# Polyfluoroalkyl, Polyethylene Glycol, 1,4-Bismethylenebenzene, or 1,4-Bismethylene-2,3,5,6-Tetrafluorobenzene Bridged Functionalized Dicationic Ionic Liquids: Synthesis and Properties as High Temperature Lubricants

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A new class of geminal dicationic ionic liquids was formed with a bridging moiety, such as a polyalkyl ether, polyfluoroalkyl, 1,4-bismethylenebenzene, or 1,4-bismethylene-2,3,5,6-tetrafluorobenzene link, between alkyl-substituted imidazolium rings. Their properties were modified by varying the linker chains and/or alkyl substituents on the imidazolium ring. The polyfluoroalkyl bridged dicationic ionic liquids exhibit the highest densities and viscosities. Although melting points are directly proportional to the length of the alkyl substituent, the densities decrease concomitantly. With 1,4-bismethylene-2,3,5,6-tetrafluorobenzene as the linking chain and with longer alkyl substituents on the imidazolium rings, the nonpolar character of the ionic liquid greatly increases, e.g., the solubilities in toluene of dicationic ionic liquids **36** and **37**, where the ring substituents are $C_{10}H_{21}$ and $C_{14}H_{29}$, increase markedly. Some of the salts exhibit higher conductivities than an equimolar tetrabutylammonium iodide solution in acetonitrile/toluene. These new ionic liquids (except with $PF_6^-$ as anion) display outstanding tribological properties in temperature ramp tests by performing very well at 300 °C, thus meeting one criterion for high-temperature lubricants.

## Introduction

Ionic liquids are low-melting salts that are stable, recyclable, and readily manipulated to allow a myriad of applications, such as (1) replacing organic solvents in chemical processes and reactions, (2) extracting organic compounds from aqueous waste streams, (3) electrolytes for various electrochemical devices, and (4) active pharmaceutical ingredients.[1,2] It is interesting and worthwhile to develop new ionic liquids that may have these or other advantageous applications.[3] Some ionic liquids currently receiving attention are highly stable geminal dicationic ionic liquids.[3b,c,4] The thermal stabilities of the geminal dicationic ionic liquids with a liquid/stability range of over 300 °C are greater than those of most traditional monocationic ionic liquids. The number of combinations of anions and geminal dications that can be used to produce ionic liquids for use as solvents for high-

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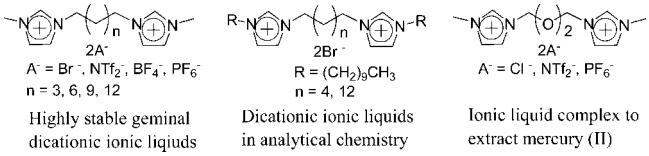
**Scheme 1. Structure of Some Known Dicationic Ionic Liquids**




temperature organic reactions,[5] additives in chromatography,[6] selectively complexing and extracting mercury(II),[7] and electrolytes[8] is huge. Some of them are shown in Scheme 1.

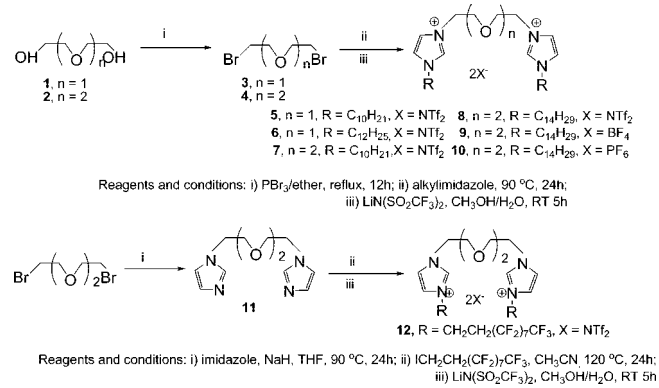
Current high-temperature aircraft lubricants can operate only up to a temperature of 150 °C. New aerospace technologies demand lubricants that can function between −40 and 330 °C. Preliminary studies have shown potential for ionic liquids as a new generation of synthetic lubricants.[3b,9] It was found that the tribological properties of ionic liquids are superior to those of conventional lubricants, such as synthetic hydrocarbons, synthetic esters, and synthetic fluorinated ethers.[10] There is interest in the development of some polyfluoroalkyl-containing ionic liquids based on imidazolium, triazolium, tetrazolium, and morpholinium cations in order to study their applications in catalytic organic synthesis,[11] as energetic materials,[12] and as lubricants.[13] Polyethylene glycol functionalized dicationic ionic liquids have been found to display outstanding thermal properties and potential for use in the next generation of high temperature lubricants.[3b,14] At low (−30 °C) and high (200 °C) temperatures, the octylimidazolium tetrafluoroborate that exhibits a lower polarity is a more effective lubricant than the hexyl-substituted moiety because of the absence of tribocorrosion processes.[15] Modification of the imidazolium-based cations with different length alkyl groups and variation of the linker chain from alkyl to polyfluoroalkyl and aryl to polyfluoroaryl markedly influences the properties of these ionic liquids. In this work, we report a series of imidazolium-based dicationic ionic liquids bridged with either a polyether, polyfluoroalkyl, 1,4-bismethylenebenzene, or 1,4-bismethylene-2,3,5,6-tetrafluorobenzene chain with different alkyl substituents on the imidazolium ring.

## Results and Discussion

Polyethylene-glycol-functionalized dicationic ionic liquids with C10−C14 alkyl or $C_8F_{17}C_2H_4$ substituents were synthesized following an earlier method as shown in Scheme 2.[3b]

When 1-iodo-1H,1H,2H,2H-perfluorodecane was employed as an electrophile with 1,8-diimidazolium-3,6-dioxaoctane (**11**), a higher reaction temperature (120 °C) and longer reaction time (24 h) were required to drive the reaction to completion. The quaternary bisimidazolium iodide was then metathesized with $LiN(SO_2CF_3)_2$ ($LiNTf_2$) in methanol/water (10:1), giving the polyfluorodecyl substituted dicationic ionic liquid **12** (51.3% fluorine) in good yield. We anticipate that use of this simple synthetic pathway will allow preparation of ionic liquids with higher fluorine content ($F > 60\%$) to substitute for the expensive, lower boiling point perfluorocarbon compounds, e. g., perfluoro(methylcyclohexane) (bp 76 °C) and perfluorodecalin (bp 142 °C) in fluorine-containing biphasic system.

**Scheme 2. Synthesis of Polyethylene-Glycol-Functionalized Dicationic Ionic Liquids with C10−C14 alkyl or $C_8F_{17}C_2H_4$ Substituents**




Fluorinated ionic liquids are hydrophobic with low hygroscopicity and can be used as surfactants[16] and lubricants.[17] Syntheses of polyfluoroalkyl bridged imidazolium-based dicationic ionic liquids by using polyfluoroalkyl iodide and alkyl imidazole were not successful, because fluorine was easily eliminated in the course of the attempted quaternization reaction. Therefore, trifluoromethanesulfonate esters, **16**–**18**, were used as precursors. The combination of polyfluoroalkyldiol (**13**–**15**) and trifluoromethanesulfonic anhydride in methylene chloride with pyridine as a base at room temperature for 24 h gave **16**–**18** (Scheme 3). The latter were further treated with alkyl imidazole (2.3 equiv) using acetonitrile as solvent at 110 °C for 12 h to give the polyfluoroalkyl-linked dicationic trifluoromethanesulfonate (OTf) salts (**19**–**22**). Metathesis reactions between compounds **19**–**22** and $LiN(SO_2CF_3)_2$ ($LiNTf_2$) in methanol/water produced the polyfluoroalkyl-bridged geminal dicationic ionic liquids **23**–**26**, the first polyfluoroalkyl bridged diimidazolium ionic liquids.

