Syntheses of 1-Alkyl-1,2,4-triazoles and the Formation of Quaternary 1-Alkyl-4-polyfluoroalkyl-1,2,4-triazolium Salts Leading to Ionic Liquids

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1,2,4-Triazole was alkylated (alkyl = methyl, butyl, heptyl, decyl) at N-1 in >90% isolated yields. The resulting 1-alkyl triazoles were quaternized at N-4 in >98% isolated yields using fluorinated alkyl halides with >98% isolated yields, under neat reaction conditions at 100−120 °C to form N1-CH_3-N4-$(CH_2)_2C_mF_{2m+1}$-triazolium (Taz) iodide ($m = 1, 6$), N1-C_4H_9-N4-$(CH_2)_2C_mF_{2m+1}$-Taz iodide ($m = 1, 4, 6$), N1-C_7H_{15}-N4-$(CH_2)_2C_mF_{2m+1}$-Taz iodide ($m = 1, 4, 6$), N1-$C_{10}H_{21}$-N4-$(CH_2)_2C_mF_{2m+1}$-Taz iodide ($m = 1, 4$), and N1-C_nH_{2n+1}-N4-$(CH_2)_2F$-Taz bromide ($n = 4, 7, 10$). Single-crystal X-ray analyses confirmed the structure of $[1\text{-}CH_3\text{-}4\text{-}CH_2CH_2CF_3\text{-Taz}]^+I^-$. It crystallized in the orthorhombic space group *Pccn*, and the unit cell dimensions were $a = 13.8289(9)$ Å, $b = 17.3603(11)$ Å, $c = 9.0587(6)$ Å ($\alpha = \beta = \gamma = 90°$). Metathesis of these polyfluoroalkyl-substituted triazolium halides with other salts led to the formation of quaternary compounds, some of which comprise ionic liquids, namely, $[R(R_f)\text{-Taz}]^+Y^-$ (Y = NTf_2, BF_4, PF_6, and OTf), in good isolated yields without the need for further purification: N1-CH_3-N4-$(CH_2)_2C_mF_{2m+1}$-Taz Y ($m = 1, 6$; Y = NTf_2), N1-C_4H_9-N4-$(CH_2)_2C_mF_{2m+1}$-Taz Y ($m = 1, 4, 6$; Y = NTf_2), N1- C_7H_{15}-N4-$(CH_2)_2C_mF_{2m+1}$-Taz Y ($m = 1, 4, 6$; Y = NTf_2), N1-$C_{10}H_{21}$-N4-$(CH_2)_2C_mF_{2m+1}$-Taz Y ($n = 1, 4$; Y = NTf_2), N1-C_nH_{2n+1}-N4-$(CH_2)_2F$-Taz Y ($n = 7, 10$; Y = NTf_2), N1-$C_{10}H_{21}$-N4-$(CH_2)_2F$-TazY (Y = OTf), N1-C_7H_{15}-N4-$(CH_2)_2F$-TazY (Y = BF_4), N1-C_4H_9-N4-$(CH_2)_2C_mF_{2m+1}$-Taz Y ($m = 4, 6$; Y = PF_6), N1-C_7H_{15}-N4-$(CH_2)_2C_4F_9$-Taz Y (Y = PF_6), N1-C_4H_9-N4-$(CH_2)_2C_mF_{2m+1}$-Taz Y ($m = 4, 6$; Y = OTf). All new compounds were characterized by ^1H, ^{19}F, and ^{13}C NMR and MS spectra and elemental analyses. T_gs and T_ms of ionic liquids were determined by DSC.

Introduction

The ionic liquid field is dominated by imidazolium salts. There are very few triazolium compounds that can be characterized as ionic liquids. Of this small number, there were none that contained polyfluoroalkyl substituents or fluorine-containing anions.[1] The parent triazoles and their derivatives have many applications in medicine and in industry.[2] The introduction of a third nitrogen impacts the various chemical properties of the ring relative to the 1,3-imidazole, e.g., the 1,2,4-triazole ring is slightly more acidic, and the resistance toward electrophilic attack and the difficulty of quaternization are increased. N-Alkylation, arylation, and acylation of 1,2,4-triazoles are readily achieved and have been extensively explored using a plethora of reagents most frequently in the presence of sodium alkoxide, sodium hydride, or sodium hydroxide as the base. In general, N-alkylation occurs at N-1 rather than N-4, but in the case of methylation, small amounts of the N-4 product are obtained that must be separated under vacuum distillation. Triazoles with alkyl, aryl, or acyl substitutents on N-1 or N-4 can be readily quaternized with powerful electrophilic agents such as the trialkyloxoniumtetrafluoroborates or methyl fluorosulfate such that maximum separation of the substituents occurs.[2d]

Ionic liquids are usually defined as thermally stable salts synthesized by combining bulky organic cations, e.g., 1-butyl-3-methylimidazolium ($BmIm^+$), with a wide variety of anions often with fluorine content, e.g., hexafluorophosphate (PF_6^-). These materials are generally liquid at room temperature or melt at temperatures <100 °C, have long liquid ranges, low vapor pressures, and are highly polar yet noncoordinating.[3−5] The most common nonmetallic salts in use are those with alkylammonium, alkylphosphonium, *N*-alkylpyridinium, and especially

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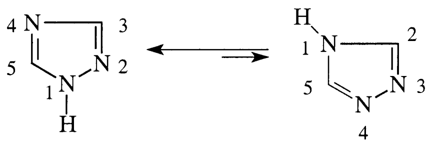
N,N′-dialkylimidazolium cations. Why these salts have such low melting points is not completely understood, but the properties of ionic liquids can be controlled to a large degree by variation in the nature of either the cation or the anion.[3,5d] While they serve as excellent solvents for large numbers of organic and organometallic compounds,[4] they often are immiscible with a number of organic solvents and thus provide a nonaqueous, polar alternative for two-phase systems. Moreover, it is possible to fine-tune their miscibility with water and common organic solvents by changing the characteristics of the side chains in the cation or of the inorganic anion. Such compounds are finding expanded applications as alternative novel reaction media for organic synthesis[4] and separation science.[5] Their unique properties have already been demonstrated by their use in a wide range of stoichiometric and catalytic reactions, as well as solvents for "green chemistry".[4,5] Much attention has been attracted through technological applications as electrolytes in batteries, photoelectrochemical cells, and other wet electrochemical devices.[6] Development of ionic liquids that are air and moisture stable has provided renewed vigor in ionic liquid chemistry. However, little, if any, work has been reported on mixed alkyl/fluoroalkyl 1,2,4-triazolium salts.

