), 4.29 (m, 2H), 7.19 (s, 1H), 7.37 (s, 1H), 8.63 (s, 1H). ^{13}C NMR: δ 31.4 (t, J = 21.5 Hz), 36.5, 42.4, 54.3, 114.0−127.0 (m), 123.3, 124.6, 137.5. Anal. Calcd for $C_{12}H_{10}F_{19}N_3O_4S_3$: C, 20.00; H, 1.39; N, 5.86. Found: C, 20.73; H, 1.60; N, 6.09.

1-Propyl- 4-$SF_5CF_2CF_2CH_2CH_2CH_2CH_2$-1, 2, 4-triazolium$^+I^-$ (8a). Yield, 82%. IR (neat): 3030, 1622, 1576, 1462, 1363, 1272, 1116, 1042, 956, 738 cm^{-1}. ^{19}F NMR: δ 65.92 (m, 1F), 44.62 (d, m, 4F), −95.70 (m, 2F), −115.52 (m, 2F). ^{1}H NMR: δ 1.02 (t, 3H, J = 7.1 Hz), 2.07 (m, 4H), 3. 48 (m, 2H), 3.68 (s, 3H), 4.56 (q, 2H, J = 7.1 Hz), 5.02 (m, 2H), 8.62 (s, 1H), 9.63 (s, 1H). Anal. Calcd for $C_{11}H_{17}F_9IN_3S$: C, 25.3; H, 3.3; N, 8.12. Found: C, 25.18; H, 3.32; N, 8.15.

1-Propyl-4-$SF_5CF_2CF_2CH_2CH_2CH_2CH_2$-1, 2, 4-triazolium$^+$N-$(SO_2CF_3)_2^-$ (12a). Liquid (mp = −54.8 °C, DSC). Yield, 88%. IR (neat): 3035, 1622, 1578, 1525, 1462, 1386, 1363, 1265, 1190, 1116, 1042, 956, 826, 738 cm^{-1}. ^{19}F NMR: δ 66.21 (m, 1F), 44.20 (d, m, 4F), −80.12 (s, 6F), −95.88 (m, 2F), −116.42 (m, 2F). ^{1}H NMR: δ1.12 (t, 3H, J = 7.0 Hz), 2.22 (m, 4H), 3. 53 (m, 2H), 3.67 (s, 3H), 4.58 (q, 2H, J = 7.0 Hz), 5.12 (m, 2H), 8.77 (s, 1H), 9.67 (s, 1H). Anal. Calcd for $C_{13}H_{16}F_{15}N_4O_4S_3$: C, 23.18; H, 2.38; N, 8.32. Found: C, 23.17; H, 2.52; N, 8.54.

1-$SF_5CF_2CF_2CH_2CH_2CH_2CH_2$-pyridazinium$^+I^-$ (9a). Mp = 145.9 °C. Yield, 82%. IR (KBr): 3054, 2950, 1581, 1196, 1118, 875, 828 cm^{-1}. ^{19}F NMR: δ d 66.18 (5m, J = 146.1 Hz, 1F), 44.45 (d, 5m, J_1 = 144.0 Hz, J_2 = 14.12 Hz, 4F), −95.07 (5m, J = 15.53 Hz, 2F), −115.44−115.56 (m, 2F). ^{1}H NMR: δ d 1.86−1.94 (m, 2H), 2.39−2.53 (m, 4H), 5.23 (t, J = 7.29 Hz, 2H), 8.81−8.85 (m, 1H), 8.91−8.94 (m, 1H), 9.78 (d, J = 4.05 Hz, 1H), 10.59 (d, J = 5.76 Hz, 1H). ^{13}C NMR: δ d 155.6, 151.3, 137.8, 137.3, 115.4−123.0 (m), 65.57, 31.64 (t, J = 22.53 Hz), 29.76, 18.04 (t, J = 4.04 Hz).