Ionic liquids with a benzene linker display good hydrophobic properties and can be used as effective conductive additives to form ionic conductive polymers.[18] The geminal dicationic liquids with 1,4-bismethylenebenzene and 1,4-bismethylene- 2,3,4,5-tetrafluobenzene linkage chains, **31**–**37**, are shown in Scheme 4.

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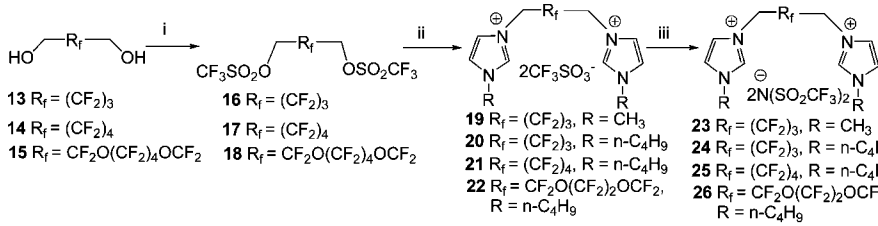
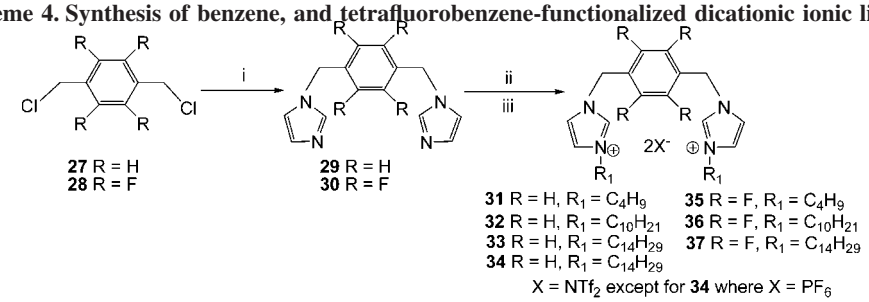
**Scheme 3. Synthesis of Polyfluoroalkyl-Functionalized Dicationic Ionic Liquids**




Reagents and conditions: i) $(CF_3SO_2)_2O$, $CH_2Cl_2$/pyridine, R. T., 24h; ii) alkylimidazole, $CH_3CN$, 110 °C, 12h; iii) $LiN(SO_2CF_3)_2$, $CH_3OH/H_2O$, R. T., 2h

**Scheme 4. Synthesis of benzene, and tetrafluorobenzene-functionalized dicationic ionic liquids**




Reagents and conditions: i) imidazole, $CH_3OH/K_2CO_3$, reflux. 18h; ii) RBr or RI, $CH_3CN$, 100 °C, 12h; iii) $LiN(SO_2CF_3)_2$ or $KPF_6$, $CH_3OH/H_2O$, R. T., 5h

1,4-Bis(imidazol-1-yl-methyl)benzene, **29**,[19] and 1,4-bis-(imidazol-1-yl-methyl)-2,3,5,6-tetrafluorobenzene, **30,**[20] were conveniently obtained by treating imidazole and 1,4-bis-(chloromethyl)benzene, **27**, and 1,4-bis(chloromethyl)tetrafluorobenzene, **28,** in methanol at reflux for 18 h. Quaternization of **29** and of **30** with alkyl bromide or iodide in acetonitrile as solvent at 100 °C for 12 h gave bromide or iodide, which when further reacted with a slight molar excess of $LiN(SO_2CF_3)_2$ ($LiNTf_2$), or $KPF_6$ resulted in ionic liquids, **31–37**.

Ionic liquids **5**–**10**, **12**, **20**, **23**–**26**, **31**–**37** and salts **19**, **21**–**22**, were characterized by their $^1H$, $^{13}C$, and $^{19}F$ NMR spectra, and elemental analysis. In Table 1 are found the properties for the 18 geminal dicationic ionic liquids and four dicationic salts prepared in this study. Solubility, density, thermal stability, and viscosity properties were measured for these materials.

**Solubility.** The solubilities of these dicationic ionic liquids were determined at room temperature. In general, they are immiscible with hexane, and diethyl ether and miscible with methanol, ethyl acetate and DMSO. The length of the alkyl chain substituent and the nature of the linking bridge exhibit a strong influence on solubility, particularly, e. g., the dicationic ionic liquids, $[C_{10}H_{21}(PhF_4)IM][NTf_2]_2$, **36**, and $[C_{14}H_{29}(PhF_4)IM][NTf_2]_2$, **37**, with 1,4-bismethylene-2,3,5,6-tetrafluobenzene links and with an alkyl, n-$C_{10}H_{21}$ or n-$C_{14}H_{29}$, substituent can dissolve in toluene at room temperature. In the case of **37**, the solubility is ~0.2 g/cm$^3$ in toluene at room temperature. However, when the substituent is n-butyl as in **35** or n-$C_{14}H_{29}$ in **33** and where the bridge is non-fluorine-containing, neither salt will dissolve in toluene. It can be seen that with the longer alkyl substituent on the ring and a fluorinated benzene linkage chain, the nonpolar character of the dicationic ionic liquids increases markedly, and the solubilities of dicationic ionic liquids, **36** and **37**, in toluene increase as well. The exceptional solubility characteristics of **37** may allow study of the electrochemical and synthetic applications of dicationic ionic liquids in low dielectric constant organic solvents.

**Table 1. Properties of Geminal Dicationic Ionic Liquids Bridged with Polyethylene Ether, Polyfluoroalkyl, 1,4-Bismethylenebenzene, Or 1,4-Bismethylene- 2,3,4,5-Tetrafluorobenzene**