In this paper, we report the syntheses of several new alkylated 1,2,4-triazoles, the subsequent formation of quaternary 1-alkyl-4-polyfluoroalkyl-1,2,4-triazolium salts, and their conversion to stable ionic liquids. Considerable attention is devoted to the change in the properties of the quaternary salts as a function of the chain length and extent of fluorination of the cation substituents, as well as the impact of a variety of anions.

Results and Discussion

1,2,4-Triazoles are cyclic hydrazidines with a hydrogen atom (or substituent) on either the hydrazide nitrogen-1 or on the amide nitrogen. The parent 1,2,4-triazole (1H form) is in tautomeric equilibrium with the 1,3,4-triazole (4H form). The interconversion of the two tautomeric forms occurs rapidly, and their separation is difficult. However, the 1,2,4-triazole tautomer **1** is preferred over the 1,3,4-triazole tautomer **2** (the less symmetrical 1H form is favored over the symmetrical 4H form) (Scheme 1).[1,7−9]

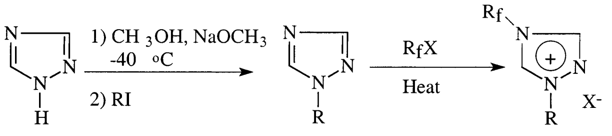
SCHEME 1



1
1,2,4-Triazole

2
1,3,4-Triazole

SCHEME 2



1 **3** **4**

Compd	R	Compd	Rf	X
3a	CH_3	**4a**	$(CH_2)_2CF_3$	I
3b	$(CH_2)_3CH_3$	**4b**	$(CH_2)_2CF_3$	I
3c	$(CH_2)_6CH_3$	**4c**	$(CH_2)_2CF_3$	I
3d	$(CH_2)_9CH_3$	**4d**	$(CH_2)_2CF_3$	I
3b	$(CH_2)_3CH_3$	**4e**	$(CH_2)_2(CF_2)_3CF_3$	I
3c	$(CH_2)_6CH_3$	**4f**	$(CH_2)_2(CF_2)_3CF_3$	I
3d	$(CH_2)_9CH_3$	**4g**	$(CH_2)_2(CF_2)_3CF_3$	I
3a	CH_3	**4h**	$(CH_2)_2(CF_2)_5CF_3$	I
3b	$(CH_2)_3CH_3$	**4i**	$(CH_2)_2(CF_2)_5CF_3$	I
3c	$(CH_2)_6CH_3$	**4j**	$(CH_2)_2(CF_2)_5CF_3$	I
3b	$(CH_2)_3CH_3$	**4k**	$(CH_2)_2F$	Br
3c	$(CH_2)_6CH_3$	**4l**	$(CH_2)_2F$	Br
3d	$(CH_2)_9CH_3$	**4m**	$(CH_2)_2F$	Br

In contrast to benzene, 1,2,4-triazoles fail to undergo nitration or sulfonation but are readily alkylated or acylated. While 1,2,4-triazoles with alkyl, aryl, or acyl substituents on N-1 or N-4 undergo quaternization when treated with powerful electrophiles such as the trialkyoxonium tetrafluoroborates, similar reagents are less available for the introduction of polyfluoroalkyl groups. There is only very little in the literature on the regioselective synthesis of fluorine-containing 1,2,4-triazolium compounds or quaternary salts.[2] Therefore, it was of interest to develop a methodology for the synthesis of this class of compounds and their concomitant quaternary salts.

One potential area for expansion of ionic liquids is the use of quaternary salts of 1-alkyl-4-polyfluoroalkyl 1,2,4-triazoles in order to determine the chemical and physical properties of these compounds. Alkylation of 1,2,4-triazoles occurred at N-1 to form 1-alkyl-1,2,4-triazoles (**3a**−**d**) in nearly quantitative yields (Scheme 2). The alkylation reactions occurred under mild conditions by addition of appropriate iodoalkane to 1,2,4-trizaole in a methanolic solution of sodium methoxide.

1-Alkyl-1,2,4-triazoles (**3a**−**d**) were quaternized at N-4 by reaction with equivalent amounts of polyfluoroalkyl iodides or bromides under neat reaction conditions at

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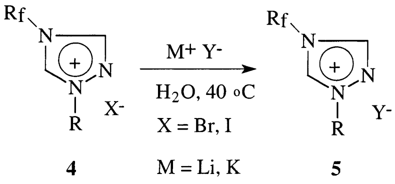
SCHEME 3



4 **5**

Compd	R	Rf	Compd	Y
4a	CH_3	$(CH_2)_2CF_3$	**5a**	NTf_2
4b	$(CH_2)_3CH_3$	$(CH_2)_2CF_3$	**5b**	NTf_2
4c	$(CH_2)_6CH_3$	$(CH_2)_2CF_3$	**5c**	NTf_2
4d	$(CH_2)_9CH_3$	$(CH_2)_2CF_3$	**5d**	NTf_2
4e	$(CH_2)_3CH_3$	$(CH_2)_2(CF_2)_3CF_3$	**5e**	NTf_2
4f	$(CH_2)_6CH_3$	$(CH_2)_2(CF_2)_3CF_3$	**5f**	NTf_2
4g	$(CH_2)_9CH_3$	$(CH_2)_2(CF_2)_3CF_3$	**5g**	NTf_2
4h	CH_3	$(CH_2)_2(CF_2)_5CF_3$	**5h**	NTf_2
4i	$(CH_2)_3CH_3$	$(CH_2)_2(CF_2)_5CF_3$	**5i**	NTf_2
4j	$(CH_2)_6CH_3$	$(CH_2)_2(CF_2)_5CF_3$	**5j**	NTf_2
4l	$(CH_2)_6CH_3$	$(CH_2)_2F$	**5k**	NTf_2
4m	$(CH_2)_9CH_3$	$(CH_2)_2F$	**5l**	NTf_2
4m	$(CH_2)_9CH_3$	$(CH_2)_2F$	**5m**	OTf
4l	$(CH_2)_6CH_3$	$(CH_2)_2F$	**5n**	BF_4
4e	$(CH_2)_3CH_3$	$(CH_2)_2(CF_2)_3CF_3$	**5o**	PF_6
4f	$(CH_2)_6CH_3$	$(CH_2)_2(CF_2)_3CF_3$	**5p**	PF_6
4i	$(CH_2)_3CH_3$	$(CH_2)_2(CF_2)_5CF_3$	**5q**	PF_6
4b	$(CH_2)_3CH_3$	$(CH_2)_2CF_3$	**5r**	OTf
4e	$(CH_2)_3CH_3$	$(CH_2)_2(CF_2)_3CF_3$	**5s**	OTf

100−120 °C to produce salts **4a**−**m** in >98% isolated yields (Scheme 2). Not surprisingly, these quaternary salts have rather high melting temperatures (Table 1).