1-$SF_5CF_2CF_2CH_2CH_2$-pyridazinium$^+$ I$^-$ (9b). Golden solid (mp = 171.8 °C, DSC). Yield, 80%. IR (KBr): 3049, 2982, 1425, 1279, 1198, 1117, 874, 812 cm^{-1}. ^{19}F NMR: δ 65.39 (5m, J = 145.1 Hz, 1F), 44.34 (d, 5m, J_1 = 145.8 Hz, J_2 = 13.67 Hz, 4F), −95.36 (5m, J = 14.97 Hz, 2F), −113.9−114.2 (m, 2F). ^{1}H NMR: δ 3.51 (ttt, J_1 = 18.77 Hz, J_2 = 7.26 Hz, J_3 = 1.60 Hz, 2H), 3.56 (s, 3H), 5.57 (t, J = 7.20 Hz, 2H), 8.88−8.91 (m, 1H), 8.96−8.99 (m, 1H), 9.81 (d, J = 4.71 Hz, 1H), 10.71 (d, J = 5.82 Hz, 1H). ^{13}C NMR: δ 155.7, 152.4, 138.5, 137.4, 114.9−123.1 (m), 58.47 (t, J = 4.38 Hz), 31.94 (t, J = 21.51 Hz). MS (solid probe) (EI) *m/z* (%) 335 (M$^+$, 100) (cation only).

1-$SF_5CF_2CF_2CH_2CH_2CH_2CH_2$-pyridazinium$^+$ N$(CF_3SO_2)_2^-$ (13a). Red liquid (T_g = −41.7 °C). Yield, 93%. IR (KBr): 3111, 2959, 1590, 1352, 1196, 1137, 1059, 880, 828, cm^{-1}. ^{19}F NMR: δ d 66.08 (5 m, J = 146.6 Hz, 1F), 44.45 (d, 5m, J_1 = 146.8 Hz, J_2 = 14.12 Hz, 4F), −79.92 (s, 6F), −95.22 (5m, J = 15.53 Hz, 2F), −115.38 to −115.70 (m, 2F). ^{1}H NMR: δ 1.83−1.93 (m, 2H), 2.37−2.51 (m, 4H), 5.19 (t, J = 7.20 Hz, 2H), 8.77−8.82 (m, 1H), 8.88−8.91 (m, 1H), 9.77 (d, J = 4.59 Hz, 1H), 10.10 (d, J = 5.82 Hz, 1H). ^{13}C NMR: δ 155.8, 151.0, 138.0, 137.3, 121.0 (q, J = 321.2 Hz), 115.3−123.2 (m), 66.06, 31.53 (t, J = 22.19 Hz), 29.91, 18.08 (t, J = 4.04 Hz). Anal. Calcd for $C_{12}H_{12}N_3F_{15}S_3O_4$: C, 23.11; H, 1.92. Found: C, 22.97; H, 2.02.

1-$SF_5CF_2CF_2CH_2CH_2$-pyradazinium$^+$N$(SO_2CF_3)_2^-$ (13b). Brown liquid, d = 1.93 g/cm^3. Yield, 85%. IR (KBr): 3115, 3046, 1484, 1437, 1351, 1191, 1137, 1059, 880, 824 cm^{-1}. ^{19}F NMR: δ 65.25 (5m, J = 145.8 Hz, 1F), 44.31 (d, 5m, J_1 = 145.8 Hz, J_2 = 13.78 Hz, 4F), −79.90 (s, 6F), −95.57 (5m, J = 15.25 Hz, 2F), −114.0 to −114.4 (m, 2F). ^{1}H NMR: δ 3.45 (tt, J_1 = 7.10 Hz, J_2 = 18.63 Hz, 2H), 5.56 (t, J = 7.10 Hz, 2H), 8.84−8.89 (m, 1H), 8.95−8.99 (m, 1H), 9.82 (d, J = 4.26 Hz, 1H), 10.25 (d, J = 5.76 Hz, 1H). ^{13}C NMR: δ 160.0, 152.1, 138.8, 137.4, 120.9 (q, J = 321.2 Hz), 114.4−123.2 (m), 58.64 (t, J = 4.38 Hz), 31.12 (t, J = 21.51 Hz). MS (solid probe) (EI) *m/z* (%) 335 (M$^+$, 100) (cation only). Anal. Calcd for $C_{10}H_8N_3F_{15}S_3O_4$: C, 19.52; H, 1.13. Found: C, 19.45; H, 1.52.