| compd[a] | $T_g$ (°C)[b] | $T_d$ (°C)[c] | density[d] | viscosity[e] | $K$[f] |
|---|---|---|---|---|---|
| **5** $[C_{10}H_{21}O_1IM]$ | 10.2 | 415.8 | 1.31 | | |
| **6** $[C_{12}H_{25}O_1IM]$ | 30.7 | 417.1 | 1.37 | | |
| **7** $[C_{10}H_{21}O_2IM]$ | −49.5 | 408.7 | 1.30 | | |
| **8** $[C_{14}H_{29}O_2IM]$ | 3.1 | 438.8 | 1.28 | 40.8 | 2.06 |
| **9** $[C_{14}H_{29}O_2IM][BF_4]_2$ | 32.9 | 360.0 | 1.13 | | |
| **10** $[C_{14}H_{29}O_2IM][PF_6]_2$ | 73.4 | 349.9 | 1.23 | | |
| **12** $[C_{10}F_{17}O_2IM]$ | 8.6 | 386.9 | 1.76 | 172.0 | |
| **19** $[CH_3(CF_2)_3IM]$ | 173.10 | 365.43 | 1.73 | | |
| **20** $[C_4H_9(CF_2)_3IM]$ | 72.80 | 345.09 | 1.48 | | |
| **21** $[C_4H_9(CF_2)_4IM]$ | 148.01 | 346.03 | 1.51 | | |
| **22** $[C_4H_9(CF_2)_4O_2IM]$ | 100.28 | 352.34 | 1.63 | | |
| **23** $[CH_3(CF_2)_3IM]$ | 59.9 | 384.6 | 1.77 | | |
| **24** $[C_4H_9(CF_2)_3IM]$ | 49.2 | 376.4 | 1.63 | 151.8 | |
| **25** $[C_4H_9(CF_2)_4IM]$ | 74.4 | 375.1 | 1.64 | 226.6 | |
| **26** $[C_4H_9(CF_2)_4O_2IM]$ | 68.2 | 354.3 | 1.67 | | |
| **31** $[C_4H_9(Ph)IM]$ | 49.3 | 374.0 | 1.53 | | |
| **32** $[C_{10}H_{21}(Ph)IM]$ | 68.4 | 386.8 | 1.36 | | |
| **33** $[C_{14}H_{29}(Ph)IM]$ | 83.0 | 381.5 | 1.31 | 106.5 | 1.90 |
| **34** $[C_{14}H_{29}$ $(Ph)IM][PF_6]_2$ | 110.7 | 304.8 | 1.24 | | |
| **35** $[C_4H_9$ $(PhF_4)IM]$ | 72.0 | 399.1 | 1.69 | 123.8 | |
| **36** $[C_{10}H_{21}(PhF_4)IM]$ | 78.2 | 374.7 | 1.45 | | 2.85 |
| **37** $[C_{14}H_{29}(PhF_4)IM]$ | 88.7 | 376.8 | 1.43 | 213.4 | 1.98 |

[a] $(NTf_2)_2$ are the anions except for **9** $(BF_4^-)_2$, and **10** and **34** $(PF_6^-)_2$, $C_4H_9$, n-butyl; $C_{10}H_{21}$, n-decyl; $C_{12}H_{25}$, n-dodecyl; $C_{14}H_{29}$, n-tetradecyl; $O_1$, $O_2$, mono or diether linkage chain; $(CF_2)_3$, 2,2,3,3,4,4-hexafluoro-1,5-pentamethylene chain; $(CF_2)_4$, 2,2,3,3,4,4,5,5-octafluoro-1,6-hexamethylene chain; $(CF_2)_4O_2$, 1H, 1H, 8H, 8H-octafluoro-3,6-dioxaoctamethylene chain; Ph, 1,4-bismethylenebenzene; $PhF_4$, 1,4-bismethylene-2,3,5,6-tetrafluorobenzene; IM, imidazole. [b] Glass-transition temperature or melting point. [c] Decomposition temperature. [d] In g cm$^{-3}$ at 25 °C. [e] Determined by drop-ball method at 85 °C ($\eta$/cP). [f] Conductivity at 25 °C, for tetrabutylammonium iodide solution (0.375 mM, toluene-acetonitrile (3:1)) conductivity = 1.73 $\mu$S cm$^{-1}$.

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**Density.** As shown in Table 1, the dicationic ionic salts have densities falling in the range from 1.13 to 1.77 g $cm^{-3}$. While the density decreases with increasing length of the alkyl substituent, the nature of the anion perhaps has a greater influence, with densities decreasing in the order of $NTf_2^-$ > $PF_6^-$ > $BF_4^-$. The dicationic ionic liquids with fluorine-containing linkers have higher densities than their polyether or 1,3-bismethylenebenzene analogues.

**Melting Points.** Melting points of the dicationic ionic liquids were determined by differential scanning calorimetry (DSC). All these dicatonic salts are liquids at <100 °C except for the salts **19**–**22**, **34**. Four factors which affect the melting points include: (1) the nature of the linkage chain; (2) the length of the linkage chain separating the cations; (3) the substituent group on the cation; and (4) the nature of the anion. The melting points of the dicationic ionic liquids with a polyfluoroalkyl linkage chain are higher than those with 1,4-bismethylenebenzene or 1,4-bismethylene-2,3,5,6-tetrafluorobenzene linkers with the same cation, e.g., $[C_4H_9(CF_2)_4IM][NTf_2]_2$, **25**, melts at 74.4 °C which is higher than $[C_4H_9(Ph)IM][NTf_2]_2$, **31**, (mp 49.3 °C), and $[C_4H_9(PhF_4)IM][NTf_2]_2$, **35**, (mp 72.0 °C). Longer polyfluoroalkyl linkers (higher molecular weight) result in an increase in the melting point, e.g., $[C_4H_9(CF_2)_4IM][NTf_2]_2$, **25**, at 74.4 °C; $[C_4H_9(CF_2)_3IM][NTf_2]_2$, **24**, at 49.2 °C. Melting points increase with increase in alkyl substituent length for liquids with a common linker and anion, e.g., when the alkyl substituent is n-$C_{14}H_{29}$, the liquids have the highest melting point in comparison with the shorter alkyl substituted compounds, for example, $[C_4H_9(Ph)IM][NTf_2]_2$, **31**, at 49.3 °C; $[C_{10}H_{21}(Ph)IM][NTf_2]_2$, **32**, at 68.4 °C; $[C_{14}H_{29}(Ph)IM][NTf_2]_2$, **33**, at 83.0 °C. The anion also plays a crucial role in determining the melting point. In nearly every case, the salts with $NTf_2^-$ anion have melting points lower than those of corresponding salts with $BF_4^-$ or $PF_6^-$ anion. This arises from the fact that the negative charge associated with the $NTf_2^-$ anion is dispersed over the entire structure and therefore does not interact as strongly with the cation.

**Thermal Stability.** Thermal stabilities, which range from 300 to 430 °C and depend on the anion and the linking chain, were determined by thermal gravimetric analysis (TGA). In general, the new salts with $BF_4^-$ or $PF_6^-$ as anion are thermally less stable, e.g., comparing with the analogous $NTf_2$ anion salts, e.g., $[C_{14}H_{29}O_2IM][BF_4]_2$, **9**, and $[C_{14}H_{29}O_2IM][PF_6]_2$, **10**, at $T_d$ 360.0 °C and $T_d$ 349.9 °C, whereas $[C_{14}H_{29}O_2IM][NTf_2]_2$, **8**, has $T_d$ 438.8 °C. The bridge also influences the thermal stability, for example, changing the linker from 1,4-dimethylene-2,3,5,6-tetrafluorobenzene to 1,4-dimethylenebenzene to polyether, gives rise to a increase in thermal stability, e.g., $[C_{14}H_{29}(PhF_4)IM][NTf_2]_2$, **37**, $[C_{14}H_{29}(Ph)IM][NTf_2]_2$, **33**, and $[C_{14}H_{29}O_2IM][NTf_2]_2$, **8**, with $T_d$ at 376.8, 381.5, and 438.8 °C, respectively.