Metathesis of polyfluoroalkyl triazolium halides **4** with other salts led to the formation of new quaternary salts (**5a**−**s**), namely, $[R(R_f)\text{-Taz}]^+Y^-$ (Y = BF_4, PF_6, NTf_2, and OTf), in excellent isolated yields (Scheme 3). Salts **5a**−**n**,**r** have T_ms or T_gs of less than 100 °C and therefore may be considered ionic liquids. On the basis of elemental analysis data, the purity of these salts is very good. The impact of fluorine concentration is clearly observed, e.g., when **5b** and **5i** are compared, where N-1 is butyl with N-4 changed from polyfluoropropyl to polyfluorooctyl, an increase in the phase transition temperature from −67 to 28 °C occurred.

Phase transition temperatures (midpoints of glass transitions and/or melting points) for compounds $[R(R_f)\text{-Taz}]^+Y^-$ (**5a**−**s**) as determined by differential scanning calorimetry (DSC) are given in Table 1. The key criterion for evaluation of an ionic liquid is, by definition, its melting point. Features discussed for cations of low-melting salts include low symmetry,[4] weak intermolecular interactions (such as little or no hydrogen bonding),[10,11] and a good distribution of charge in the cation.[12] Therefore, of particular interest is the relationship between the structure and chemical composition of an ionic liquid and its melting point. Comparison of the melting points of different hexafluorophosphate (PF_6), trifluoromethanesulfonate (OTf), and bis(trifluoromethane-sulfonyl)amide (NTf_2) triazolium salts clearly illustrates the influence of the cation. For example, with bis(trifluoromethanesulfonyl)amide as the anion, 1*H*,1*H*,2*H*,2*H*-perfluorooctyl or 1*H*,1*H*,2*H*,2*H*-perfluorohexyl as the substitutent at N-4, and variation of the N-1 alkyl groups from methyl to butyl to heptyl, the melting points decreased from 69 to 28 to 22°C or from 69 to 55 to 53 °C, respectively. However, these changes in phase transition temperatures are not predictable except in a very qualitative way. Interestingly, again with a constant R_f (3,3,3-trifluoropropyl), $^-NTf_2$ as the anion, and varying R from methyl to butyl to heptyl to decyl, the T_g is lowered from −58 to −67 °C and then remains unchanged for C_7 (heptyl) and C_{10} (decyl). Holding R constant at C_7, a constant $^-NTf_2$ anion, and varying R_f from C_3 to C_6 to C_8 leads to a discontinuous change in T_g/T_m, from −67 to 55 to 22 °C. However, when the anion is PF_6^-, R_f is C_6, and R changes from butyl to heptyl, both salts melt at ~297 °C. Generally, a decrease in cation symmetry contributes to poorer packing in the crystalline lattice and thus a lower melting point.

TABLE 1. Phase Transtion Temperatures and Thermal Decomposition of Quaternary Salts $[R(R_f)\text{-Taz}]^+Y^-$

compd	T_m (°C)[a]	T (°C)[b]	compd	T_m (°C)[a]	T (°C)[b]
4a	98	296	**5d**	−68 (T_g)	400
4b	123	274	**5e**	69	394
4c	174	303	**5f**	55	396
4d	192	280	**5g**	53	396
4e	277	288	**5h**	62	381
4f	270	292	**5i**	28	368
4g	255	303	**5j**	22	405
4h	225	347	**5k**	−70 (T_g)	359
4i	279	296	**5l**	−62 (T_g)	425
4j	276	300	**5m**	46	362
4k	167	216	**5n**	52	336
4l	125	320	**5o**	296	357
4m	129	312	**5p**	298	354
5a	−58 (T_g)	376	**5q**	289	361
5b	−67 (T_g)	395	**5r**	33	379
5c	−67 (T_g)	402	**5s**	173	391

[a] Phase transition temperature. [b] Thermal degradation.

The anion appears to exhibit a major influence on the melting point in a more predictable manner. For example, for R = C_3 and R_f = C_3, changing the anion from ^-OTf to $^-NTf_2$ lowers the melting point from 33 °C to a T_g of −67 °C; with the same anions and R = C_{10} and R_f = C_2, the melting point is reduced from 46 °C to a T_g of −52 °C. For R = C_4 and R_f = C_6 and changing from ^-OTf to PF_6^-, the melting point moves from 173 to 296 °C; for R = C_7 and R_f = C_2, changing from BF_4^- to $^-NTf_2$ lowers the phase transition temperature from 52 to −70 °C. The reduction in T_ms (T_gs) by introducing the NTf_2 ion is consistent throughout this entire family of compounds

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TABLE 2. Miscibility of Various Ionic Salts and Ionic Liquids in Organic Solvents[a] with the Dielectric Constant ϵ[b]

compd	THF	hexane	CH_2Cl_2	EtOAc	H_2O	acetone
4a–d	m	nm	m	m	m	m
4e–f	m	nm	m	m	pm	m
4g	m	nm	m	m	nm	m
4h	m	nm	m	m	pm	m
4i–j	m	nm	m	m	nm	m
4k–l	m	nm	pm	pm	m	pm
4m	pm	nm	nm	pm	pm	pm
5a–d	m	nm	m	m	pm	m
5e–h	m	nm	m	m	nm	m
5i	m	nm	pm	m	nm	m
5j–k	m	nm	pm	m	pm	m
5l	m	nm	m	m	pm	m
5m	m	nm	m	m	nm	m
5n	m	nm	m	m	m	m
5o–q	m	nm	pm	m	nm	m
5r	m	nm	m	m	nm	m
5s	m	nm	m	m	pm	m

[a] m = miscible; nm = nonmiscible; pm = partially miscible. [b] Dielectric constant ϵ at 25 °C; THF = 7.58; CH_2Cl_2 = 8.93; EtOAc = 6.02; H_2O = 78.54; acetone = 20.7; hexane = 1.89/20°C.

and appears to be independent of either of the substituents on the triazolium ring.