1-$CF_3(CF_2)_5(CH_2)_2$-3-methylimidazolium$^+$N$(SO_2CF_3)_2^-$ (14). To 2 mmol of 1-methylimidazole was added 1.5 mmol of $CF_3(CF_2)_5(CH_2)_2I$, and the mixture was maintained at 65 °C for 2 days to give 1-$CF_3(CF_2)_5(CH_2)_2$-3-methyl-imidazonium iodide. To a magnetically stirred solution of the latter (0.25 mmol) in water (1 mL) was added lithium bis(trifluoromethanesulfonyl)amide (0.3 mmol). After 5 min at room temperature, the water was decanted and the residue was washed with water (2.1 mL) that was removed in vacuo (0.3 mm Hg) at 40 °C for 24 h to leave **14.** Yellow liquid (T_g = −49.9 °C). Yield, 96%. ^{19}F NMR: δ −79.98 (s, 6F), −81.67 (tt, J_1 = 2.82 Hz, J_2 = 9.88 Hz, 3F), −114.3 to −115.5 (m, 2F), −122.4 (bs, 2F), −123.4 (bs, 2F), −124.1 (bs, 2F), −126.7 to −126.8 (m, 2F). ^{1}H NMR: δ 3.15 (tt, J_1 = 7.19 Hz, J_2 = 18.96 Hz, 2H), 4.05 (s, 3H), 4.89 (t, J = 7.19 Hz, 2H), 7.81 (t, J = 1.79 Hz, 1H), 7.97 (t, J = 1.79 Hz, 1H), 9.25 (s, 1H). ^{13}C NMR: δ 138.2, 125.1, 123.7, 120.9 (q, J = 321.1 Hz), 127.6−109.0 (m), 42.73 (t, J = 5.06 Hz), 36.79, 31.82 (t, J = 21.13 Hz). Anal. Calcd for $C_{14}H_{10}F_{19}N_3O_4S_2$: C, 23.70; H, 1.41. Found: C, 23.68; H, 1.56.

1-$CF_3(CF_2)_5(CH_2)_2$-$NC_5H_5$$^+N(SO_2CF_3)_2^-$ (15). The iodide and bis(trifluorosulfonyl)amide (**15**) were prepared as above. Solid (mp = 38.4 °C). Yield, 91%. IR (KBr): 3143, 3096, 1493, 1351, 1193, 1140, 1059 cm^{-1}. ^{19}F NMR: δ −79.98 (s, 6F), −81.70 (tt, J_1 = 2.82 Hz, J_2 = 12.71 Hz, 3F), −113.9 to −114.0 (m, 2F), −122.4 (bs, 2F), −123.5 (bs, 2F), −124.0 (bs, 2F), −126.8 to −126.9 (m, 2F). ^{1}H NMR: δ 3.40 (tt, J_1 = 7.39 Hz, J_2 = 18.94 Hz, 2H), 5.35 (t, J = 7.41 Hz, 2H), 8.37 (t, J = 7.84 Hz, 2H), 8.84 (tt, J_1 = 1.24 Hz, J_2 = 7.84 Hz, 1H), 9.40 (d, J = 5.51 Hz, 2H). ^{13}C NMR: δ 147.8, 146.3, 129.6, 121.0 (q, J = 321.2 Hz), 105.0−124.0 (m), 54.83 (t, J = 4.75 Hz), 32.40 (t, J = 21.01 Hz). Anal. Calcd for $C_{15}H_9F_{19}N_2O_4S_2$: C, 25.50; H, 1.27; Found: C, 25.36; H, 1.39.

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