**Viscosity.** Viscosity is a very important physical property for dicationic ionic liquids used as the potential lubricant. The viscosities of seven dicationic ionic liquids were measured at 85 °C and are shown in Table 1. The bridging polyfluoroalkyl chains have an uneven influence on the viscosities of the salts. The ionic liquids with the polyfluoroalkyl linkage chain have higher viscosities than those with polyethers, 1,4-bismethylenebenzene, or 1,4-bismethylene-2,3,5,6-tetrafluorobenzene. The introduction of a polyfluoroalkyl group increases the van der Waals interactions that contribute to the viscosity of the ionic liquids. The more viscous ionic liquids are preferable for some applications, such as a stationary phase for gas–liquid chromatography. Longer chain alkyl substituents result in higher viscosities because of stronger van der Waals interactions, e. g., changing from the n-butyl substituent to n-tetradecane, the viscosity increases by nearly 90 cP, e.g., $[C_4H_9(PhF_4)IM][NTf_2]_2$, **35**, $\eta$ = 123.8 cP, $[C_{14}H_{29}(PhF_4)IM][NTf_2]_2$, **37**, $\eta$ = 213.4 cP.

**Conductivity.** Ionic liquids have good chemical and electrochemical properties that can be applied for example in lithium ion batteries,[21] or fuel cells as nonaqueous electrolytes.[22] The conductivities of four new ionic liquids were determined in 0.375 mM toluene−acetonitrile (toluene: acetonitrile = 3:1) solutions. When compared with tetrabutylammonium iodide, $[(n\text{-buty})_4NH_4]I$ solutions of the same concentration (0.375 mM) in toluene-acetonitrile (toluene: acetonitrile = 3:1), the salts exhibited higher conductivities, e.g., $[C_{14}H_{29}O_2IM][NTf_2]_2$, **8**, 2.06 $\mu$S $cm^{-1}$, $[C_{14}H_{29}(Ph)IM][NTf_2]_2$, **33**, 1.90 $\mu$S $cm^{-1}$, $[C_{10}H_{21}(PhF_4)IM][NTf_2]_2$, **36**, 2.85 $\mu$S $cm^{-1}$, $[C_{14}H_{29}(PhF_4)IM][NTf_2]_2$, **37**, 1.98 $\mu$S $cm^{-1}$, $[(n\text{-buty})_4NH_4]I$, 1.73 $\mu$S $cm^{-1}$. This is not surprising, since these dicationic ionic liquids have two carrier ions that would be expected to contribute more favorably to a higher conductivity. The salt, $[C_{10}H_{21}(PhF_4)IM][NTf_2]_2$, **36**, for instance, is more conducting than the corresponding $[C_{14}H_{29}(PhF_4)IM][NTf_2]_2$, **37**, with the same linker and it has the shorter n-$C_{10}H_{21}$ alkyl substituent. The shorter alkyl substituent causes the salt, $[C_{10}H_{21}(PhF_4)IM][NTf_2]$, **36**, to have a the smaller cation size than $[C_{14}H_{29}(PhF_4)IM][NTf_2]$, **37**, and therefore, increases the conductivity.

**Tribological Characteristics.** Six thermally stable ionic liquids (**8**, **10**, **12**, **33**, **35**, **37**) were used as candidates for a temperature ramp test, where pure ionic liquids were put onto the surface of a steel vs steel contact (M50 steel) and the temperature increased every 5000 cycles. The data from ionic liquids $[C_{14}H_{29}O_2IM][NTf_2]_2$, **8**, $[C_{14}H_{29}(Ph)IM][NTf_2]_2$ **33**, $[C_4H_9(PhF_4)IM][NTf_2]_2$, **35**, and $[C_{14}H_{29}(PhF_4)IM][NTf_2]_2$, **37** are very similar with low friction values and with slight instability at 100−300 °C (Figure 1a−c). At 400 °C, signs of fluid breakdown start occurring and failure occurs within a few thousand cycles in each case. The results show the dicationic ionic liquids bridged with polyethylene ether, **8**, 1,4-bismethylenebenzene, **33**, and 1,4-bismethylene-2,3,5,6-tetrafluorobenzene, **37**, with an n-$C_{14}H_{29}$ substituent have similar high temperature lubricant properties. The polyfluorodecyl-substituted dicationic ionic liquid $[C_{10}F_{17}O_2IM]$, **12** (51% fluorine), showed stability and consistent low friction up to a temperature of 300 °C (Figure 1b). When the temperature was raised to 400 °C, the friction trace shows instability and eventually failure. This results from the existence of higher fluorine content (**12** (51% fluorine) vs **8** (18.9% fluorine)), which favorably boosts the high-temperature lubricant property. Ionic liquid $[C_{14}H_{29}O_2IM][PF_6]_2$ **10**

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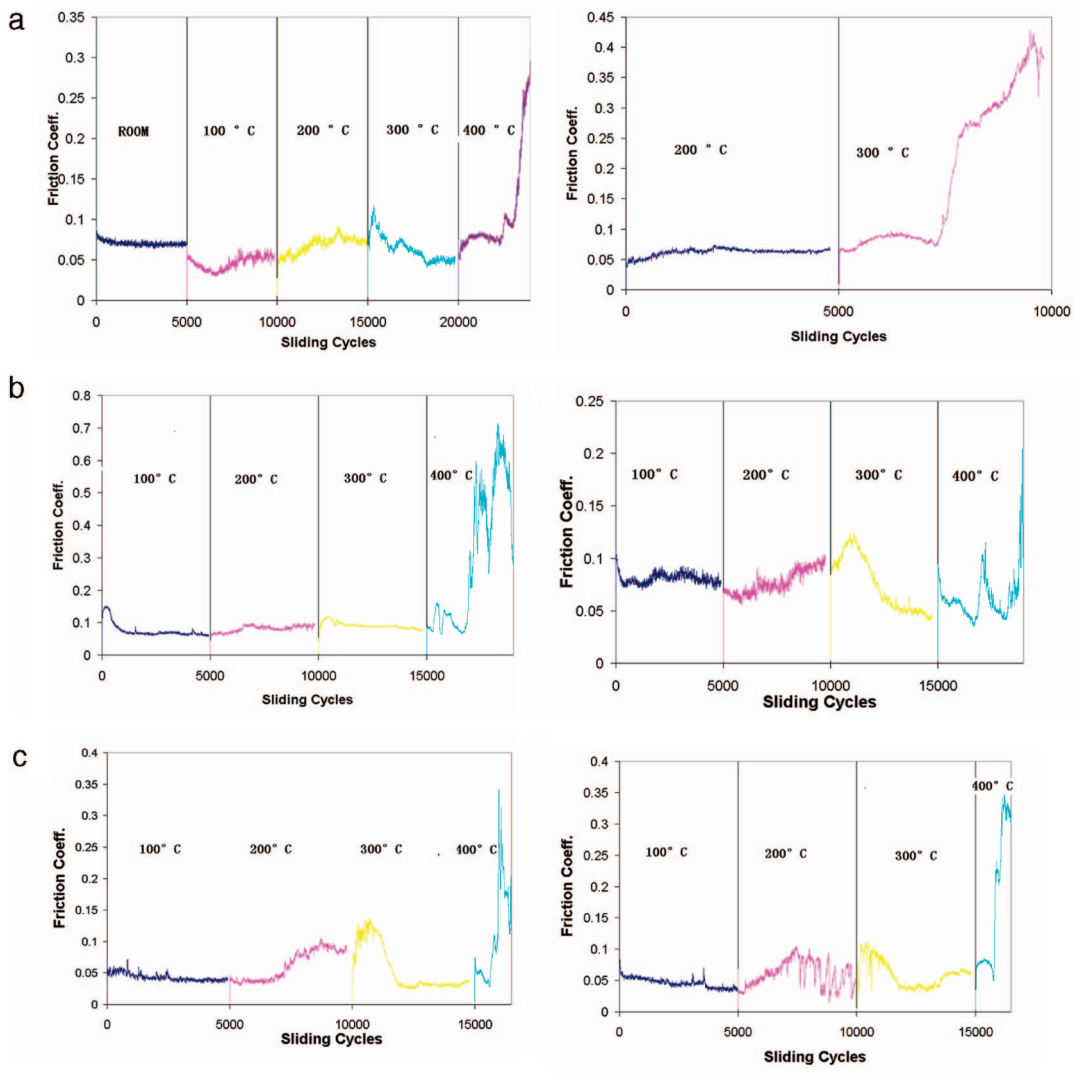