The density of the 1-alkyl-1,2,4-triazoles decreased as the bulkiness of the alkyl group increased **3a** > **3b** > **3c** > **3d** (methyl > butyl > heptyl > decyl). The same trend was observed for the ionic liquids with constant anion (NTf_2) and fluoroalkyl ($CF_3CH_2CH_2$) group on N-4 where **5a** > **5b** > **5c** > **5d** (d = 1.66, 1.60, 1.52, 1.49 g/cm^3). This is also the case with 4-fluoroethyl and NTf_2 where heptyl > decyl (d = 1.39, 1.37 g/cm^3). It appears that the density of ionic liquids with a constant anion is a function not only of the type and bulkiness of alkyl group at N-1 but also of the type and bulkiness of the fluoroalkyl group at the N-4 position, i.e., with an increase in the number of fluorine atoms and in the bulkiness of the fluoroalkyl group (constant alkyl), the density increases **5c** > **5k** ($CF_3CH_2CH_2$ > FCH_2CH_2, N-1 heptyl, d = 1.52, 1.39 g/cm^3) and **5d** > **5l** ($CF_3CH_2CH_2$ > FCH_2CH_2, N-1 decyl, d = 1.49, 1.37 g/cm^3). It is likely that with slight structural changes in the cation, densities of these liquids can be fine-tuned.

The tuning of solubility properties of an ionic liquid by careful choice of cation and anion deserves particular attention. When the dielectric constants of the organic solvents (THF, EtOAc, acetone, and dichloromethane) exceed a characteristic limit, Taz-ionic liquids (**5a–h** and **5l–p**) are completely miscible with these materials. This limit appears to be specific for each cation/anion combination (Table 2).

The influence of the cation, for example, is shown by the investigations of the solubility of **5a–l**, **4a–j**, and **4l–m**. It can be seen that with elongation of the alkyl and fluoroalkyl groups on the cation, the solubility of the ionic compound in organic solvents (THF, EtOAc, acetone, and dichloromethane) increases and decreases in H_2O; i.e., while **4a–d** are completely miscible in H_2O, **4f–h**, **5b–c**, **5k**, and **5l** are partially miscible and **5e–j** immiscible. These examples show that stepwise variation of the solubility properties can be achieved by variation of the alkyl group on the cation.

The influence of the anion on the solubility characteristics of the ionic liquids and quaternary salts can be demonstrated by the example of solubility of different melts containing the $^-NTf_2$, ^-OTf, I^-, and PF_6^- anions. While compounds **4a–j** are organic soluble, ionic liquids **5o–q** with the same cation but with the PF_6^- anion form biphasic mixtures with water.

X-ray Crystal Structure of 4a. Compound **4a** was crystallized from a mixture of EtOAc and hexane. The crystal structure confirms that the first alkylation took place at N-1 and the second alkylation at N-4. The structure was confirmed by single-crystal X-ray. The compound crystallizes as colorless crystals in the space group *Pccn*. The asymmetric unit consists of a molecule of the triazole and an iodine atom. The triazole moiety shows no unusual features; the triazole ring is planar, and the fluoroalkyl chain bends up, orthogonal to the ring as shown in Figure 1 in Supporting Information. The iodine atom is spatially separated from the triazole moiety and is 2.805(3) Å from H2a and 2.920(4) Å from asymmetry-related H3a. All other iodine interactions are >3.15 Å. Details of the data collection given in Table 1 and additional information are both given in Supporting Information.

Conclusion

An efficient procedure for the synthesis of new families of fluoroalkyl-containing triazolium quaternary salts and triazolium ionic liquids in good isolated yields has been developed. Regardless of the cation, when the anion is halide, the melting points are high. However, introduction of other anions, particularly NTf_2, reduces the melting points drastically. Similarly, as the length of the alkyl and polyfluoroalkyl substituents on the cations increases, causing less efficient packing in the solid, the melting points are observed to decrease. The density increases with elongation of the fluoroalkyl substituent and fluorine concentration and decreases as the alkyl group becomes bulkier. Work is continuing in an effort to understand changes in physical and chemical properties as functions of molecular composition.

Experimental Section

General. ^1H, ^{13}C, and ^{19}F NMR spectra were recorded in acetone-d_6, DMSO-d_6, and $CDCl_3$ (unless otherwise stated) on a 500 MHz spectrometer operating at 500.13, 125.75, and 470.56 MHz, respectively. GC/MS spectra were determined on an appropriate spectrometer. Mass spectra for ionic compounds were determined by insertion using the solid probe. M^+ is the mass of the cation. T_m and T_g were recorded on a differential scanning calorimeter at a scan rate of 10 °C/min. Chemical shifts are reported in parts per million relative to the appropriate standard. IR spectra were recorded using NaCl plates for neat liquids and KBr pellets for solids. Densities were measured at 24 °C using a pycnometer. Elemental analyses were perfomed by Desert Analytics Laboratory, Tucson, AZ, and the Shanghai Institute of Organic Chemistry.

X-ray Crystallographic Studies. Crystals of compound **4a** were removed from the flask and covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber and placed in the low-temperature nitrogen stream.[13] Data for compound **4a** were collected at 203(2) K (Mo Kα radiation, $\lambda = 0.71073$ Å) on an instrument equipped with a low-temperature device. Data were measured using omega scans of 0.3° per frame for 10 s, and a half sphere of data was collected. A total of 1471 frames were collected with a final resolution of 0.71 Å. The first 50 frames were recollected at the end of data collection to monitor the decay. Cell parameters were retrieved using SMART[14] software and refined using SAINTPlus[15] on all observed reflections. Data reduction and correction for Lp and decay were performed using SAINTPlus software. Absorption corrections were applied using SADABS.[16] The structure was solved by direct methods and refined by the least-squares method of F2 using the SHELXTL program package.[17] The structure was solved in the space group *Pccn* by analysis of systematic absences. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added geometrically and refined with a riding model with their parameters constrained to the parent atom site. No decomposition was observed during data collection. Some details of the data collection and refinement are given in the Experimental Section. Further details are provided in Supporting Information.

General Procedure for the Preparation of 3a–d. This synthesis is a modification of the procedure of Atkinson and Polya.[12] 1-Bromoalkane (102 mmol) was slowly added to a cooled methanolic (50 mL) solution of sodium methoxide (from 101 mmol of sodium) containing 1,2,4-triazole (101 mmol). The stoppered reaction flask was stirred at ambient temperature for 2 h and then warmed at 60 °C for 20 h. Methanol was removed to give an oil. The product was extracted from the oil with hot benzene (60 mL) and then hot chloroform (3 × 60 mL) and isolated under vacuum distillation.