**Figure 1.** (a) Temperature-ramp friction testing results for polyalkyl ether bridged ionic liquids $[C_{14}H_{29}O_2IM][NTf_2]_2$ **8**, (left) and $[C_{14}H_{29}O_2IM][PF_6]_2$ **10** (right). (b) Temperature-ramp friction testing results for high fluorine content ionic liquids $[C_{10}F_{17}O_2IM]$ $[NTf_2]_2$ **12** (51.3% fluorine) (left) and 1,4-bismethylene-2,3,5,6- tetrafluorobenzene bridged ionic liquid $[C_4H_9$ $(PhF_4)IM][NTf_2]_2$ **35** (right). (c) Temperature-ramp friction testing results for 1,3-bismethylenebenzene bridged ionic liquid $[C_{14}H_{29}$ $(Ph)IM][NTf_2]_2$ **33** (left) and 1,4-bismethylene-2,3,5,6-tetrafluorobenzene bridged ionic liquid $[C_{14}H_{29}$ $(PhF_4)IM][NTf_2]_2$ **37** (right).

with $PF_6^-$ as anion was the only ionic liquid tested that failed prior to 400 °C. Ionic liquids **8**, **12**, **33**, **35**, and **37** compared favorably with previous results[3b] where polyethylene-glycol-functionalized dicationic ionic liquids tested failed immediately at 400 °C. The friction for ionic liquids at low temperatures (room, 100 °C) is very consistent, and an increase to 100 °C causes a slight reduction due to a decrease in viscosity. At 200 °C, the continuing decrease in viscosity will cause increasing asperity contact and possibly the first signs of the reaction that leads to increased friction. At >300 °C, the surface reaction between the steel and the ionic liquid causes the friction to increase dramatically. These results indicate that during operation at elevated temperatures, ionic liquids can form thin, durable, and stable surface boundary layers that maintain low friction and wear (Figure 1).

To put these results in perspective, it is enlightening to compare our data with those obtained for perfluoropolyalkylether (PFPAE) fluids.[23] It can be seen that our ionic liquid systems compete reasonably well with these type of fluids at least in the presence of steel. However, the PFPAE fluids tend to be more stable thermally approaching 500 °C.

## Conclusion

A new class of dicationic ionic liquids was synthesized that employ polyfluoroalkyl, polyether, 1,4-bismethenebenzene, and 1,4-bismethene-2,3,5,6-tetrafluorobenzene as linkage chains between imidazolium cations with traditional anions, i.e., $NTf_2^-$, $BF_4^-$, $PF_6^-$. Their melting points, decomposition temperatures, solubilities in common solvents, densities, viscosities, and conductivities were measured. The properties of these ionic liquids can be adjusted by using different linkers. When polyfluoroalkyl linkage chains are used to bridge the rings, the melting points, densities, and viscosities increase. Melting points increase with the increase of the alkyl substituent length for these liquids containing a common linker and anion, whereas the densities decrease concomitantly. Using longer alkyl n-$C_{10}H_{21}$ or n-$C_{14}H_{29}$ substituent and fluorinated benzene as the linker greatly

increases the nonpolar character of the dicationic ionic liquids, and the solubility of dicationic ionic liquids **36** and **37** in toluene increases markedly. Some exhibit higher conductivities than an equimolar tetrabutylammonium iodide solution in acetonitrile/toluene. These new ionic liquids display very good high- temperature tribological characteristics at 300 °C, meeting one of the criteria for high-temperature lubricants.

## Experimental Section

**General Considerations.** All the reagents used were analytical reagents purchased from commercial sources and used as received. The following materials were prepared and purified according to the reported procedures: polyether dibromide,[24] 1-decyl-imidazole,[25] 1-dodecyl-imidazole,[25] 1-tetradecyl-imidazole,[25] 1,8-diimidazolium-3,6-dioxaoctane,[26] 1,4-bis(imidazol-1-yl-methyl)benzene,[19] 2,3,5,6-tetrafluoro-1,4-bis(2-methylimidazol-1-yl-methyl)benzene.[20] $^1$H, $^{19}$F, and $^{13}$C NMR spectra were recorded on a 300 MHz nuclear magnetic resonance spectrometer operating at 300.13, 282 and 75.48 MHz, respectively. Chemical shifts were reported relative to $Me_4Si$ for $^1$H and $^{13}$C, and $CCl_3F$ for $^{19}$F. The solvent was either $CDCl_3$ or $CD_3CN$ unless otherwise specified. The melting and decomposition points were recorded on a differential scanning calorimeter and a thermogravimetric analyzer at a scan rate of 10 °C/min, respectively. Conductivity was determined on a model 1056 EC METER. Density was measured at room temperature using a Micromeritics Accupyc 1330 gas pycnometer. Viscosity was obtained by a drop-ball method (Minivis II). Elemental analyses were performed on an EXETER CE-440 elemental analyzer.

**General Procedure for the Preparation of Polyether Linkage Chain Dicationic Ionic Liquids 5–10.** The synthesis is a slightly modified version of a previous procedure.[2b] 1-Decyl-imidazole (2 mmol), 1-dodecyl-imidazole (2 mmol), 1-tetradecyl-imidazole (2 mmol), or polyethylene glycol dibromide (3–4, 1 mmol) were placed in a Pyrex glass tube, sealed, heated at 90 °C for 24 h, and then cooled to room temperature to give the quaternization product. The latter product was dissolved in methanol (30 mL); an aqueous solution (5 mL) of lithium bis(trifluoromethanesulfonyl)amide (2.3 mmol) was then added and stirred at room temperature for 5 h. The solvent was removed via rotavap and extracted with ethyl acetate (3 × 20 mL), and then washed with water (3 × 10 mL) and dried over anhydrous magnesium sulfate. The solvent was removed under vacuum at 90 °C for 6 h to give the $NTf_2^-$ salts **5–8**.

To prepare $BF_4^-$ or $PF_6^-$ salts, we dissolved the quaternized subtrate (1 mmol) in methanol and water (10:1, 40 mL), added sodium tetrafluoroborate or potassium hexafluoroborate (2.3 mmol), and stirred the solution at room temperature. After 5 h, methanol was removed at reduced pressure and the insoluble product was separated by filtration from water. The product was washed with water (3 × 10 mL), recrystallized with methanol−diethyl ether (1:15), and then dried under a vacuum at 90 °C for 6 h to give the $BF_4^-$ or $PF_6^-$ salt, **9** or **10**.

**Synthesis of Dicationic Ionic Liquid 12.** 1,8-Diimidazolium-3,6-dioxaoctane 11 (1 mmol), 1-iodo-1H, 1H, 2H, 2H-perfluorodecane (2.4 mmol) and 10 mL acetonitrile were sealed in a Pyrex glass tube in vacuo by cooling to liquid nitrogen temperature and then heated at 120 °C for 24 h. After cooling, 30 mL of methanol was added and the reaction mixture was dried in a vacuum. The residue was washed with ethyl ether (3 × 10 mL) to remove the excess perfluoroalkyl iodide and then recrystallized using $CH_3OH$/$Et_2O$ (15:1 v/v) to give the perfluoroalkyl quaternization product. This iodo salt (0.5 mmol) was dissolved in methanol (20 mL); an aqueous solution (5 mL) of lithium bis(trifluoromethanesulfonyl)-amide (2.3 mmol) was added and stirred at room temperature for 5 h. The organic solvent was removed and extracted with ethyl acetate (3 × 20 mL); it was then washed with water (3 × 10 mL) and dried over anhydrous magnesium sulfate. The solvent was removed under a vacuum at 90 °C for 6 h to give product **12**.

**General Procedure for the Preparation of Polyfluoroalkyl Linked Dicationic Ionic Liquids 23–26.** 2,2,3,3,4,4-Hexafluoro-1,5-pentanediol, **13** (1 mmol), 2,2,3,3,4,4,5,5-octafluoro-1,6-hexanediol, **14** (1 mmol), or 1H,1H,8H,8H-octafluoro-3,6-dioxaoctane-1,8-diol, **15** (1 mmol), pyridine (2.3 mmol), and dichloromethylene (20 mL) were stirred at room temperature under a nitrogen atmosphere. After 20 min, trifluoromethanesulfonic anhydride (2.5 mmol) was slowly added (over 1 h) by using an addition funnel. The mixture was stirred for 24 h, washed with water (3 × 10 mL) and then 10% sodium bicarbonate (2 × 10 mL), and dried over anhydrous sodium sulfate. The solvent was removed under a vacuum to give trifluoromethansulfonate ester, **16–18**.

The trifluoromethansulfonate ester, **16–18** (1 mmol), 1-methyl-imidazole (2.4 mmol), or 1-butyl-imidazole (2.4 mmol) and 10 mL of acetonitrile were placed in a Pyrex glass tube. The tube was sealed and heated at 110 °C for 12 h. After being cooled, the solvent was removed and the residue was washed with ethyl ether (3 × 10 mL) to remove any excess alkyl imidazole. To the residue was added 20 mL of methanol; it was then filtered, and the filtrate was dried under a vacuum at 80 °C for 5 h to give alkyl imidazolium trifluoromethanesulfonate product, **19–22**.

This salt, **19–22** (0.5 mmol), was dissolved in methanol (20 mL). An aqueous solution (5 mL) of lithium bis(trifluoromethanesulfonyl)amide (2.3 mmol) was added and stirred at room temperature for 5 h. The organic solvent was removed and extracted with ethyl acetate (3 × 20 mL); it was then washed with water (3 × 10 mL) and dried over anhydrous sodium sulfate. The solvent was removed under a vacuum at 90 °C for 6 h to give polyfluoroalkyl linked dicationic ionic liquids, **23–26**.

**General Procedure for the Preparation of 1,4-Bismethylenebenzene or 1,4-Bismethylene-2,3,5,6-Tetrafluorobenzene Linker Dicationic Salts, 31–37.** 1,4-Bis(imidazol-1-yl-methyl)benzene, **29**,[19] (1 mmol), or 2,3,5,6-tetrafluoro-1,4-bis(2-methylimidazol-1-yl-methyl)benzene, **30**,[20] (1 mmol), and alkyl bromide or iodide (n-$C_4H_9I$, n-$C_{10}H_{21}Br$, n-$C_{14}H_{29}Br$, 2.3 mmol) were placed in a Pyrex glass tube, sealed, and heated at 100 °C for 12 h. After cooling, the organic solvent was removed and the residue was washed with ethyl ether (3 × 10 mL) to remove the excess alkyl halide to leave the quaternized product. This product (1 mmol) was dissolved in methanol (30 mL); an aqueous solution (2 mL) of lithium bis(trifluoromethanesulfonyl)amide (2.3 mmol) was added and stirred at room temperature for 5 h. The solvent was removed and extracted with ethyl acetate (3 × 20 mL); it was then washed with water (3 × 10 mL) and dried over anhydrous sodium sulfate. The solvent was removed under a vacuum at 90 °C for 6 h to give the $NTf_2^-$ salts, **31–33** and **35–37**.

To form the $PF_6^-$ salt, the quaternized product (1 mmol) was dissolved in acetone and water (10:1, 40 mL), and potassium

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hexafluorophosphate (2.3 mmol) was added and stirred at room temperature. After 5 h, acetone was removed at reduced pressure and the insoluble product was separated by filtration from water. The product was washed with water (3 × 10 mL), recrystallized from methanol−diethyl ether (1:15), and then dried under a vacuum at 90 °C for 6 h to give the $PF_6^-$ salt, **34**.

**(5) 1,1′-(3-Oxapentane-1,5-diyl)bis(3-decyl-1*H*-imidazolium-1-yl) di[bis(trifluoromethanesulfonyl)amide].** 82% yield, colorless liquid. $^1$H NMR ($CDCl_3$): $\delta$ 8.79 (s, 2H), 7.48 (s, 2H), 7.33 (s, 2H), 4.41 (t, $J$ = 4.6 Hz, 4H), 4.19 (t, $J$ = 7.4 Hz, 4H), 4.19 (t, $J$ = 4.6 Hz, 4H), 1.88 (m, 4H), 1.28 (m, 32H), 0.89 (t, $J$ = 6.8 Hz, 6H). $^{13}$C NMR: $\delta$ 136.60, 122.87 [q, $J_{CF}$ = 360.9 Hz, $N(SO_2CF_3)_2$], 122.73, 118.48, 69.51, 51.15, 50.53, 32.66, 30.87, 30.23, 30.13, 30.04, 29.69, 26.99, 23.47, 14.88. $^{19}$F NMR: $\delta$ –78.87 (s, $N(SO_2CF3)_2$, 12F). Anal. Calcd (%) for $C_{34}H_{56}F_{12}N_6O_9S_4$ (1048.48): C, 38.93; H, 5.38; N, 8.01. Found: C, 38.66; H, 5.74; N, 7.28.