1-Decyl-1,2,4-triazole (3d): 14.43 g, 90% yield, colorless viscous oil (bp 47–48 °C, 0.27 Torr, bath temperature = 95 °C); $d_{24\,°\mathrm{C}} = 0.921$ g/cm^3; IR (neat) 3117, 2925, 2854, 1747, 1506, 1465, 1377, 1273, 1206, 1012, 873 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.79 (t, $J = 6.9$ Hz, 3H), 1.21 (m, $J = 5.1$ Hz, 14H), 1.81 (p, $J = 7.2$ Hz, 2H), 4.07 (t, $J = 7.19$ Hz, 2H), 7.85 (s, 1H), 7.97 (s, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 152.17, 143.12, 50.06, 32.18, 30.11, 29.91, 29.79, 29.72, 29.58, 29.42, 29.33, 26.78, 22.99, 14.43; GC-MS (CI) *m/z* (%) 210 (M$^+$ + H, 100), 209 (M$^+$, 8). Anal. Calcd for $C_{12}H_{23}N_3$: C, 68.85; H, 11.07; N, 20.07. Found: C, 68.91; H, 10.82; N, 20.27.

General Procedure for the Preparation of 4a–m: 1-Methyl-4-(3,3,3-trifluoropropyl)-1,2,4-triazolium Iodide (4a). (3,3,3-Trifluoropropyl)iodide (1.11 g, 4.518 mmol) and 1-methyl-1,2,4-triazole (0.38 g, 4.518 mmol) were put into a Pyrex glass tube that was evacuated, sealed, and heated at 85 °C for 20 h and then at 105 °C for 24 h. The orange residue was dissolved in dichloromethane and recrystallized (EtOAc–hexane) to a white solid: 1.38 g, 99% yield; mp 98 °C; $d_{\mathrm{calcd}} = 1.876$ g/cm^3; IR (KBr) 3112, 3039, 2996, 2882, 1584, 1537, 1536, 1393, 1286, 1254, 1150, 1075, 1027, 999, 956 cm^{-1}; ^{1}H NMR (500 MHz, acetone-d_6) 3.24 (m, $J = 7.43$ Hz, 2H), 4.26 (s, 3H), 4.95 (t, $J_{\mathrm{HH}} = 7.18$ Hz, 2H), 9.40 (s, 1H), 10.82 (s, 1H); ^{13}C NMR (125 MHz, acetone-d_6) δ 144.68, 142.92, 125.50 (q, $J_{\mathrm{C-F}} = 276$ Hz), 41.65, 39.05, 33.21 (q, $J = 29.47$ Hz); ^{19}F NMR (470 MHz, acetone-d_6) δ −65.62 (m, $J_{\mathrm{H-F}} = 10.35$ Hz, $J_{\mathrm{H-H-F}} = 2.35$ Hz, 3F); MS (solid probe) (EI) *m/z* (%) 181 (M$^+$ + 1, 7), 180 (M$^+$, 84), 42 (100). X-ray crystallographic data: crystal system, orthorhombic; space group, *Pccn*; unit cell dimensions, $a = 13.8289(9)$ Å, $b = 17.3603(11)$ Å, $c = 9.0587(6)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$; $Z = 8$; F(000) = 1168; crystal size = 0.39 × 0.05 × 0.04 mm^3; $R_1 = 0.0484$, w$R_2 = 0.0867$. Anal. Calcd for $C_6H_9F_3I_1N_3$: C, 23.47; H, 2.95; F, 18.56. Found: C, 23.44; H, 2.67; F, 18.79.

1-Decyl-4-(1*H*,1*H*,2*H*,2*H*-perfluorohexyl)-1,2,4-triazolium Iodide (4g): 1.18 g, 98% yield, pale yellow solid; mp 255 °C; IR (KBr) 3107, 3020, 2963, 2932, 2859, 1638, 1581, 1531, 1467, 1381, 1356, 1234, 1172, 1136, 1060, 1014, 998, 880 cm^{-1}; ^{1}H NMR (500 MHz, acetone-d_6) δ 0.86 (t, $J = 6.86$ Hz, 3H), 1.26–1.42 (m, $J = 6.10, 4.44$ Hz, 14H), 2.01 (m, 2H), 3.31 (m, $J = 8.05$ Hz, 2H), 4.58 (t, $J_{\mathrm{HH}} = 7.20$ Hz, 2H), 5.05 (t, $J_{\mathrm{HH}} = 7.41$ Hz, 2H), 9.45 (s, 1H), 11.01 (s, 1H); ^{13}C NMR (125 MHz, acetone-d_6) δ 144.88, 143.36, 120.00–106.00 (m), 52.63, 40.70 (t, $J = 5.96$ Hz), 31.74, 30.78 (t, $J_{\mathrm{C-C-F}} = 20.78$ Hz), 29.34, 29,25, 28.81, 28.42, 28.37, 25.87, 22.45, 13.47; ^{19}F NMR (470 MHz, acetone-d_6) δ −82.36 (tt, $J_{\mathrm{H-F}} = 9.88$ Hz, $J_{\mathrm{H-H-F}} = 4.70$ Hz, 3F), −114.80 (s, 2F), −125.28 (s, 2F), −127.07 (m, $J = 14.11, 4.59$ Hz, 2F); MS (solid probe) (EI) *m/z* (%) 456 (M$^+$, 100). Anal. Calcd for $C_{18}H_{27}F_9I_1N_3$: C, 37.06; H, 4.67; N, 7.20; F, 29.31. Found: C, 37.19; H, 4.45; N, 7.13; F, 29.65.

1-Methyl-4-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-1,2,4-triazolium Iodide (4h): 2.97 g, 98% yield, tan solid; mp 225 °C; IR (KBr) 3023, 2976, 1585, 1539, 1235, 1192, 1146, 1082, 960 cm^{-1}; ^{1}H NMR (500 MHz, acetone-d_6) δ 3.33 (sep, $^3J_{\mathrm{HF}} = 11.7$ Hz, 2H), 4.27 (s, 3H), 5.06 (t, $J_{\mathrm{HH}} = 7.32$ Hz, 2H), 9.47 (s, 1H), 10.86 (s, 1H); ^{13}C NMR (125 MHz, acetone-d_6) δ 145.1, 144.28, 118.4 (q, $J_{\mathrm{C-F}} = 325$ Hz), 52.6, 41.1 (t, $J = 11.94$ Hz), 39.4, 31.5, 31.3, 31.2; ^{19}F NMR (470 MHz, acetone-d_6) δ −82.15 (tt, $^3J_{\mathrm{FF}} = 9.88$ Hz, $^4J_{\mathrm{FF}} = 1.42$ Hz, 3F), −114.54 (p, $^3J_{\mathrm{H-F}} = 14.1$ Hz, 2F), −122.83 (s, 2F), −123.85 (p, $J_{\mathrm{H-F}} = 9.41$ Hz, 2F), −124.34 (d, $J_{\mathrm{H-F}} = 14.1$ Hz, 2F), −127.22 (m, $^3J_{\mathrm{FF}} = 9.41$ Hz, 2F); MS (solid probe) (EI) *m/z* (%) 430 (M$^+$, 100). Anal. Calcd for $C_{11}H_9F_{13}I_1N_3$: C, 23.72; H, 1.63; N, 7.54; F, 44.33. Found: C, 23.90; H, 1.81; N, 7.52; F, 44.75.

1-Butyl-4-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-1,2,4-triazolium Iodide (4i): 0.93 g, 98% yield, white solid; mp 279 °C; IR (KBr) 3120, 3017, 2965, 2879, 1727, 1578, 1530, 1507, 1462, 1384, 1364, 1356, 1317 1241, 11124, 1080, 997, 962 cm^{-1}; ^{1}H NMR (500 MHz, acetone-d_6) δ 0.95 (t, $J = 7.4$ Hz, 3H), 1.44 (hext, $J = 7.5$ Hz, 2H), 1.99 (m, $J = 7.5$ Hz, 2H), 3.34 (m, $J = 7.8$ Hz, 2H), 4.59 (t, $J_{\mathrm{HH}} = 7.20$ Hz, 2H), 5.06 (t, $J_{\mathrm{HH}} = 7.3$ Hz, 2H), 9.44 (s, 1H), 10.99 (s, 1H); ^{13}C NMR (125 MHz, acetone-d_6) δ 144.9, 143.4, 120.26 (m, $J_{\mathrm{C-F}} = 243$, 32.79, 8.3 Hz), 106.52, 52.36, 40.77 (t, $J = 5.4$ Hz), 30.87 (t, $J = 20.9$ Hz), 30.36, 30.34, 19.08, 12.82; ^{19}F NMR (470 MHz, acetone-d_6) δ −82.13 (tt, $J_{\mathrm{H-F}} = 9.9$ Hz, $J_{\mathrm{H-H-F}} = 2.82$ Hz, 3F), −114.53 (t, $J_{\mathrm{F-F}} = 14.0$ Hz, 2F), −122.81 (s, 2F), −123.84 (s, 2F), −124.35 (s, 2F), −127.20 (m, $^3J_{\mathrm{FF}} = 9.5$ Hz, 2F); MS (solid probe) (EI) *m/z* (%) 472 (M$^+$, 100). Anal. Calcd for $C_{14}H_{15}F_{13}I_1N_3$: C, 28.06; H, 2.52; N, 7.01; F, 41.22. Found: C, 28.05; H, 2.79; N, 7.07; F, 41.07.

1-Heptyl-4-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-1,2,4-triazolium Iodide (4j): 1.47 g, 98% yield, white solid; mp 276 °C; IR (KBr) 3122, 2932, 2860, 1578, 1507, 1462, 1356 1242, 1209, 1067, 1009 cm^{-1}; ^{1}H NMR (500 MHz, acetone-d_6) δ 0.84 (t, $J = 6.8$ Hz, 3H), 1.26 (m, $J = 2.4$ Hz, 8H), 1.99 (m, $J = 7.2$ Hz, 2H), 3.33 (t, $J = 7.20$ Hz, 2H), 4.60 (t, $J_{\mathrm{HH}} = 7.20$ Hz, 2H), 5.06 (t, $J_{\mathrm{HH}} = 7.3$ Hz, 2H), 9.47 (s, 1H), 11.01 (s, 1H); ^{13}C NMR (125 MHz, acetone-d_6) δ 144.9, 143.4, 116.5 (q, $J_{\mathrm{C-F}} = 320$ Hz), 52.62, 40.78 (t, $J = 11.93$ Hz), 31.44, 31.0, 30.87, 28.4, 28.5, 25.82, 22.31, 13.41; ^{19}F NMR (470 MHz, acetone-d_6) δ −82.13 (tt, $J_{\mathrm{H-F}} = 10.81$ Hz, $J_{\mathrm{H-H-F}} = 2.82$ Hz, 3F), −114.54 (p, $J_{\mathrm{H-F}} = 14.0$ Hz, 2F), −122.82 (s, 2F), −123.85 (s, 2F), −124.33 (s, 2F), −127.22 (m, $^3J_{\mathrm{FF}} = 9.4$ Hz, 2F); MS (solid probe) (EI) *m/z* (%) 514 (M$^+$, 100). Anal. Calcd for $C_{17}H_{21}F_{13}I_1N_3$: C, 31.84; H, 3.30; N, 6.55; F, 38.52. Found: C, 31.91; H, 3.26; N, 6.57; F, 38.67.

General Procedure for the Preparation of Ionic Liquids 5a–s. To a magnetically stirred solution of 1-alkyl-4-fluoroalkyl-1,2,4-triazolium halide (1.09 mmol) in water (5 mL) was added lithium bis(trifluoromethanesulfonyl)amide (LiNTf$_2$, 1.09 mmol). After 8 h at 40 °C, the lower ionic liquid layer

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(13) Hope, H. *Prog. Inorg. Chem.* **1995**, *41*, 1–3.

(14) *SMART*: *version 5.625, Bruker Molecular Analysis Research Tool*; Bruker AXS: Madison, WI, 2001.

(15) *SAINTPlus: version 6.22, Data Reduction and Correction Program*; Bruker AXS: Madison, WI, 2001.

(16) Sheldrick, G. M. *SADABS: version 2.01, An Empirical Absorption Correction Program*; Bruker AXS: Madison, WI, 2001.

(17) Sheldrick, G. M. *SHELXTL: version 6.10, Structure Determination Software Suite*; Bruker AXS, Madison, WI, 2001.

was separated and dissolved in dichloromethane (8 mL). The dichloromethane solution was washed with water (2 × 15 mL) and evaporated in vacuo. Benzene was added to the residue and the solution dried using a Dean−Stark apparatus. After removal of the benzene, the residue was dried in vacuo (0.3 mmHg) at 40 °C.