**(6) 1,1′-(3-Oxapentane-1,5-diyl)bis(3-dodecyl-1*H*-imidazolium-1-yl) Di[bis(trifluoromethanesulfonyl)amide].** 80% yield, colorless semisolid. $^1$H NMR ($CDCl_3$): $\delta$ 8.77 (s, 2H), 7.48 (t, $J$ = 1.7 Hz, 2H), 7.29 (t, $J$ = 1.7 Hz, 2H), 4.40 (t, $J$ = 4.4 Hz, 4H), 4.18 (t, $J$ = 7.3 Hz, 4H), 3.86 (t, $J$ = 4.4 Hz, 4H), 1.88 (m, 4H), 1.27 (m, 40H), 0.89 (t, $J$ = 6.3 Hz, 6H). $^{13}$C NMR: $\delta$ 133.12, 120.78 [q, $J_{CF}$ = 363.8 Hz, $N(SO_2CF_3)_2$], 115.62, 111.26, 66.16, 47.71, 47.09, 29.35, 27.51, 27.04, 27.03, 26.93, 26.78, 26.34, 23.61, 20.13, 11.55. $^{19}$F NMR: $\delta$ –78.95 (s, $N(SO_2CF_3)_2$, 12F). Anal. Calcd (%) for $C_{38}H_{64}F_{12}N_6O_9S_4$ (1104.34): C, 41.30; H, 5.84; N, 7.60. Found: C, 41.13; H, 5.73; N, 7.78.

**(7) 1,1′-(3,6-Dioxaoctane-1,8-diyl)bis(3-decyl-1*H*-imidazolium-1-yl) Di[bis(trifluoromethanesulfonyl)amide].** 85% yield, colorless liquid. $^1$H NMR ($CDCl_3$): $\delta$ 8.75 (s, 2H), 7.48 (s, 2H), 7.34 (s, 2H), 4.38 (t, $J$ = 3.7 Hz, 4H), 4.17 (t, $J$ = 6.9 Hz, 4H), 3.85 (t, $J$ = 3.7 Hz, 4H), 3.64 (s, 4H), 1.88 (m, 4H), 1.27 (m, 28H), 0.90 (t, $J$ = 4.6 Hz, 6H). $^{13}$C NMR: $\delta$ 135.52, 123.32 [q, $J_{CF}$ = 398.7 Hz, $N(SO_2CF_3)_2$], 117.59, 113.34, 70.39, 68.61, 50.11, 49.86, 31.71, 29.93, 29.28, 29.18, 29.09, 28.74, 26.01, 22.51, 13.93. $^{19}$F NMR: $\delta$ –78.94 (s, $N(SO_2CF3)_2$, 12F). Anal. Calcd (%) for $C_{36}H_{60}F_{12}N_6O_{10}S_4$ (1076.31): C, 39.55; H, 5.53; N, 7.69. Found: C, 39.65; H, 5.58; N, 7.68.

**(8) 1,1′-(3,6-Dioxaoctane-1,8-diyl)bis(3-tetradecyl-1*H*-imidazolium-1-yl) Di[bis(trifluoromethanesulfonyl)amide].** 80% yield, colorless semisolid. $^1$H NMR ($CDCl_3$): $\delta$ 8.73 (s, 2H), 7.48 (t, $J$ = 1.6 Hz, 2H), 7.33 (t, $J$ = 1.6 Hz, 2H), 4.38 (t, $J$ = 4.6 Hz, 4H), 4.18 (t, $J$ = 7.4 Hz, 4H), 3.84 (t, $J$ = 4.6 Hz, 4H), 3.64 (s, 4H), 1.88 (m, 4H), 1.27 (m, 44H), 0.89 (t, $J$ = 6.5 Hz, 6H). $^{13}$C NMR: $\delta$ 135.53, 122.61 [q, $J_{CF}$ = 408.3 Hz, $N(SO_2CF_3)_2$], 117.60, 113.34, 70.42, 68.62, 50.13, 49.89, 31.81, 29.94, 29.53, 29.48, 29.37, 29.23, 28.77, 26.04, 22.57, 13.97. $^{19}$F NMR: $\delta$ –78.91 (s, $N(SO_2CF_3)_2$, 12F). Anal. Calcd (%) for $C_{44}H_{76}F_{12}N_6O_{10}S_4$ (1204.43): C, 43.84; H, 6.36; N, 6.97. Found: C, 44.19; H, 6.35; N, 7.12.

**(9) 1,1′-(3,6-Dioxaoctane-1,8-diyl)bis(3-tetradecyl-1*H*-imidazolium-1-yl) Ditetrafluoroborate.** 85% yield, colorless solid. $^1$H NMR ($CD_3CN$): $\delta$ 8.50 (s, 2H), 7.41 (t, $J$ = 1.6 Hz, 2H), 7.38 (t, $J$ = 1.6 Hz, 2H), 4.26 (t, $J$ = 4.6 Hz, 4H), 4.12 (t, $J$ = 7.2 Hz, 4H), 3.76 (s, $J$ = 4.6 Hz, 4H), 3.57 (s, 4H), 1.82 (m, 4H), 1.26 (m, 44H), 0.87 (t, $J$ = 6.5 Hz, 6H). $^{13}$C NMR: $\delta$ 136.60, 123.90, 122.98, 70.85, 69.23, 50.51, 50.41, 30.48, 30.26, 30.24, 30.22, 30.11, 29.97, 29.93, 29.48, 26.58, 14.11. $^{19}$F NMR: $\delta$ –151.60 (s, $BF_4$, 8F). Anal. Calcd (%) for $C_{40}H_{76}B_2F_8N_4O_2$ (818.60): C, 58.68; H, 9.36; N, 6.84. Found: C, 58.90; H, 9.41; N, 6.72.

**(10) 1,1′-(3,6-Dioxaoctane-1,8-diyl)bis(3-tetradecyl-1*H*-imidazolium-1-yl) Dihexafluorophosphate.** 85% yield, colorless solid. $^1$H NMR ($CD_3CN$): $\delta$ 8.44 (s, 2H), 7.40 (s, 2H), 7.38 (s, 2H), 4.30 (t, $J$ = 4.6 Hz, 4H), 4.15 (t, $J$ = 7.2 Hz, 4H), 3.76 (t, $J$ = 4.6 Hz, 4H), 2.14 (s, 4H), 1.31 (m, 4H), 1.26 (m, 44H), 0.91 (t, $J$ = 5.9 Hz, 6H). $^{13}$C NMR: $\delta$ 135.04, 122.48, 121.57, 67.87, 49.13, 48.85, 29.06, 28.85, 28.81, 28.72, 28.58, 28.52, 28.10, 25.21, 21.84, 12.83. $^{19}$F NMR: $\delta$ –71.54 to –74.04 (d, $J_{P-F}$ = 705.0 Hz, 12F). Anal. Calcd (%) for $C_{40}H_{76}F_{12}N_4O_2P_2$ (934.53): C, 51.38; H, 8.19; N, 5.99. Found: C, 51.57; H, 8.50; N, 6.59.

**(12) 1,1′-(3,6-Dioxaoctane-1,8-diyl)bis(3-perfluorodecyl-1*H*-imidazolium-1-yl) di[bis(trifluoromethanesulfonyl)amide].** 70% yield, colorless semisolid. $^1$H NMR ($CD_3CN$): $\delta$ 8.60 (s, 2H), 7.50 (s, 2H), 7.47 (s, 2H), 4.55 (t, $J$ = 6.9 Hz, 4H), 4.31 (t, $J$ = 4.6 Hz, 4H), 3.79 (t, $J$ = 4.6 Hz, 4H), 3.60 (s, 4H), 2.89 (m, 4H). $^{13}$C NMR: $\delta$ 135.81, 122.90, 121.78, 69.36, 67.71, 49.21, 41.22, 30.26 (t, $J_{CF}$ = 79.1 Hz, -$CH_2CF_2$). $^{19}$F NMR: $\delta$ –81.13 (s, $CF_3$, 6F), –81.51 (s, $N(SO_2CF_3)_2$, 12F), –114.10 (s, $-CF_2CF_3$, 4F), –122.23 [s, $-(CF_2)_3CF_3$, 12F], –123.05 [s, $-CF_2(CF_2)_3CF_3$, 4F], –123.94 [s, $-CF_2(CF_2)_4CF_3$, 4F], –126.48 [s, $-CH_2CH_2CF_2(CF_2)_6CF_3$, 4F]. Anal. Calcd (%) for $C_{36}H_{26}F_{46}N_6O_{10}S_4$ (1703.99): C, 25.36; H, 1.54; N, 4.93. Found: C, 25.77; H, 1.31; N, 5.15.