1-Butyl-4-(3,3,3-trifluoropropyl)-1,2,4-triazolium Bis(trifluoromethane sulfonyl)amide (5b): 0.97 g, 98% yield, pale yellow viscous oil; mp −67 °C; $d_{24\ °C} = 1.603$ g/cm^3; IR (KBr) 3141, 3087, 2969, 2881, 1578, 1532, 1466, 1351, 1258, 1196, 1136, 1056, 999, 959, 888, 791 cm^{-1}; ^{1}H NMR (500 MHz, acetone-d_6) δ 0.95 (t, $J = 7.40$ Hz, 3H), 1.41 (m, $J_{HH} = 7.45$ Hz, 2H), 1.98 (m, $J_{HH} = 6.68$ Hz, 2H), 3.17 (m, $J = 3.50$ Hz, 2H), 4.58 (t, $J = 7{,}10$ Hz, 2H), 4.89 (t, $J_{HH} = 6.76$ Hz, 2H), 9.23 (s, 1H), 10.15 (s, 1H); ^{13}C NMR (125 MHz, acetone-d_6) δ 145.01, 142.75, 124.21 (m), 52.48, 41.80, 33.40 (q, $J = 29{,}50$ Hz), 30.46, 18.99, 12.72; ^{19}F NMR (470 MHz, acetone-d_6) δ −66.37 (m, 3F), −80.41 (d, $J = 1.88$ Hz, 3F); MS (solid probe) (EI) m/z (%) 222 (M$^+$, 100). Anal. Calcd for $C_{11}H_{15}F_9N_4O_4S_2$: C, 26.30; H, 3.01; N, 11.15; F, 34.04. Found: C, 26.11; H, 3.06; N, 11.24.

1-Butyl-4-(1*H*,1*H*,2*H*,2*H*-perfluorohexyl)-1,2,4-triazolium Bis(trifluoromethanesulfonyl)amide (5e): 0.635 g, 98% yield, white wax; mp 69 °C; IR (KBr) 3146, 3090, 2970, 2882, 1580, 1533, 1468, 1349, 1227, 1197, 1137, 998, 882, 793 cm^{-1}; ^{1}H NMR (500 MHz, acetone-d_6) δ 0.95 (t, $J = 7.37$ Hz, 3H), 1.41 (hex, $J = 7.39$ Hz, 2H), 1.99 (m, $J = 7.53$ Hz, 2H), 3.22 (m, $J = 7.67$ Hz, 2H), 4.60 (t, $J_{H-H} = 6.16$ Hz, 2H), 5.02 (t, $J_{H-H} = 6.43$ Hz, 2H), 9.29 (s, 1H), 10.22 (s, 1H); ^{13}C NMR (125 MHz, acetone-d_6) δ 145.14, 142.88, 120.48 (m), 114.0−116.0 (m), 52.48, 40.73 (t, $J_{C-C-C-F} = 4.65$ Hz), 30.59 (t, $J_{C-C-F} = 20.62$ Hz), 30.48, 19.01, 12.73; ^{19}F NMR (470 MHz, acetone-d_6) δ −80.43 (q, $J = 4.71$ Hz, 3F), −82.39 (m, $J = 4.71$ Hz, 9.42 Hz, 3F), −115.03 (t, $J = 14.12$ Hz, 2F), −125.48 (m, $J_{FF} = 4.71$ Hz, 2F), −127.11 (t, $J = 14.11$ Hz); MS (solid probe) (EI) m/z (%) 372 (M$^+$, 100). Anal. Calcd for $C_{14}H_{15}F_{15}N_4O_4S_2$: C, 25.77; H, 2.32; N, 8.59; F, 43.68. Found: C, 25.70; H, 2.35; N, 8.56; F, 43.51.

1-Heptyl-4-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-1,2,4-triazolium Bis(trifluoromethanesulfonyl)amide (5j): 0.62 g, 98% yield, colorless wax; mp 22 °C; IR (KBr) 3147, 3092, 2933, 2864, 1580, 1468, 1350, 1237, 1193, 1144, 1059, 890, 849 cm^{-1}; ^{1}H NMR (500 MHz, acetone-d_6) δ 0.86 (t, $J = 7.06$ Hz, 3H), 1.28 (m, 4H), 1.38 (m, 4H), 1.99 (m, 2H), 3.22 (m, $J = 10.98$ Hz, 2H), 4.59 (p, $J = 5.7$ Hz, 2H), 4.99 (t, $J_{HH} = 2.78$ Hz, 2H), 9.27 (s, 1H), 10.20 (s, 1H); ^{13}C NMR (125 MHz, acetone-d_6) δ 145.12, 142.83, 125.87 (q, $J_{C-F} = 318$ Hz), 116.6 (q, $J_{C-F} = 285$ Hz), 52.72, 40.74 (t, $J_{C-C-C-F} = 4.92$ Hz), 30.68 (q, $J_{C-C-F} = 21.1$ Hz), 28.52, 28.41, 25.75, 22.27, 13.35; ^{19}F NMR (470 MHz, acetone-d_6) δ −80.44 (m, $J_{F-F} = 2.35$ Hz, 3F), −82.17 (m, $J = 8.0$ Hz, 3F), −122.86, −123.88, −124.57, −127.24; MS (solid probe) (EI) m/z (%) 514 (M$^+$, 100). Anal. Calcd for $C_{19}H_{21}F_{19}N_4O_4S_2$: C, 28.72; H, 2.66; N, 7.05; F, 45.43;. Found: C, 28.73; H, 2.96; N, 7.09; F, 45.68.

1-Heptyl-4-(1-fluoroethyl)-1,2,4-triazolium Bis(trifluoromethanesulfonyl)amide (5k): 0.53 g, 98% yield, pale yellow oil; mp −70 °C; $d_{24\ °C} = 1.393$ g/cm^3; IR (KBr) 3030, 2956, 2927, 2853, 1813, 1574, 1462, 1265, 1158, 1027 cm^{-1}; ^{1}H NMR (500 MHz, acetone-d_6) δ 0.87 (t, $J = 7.1$ Hz, 3H), 1.28 (m, $J = 1.5$ Hz, 4H), 1.30 (m, $J = 3.7$ Hz, 4H), 4.60 (t, $J = 7.2$ Hz, 2H), 4.89 (dt, $J_{H-H} = 3.88$ Hz, $J_{H-F} = 11.68$ Hz, 2H), 4.99 (dt, $J_{H-H} = 5.0$ Hz, $J_{H-F} = 31.1$ Hz, 2H), 9.15 (s, 1H), 10.09 (s, 1H); ^{13}C NMR (125 MHz, acetone-d_6) δ 145.4, 143.0, 120.5 (q, $J_{C-F} = 321$ Hz), 81.5 (d, $J_{C-F} = 168.8$ Hz), 53.0, 49.1 (d, $J_{C-C-F} = 19.5$ Hz), 31.8, 26.2, 22.7, 13.8; ^{19}F NMR (470 MHz, acetone-d_6) δ −80.4, −224.8 (tt, $J_{H-F} = 47.1$ Hz, $J_{H-F} = 28.2$ Hz, 1F); MS (solid probe) (EI) m/z (%) 214 (M$^+$, 100). Anal. Calcd for $C_{13}H_{21}F_7N_4O_4S_2$: C, 31.58; H, 4.28; N, 11.33; F, 26.90. Found: C, 31.51; H, 4.37; N, 11.24; F, 26.82.

1-Heptyl-4-(1-fluoroethyl)-1,2,4-triazolium Tetrafluoroborate (5n): 0.10 g, 18% yield, colorless wax; mp 52 °C; IR (KBr) 3147, 3101, 2957, 2929, 2859, 1670, 1582, 1534, 1467, 1446, 1387, 1253,1165, 1037, 857 cm^{-1}; ^{1}H NMR (500 MHz, acetone-d_6) δ 0.87 (t, $J = 7.14$ Hz, 3H), 1.29 (m, $J = 4.0$ Hz, 4H), 1.39 (m, $J = 3.7$ Hz, 4H), 4.55 (t, $J = 7.27$ Hz, 2H), 4.83 (dt, $J_{H-H} = 4.79$ Hz, $J_{H-F} = 27.4$ Hz, 2H), 4.93 (dt, $J_{H-H} = 3.98$ Hz, $J_{H-F} = 46.82$ Hz, 2H), 9.06 (s, 1H), 9.90 (s, 1H); ^{13}C NMR (125 MHz, acetone-d_6) δ 144.92, 142.75, 81.25 (d, $J_{C-F} = 167.88$ Hz), 52.51, 48.60 (d, $J_{C-C-F} = 19.49$ Hz), 31.43, 28.50, 28.47, 25.82, 25.81, 25.80, 22.32,13.40; ^{19}F NMR (470 MHz, acetone-d_6) δ −151.28 (dd, $J_{F-F} = 4.7$ Hz), −225.01 (tt, $J_{H-F} = 47.1$ Hz, $J_{H-F} = 28.2$ Hz, 1F); MS (solid probe) (EI) m/z (%) 214 (M$^+$, 100). Anal. Calcd for $C_{11}H_{21}B_1F_5N_3$: C, 43.88; H, 7.03; N, 13.96. Found: C, 43.93; H, 6.86; N, 13.63.

1-Heptyl-4-(1*H*,1*H*,2*H*,2*H*-perfluorohexyl)-1,2,4-triazolium Hexafluorophosphate (5p): 0.31 g, 94% yield, white solid; mp 298 °C; IR (KBr) 3160, 2960, 2931, 2861, 1972, 1718,-1579, 1534, 1470, 1361, 1136, 998, 883, 826, 747 cm^{-1}; ^{1}H NMR (500 MHz, acetone-d_6) δ 0.84 (t, $J = 6.91$ Hz, 3H), 1.27 (m, $J = 4.26$ Hz, 4H), 1.37 (m, 4H), 1.99 (m, 2H), 3.21 (m, 2H), 4.58 (t, $J_{H-H} = 7.06$ Hz, 2H), 4.97 (m, 2H), 9.27 (s, 1H), 10.19 (s, 1H); ^{13}C NMR (125 MHz, acetone-d_6) δ 145.07, 142.89, 114−122 (m), 106−112 (m), 52.71, 40.69 (t), 31.41, 30.54 (t, $J_{C-C-F} = 21.72$ Hz), 28.49, 28.44, 25.76, 22.28, 13.39; ^{19}F NMR (470 MHz, acetone-d_6) δ −72.29 to −73.79 (d, $J_{P-F} = 706$ Hz, 6F), −82.38 (tt, $J_{F-F} = 9.88$, 3.29 Hz, 3F), −115.01 (pent, $J = 18.82$ Hz, 2F), −125.45 (m, 2F), −127.10 (m, $J = 9.4$, 4.71 Hz, 2F); MS (solid probe) (EI) m/z (%) 414 (M$^+$, 88), 316 (M$^+$ − CF_3-CH_2CH_3,100). Anal. Calcd for $C_{15}H_{21}F_{15}N_3P_1$: C, 32.21; H, 3.78; N, 7.51. Found: C, 32.21; H, 3.71; N, 7.51.

1-Butyl-4-(3,3,3-trifluoropropyl)-1,2,4-triazolium Trifluoromethanesulfonate (5r): 0.66 g, 68% yield, yellow wax; mp 33 °C; IR (KBr) 3133, 3081, 2964, 2906, 2818, 1580, 1466, 1392, 1340, 1260, 1030, 1001, 796 cm^{-1}; ^{1}H NMR (500 MHz, acetone-d_6) δ 0.95 (t, $J = 7.40$ Hz, 3H), 1.41 (hex, $J = 7.38$ Hz, 2H), 1.99 (m, $J = 7.46$, 1.71 Hz, 2H), 3.19 (m. $J = 3.50$, Hz, 2H), 4.58 (t, $J_{H-H} = 7.15$ Hz, 2H), 4.88 (t, $J_{H-H} = 7.10$ Hz, 2H), 9.27 (s, 1H), 10.26 (s, 1H); ^{13}C NMR (125 MHz, acetone-d_6) δ 144.98, 143.05, 125.94 (q, $J_{C-F} = 276.04$ Hz), 120, 52.34, 41.72 (q, $J_{C-C-C-F} = 3.94$ Hz), 33.25 (q, $J_{C-C-F} = 29.42$ Hz), 30.45, 19.01, 12.77; ^{19}F NMR (470 MHz, acetone-d_6) δ −66.30 (t, $J_{H-F} = 10.35$ Hz, 3F), −79.53 (s, 3F); MS (solid probe) (EI) m/z (%) 222 (M$^+$, 100). Anal. Calcd for $C_{10}H_{15}F_6N_3O_3S_1$: C, 32.35; H, 4.07; N, 11.32. Found: C, 31.95; H, 4.14; N, 11.13.

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Supporting Information Available: Tables of data collection parameters, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates of **4a** and experimental data for compounds **3a**−**c**; **4b**−**f**,**k**−**m**; and **5a**,**c**−**d**,**f**−**i**,**l**,**m**,**o**,**q**,**s**. This material is available free of charge via the Internet at http://pubs.acs.org.

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