**(19) 1,1′-(2,2,3,3,4,4-Hexafluoropentane-1,5-diyl)bis(3-methyl-1*H*-imidazolium-1-yl) Ditrifluoromethanesulfonate.** 85% yield, brown solid. $^1$H NMR ($CD_3CN$): $\delta$ 8.70 (s, 2H), 7.54 (s, 2H), 7.47 (s, 2H), 5.05 (t, $J$ = 15.8 Hz, 4H), 3.89 (s, 6H). $^{13}$C NMR: $\delta$ 139.33, 125.49, 125.14, 48.99, 37.54. $^{19}$F NMR: $\delta$ –79.32 ($SO_3CF_3$, 6F), –117.76 ($-CF_2CF_2CF_2$, 4F), –125.12 [$-CF_2CF_2CH_2$, 2F]. Anal. Calcd (%) for $C_{15}H_{16}F_{12}N_4O_6S_2$(604.03): C, 28.13; H, 2.52; N, 8.75. Found: C, 28.46; H, 2.42; N, 8.72.

**(20) 1,1′-(2,2,3,3,4,4-Hexafluoropentane-1,5-diyl)bis(3-butyl-1*H*-imidazolium-1-yl) Ditrifluoromethanesulfonate.** 85% yield, brown solid. $^1$H NMR ($CD_3CN$): $\delta$ 8.77 (s, 2H), 7.56 (s, 2H), 7.53 (s, 2H), 5.06 (t, $J$ = 15.2 Hz, 4H), 4.20 (t, $J$ = 7.1 Hz, 4H), 1.84 (m, 4H), 1.35 (m, 4H), 0.94 (t, $J$ = 7.2 Hz, 6H). $^{19}$F NMR: $\delta$ –79.27 ($SO_3CF_3$, 6F), –117.70 ($-CF_2CH_2$, 4F), –125.51 ($-CF_2CF_2$, 2F). Anal. Calcd (%) for $C_{22}H_{28}F_{14}N_4O_6S_2$ (774.12): C, 34.81; H, 3.89; N, 7.73. Found: C, 35.03; H, 3.93; N,7.91.

**(21) 1,1′-(2,2,3,3,4,4,5,5-Octafluorohexane-1,6-diyl)bis(3-butyl-1*H*-imidazolium-1-yl) Ditrifluoromethanesulfonate.** 85% yield, brown solid. $^1$H NMR ($CD_3CN$): $\delta$ 8.77 (s, 2H), 7.56 (s, 2H), 7.53 (s, 2H), 5.06 (t, $J$ = 15.2 Hz, 4H), 4.20 (t, $J$ = 7.1 Hz, 4H), 1.84 (m, 4H), 1.35 (m, 4H), 0.94 (t, $J$ = 7.2 Hz, 6H). $^{19}$F NMR: $\delta$ –73.88 ($SO_3CF_3$, 6F), –119.62 ($-CF_2CF_2$, 4F), –122.89 ($-CF_2CH_2$, 2F). Anal. Calcd (%) for $C_{22}H_{28}F_{14}N_4O_6S_2$ (774.12): C, 34.11; H, 3.64; N, 7.23. Found: C, 33.95; H, 3.38; N,6.99.

**(22) 1,1′-(2,2,4,4,5,5,7,7-Octafluoro-3,6-dioxaoctane-1,8-diyl)-bis(3-butyl-1*H*-imidazol-ium-1-yl) Ditrifluoromethanesulfonate.** 85% yield, colorless solid. $^1$H NMR ($CD_3CN$): $\delta$ 8.76 (s, 2H), 7.52 (s, 2H), 7.51 (s, 2H), 4.99 (t, $J_{HF}$ = 9.5 Hz, 4H), 4.20 (t, $J$ = 7.0 Hz, 4H), 1.86 (m, 4H), 1.33 (m, 4H), 0.93 (t, $J$ = 7.3 Hz, 6H). $^{13}$C NMR: $\delta$ 138.40, 124.89, 124.35, 51.64, 51.01, 32.31, 19.91, 13.59. $^{19}$F NMR: $\delta$ –75.90 ($-OCF_2CF_2O$, 4F), –79.32 ($SO_3CF_3$, 6F), –89.29 (-$CH_2CF_2O$, 4F). Anal. Calcd (%) for $C_{24}H_{28}F_{20}N_6O_{10}S_4$ (806.11): C, 32.76; H, 3.50; N, 6.95. Found: C, 32.74; H, 3.33; N, 6.81.

**(23) 1,1′-(2,2,3,3,4,4-Hexafluoropentane-1,5-diyl)bis(3-methyl-1*H*-imidazolium-1-yl) Di[bis(trifluoromethanesulfonyl)amide].** 75% yield, brown solid. $^1$H NMR ($CD_3CN$): $\delta$ 8.62 (s, 2H), 7.52 (s, 2H), 7.47 (s, 2H), 5.05 (m, 4H), 4.02 (s, 6H). $^{13}$C: $\delta$ 139.18, 125.32, 124.97, 48.81, 37.36. $^{19}$F NMR: $\delta$ –81.51 (s, $N(SO_2CF_3)_2$, 12F), –117.76 (s, $-CF_2CF_2CF_2$, 4F), –124.88 [s, $-CF_2CF_2CH_2$, 2F]. Anal. Calcd (%) for $C_{17}H_{16}F_{18}N_6O_8S_4$ (901.96): C, 22.62; H, 1.79; N, 9.31. Found: C, 21.67; H, 1.51; N, 8.70.

**(24) 1,1′-(2,2,3,3,4,4-Hexafluoropentane-1,5-diyl)bis(3-butyl-1*H*-imidazolium-1-yl) Di[bis(trifluoromethanesulfonyl)amide].** 75% yield, brown solid. $^1$H NMR ($CD_3CN$): $\delta$ 8.67 (s, 2H), 7.55 (s, 2H), 7.53 (s, 2H), 5.06 (m, 4H), 4.20 (t, $J$ = 7.2 Hz, 4H), 1.86 (m, 4H), 1.34 (m, 4H), 0.94 (t, $J$ = 7.3 Hz, 6H). $^{13}$C NMR: $\delta$

139.39, 125.35, 123.10, 51.08, 49.06, 32.29, 19.94, 12.60. $^{19}$F NMR: $\delta$ –80.12 (s, $N(SO_2CF_3)_2$, 12F), –117.68 (s, $-CF_2CH_2$, 4F), –124.86 (s, $-CF_2CF_2CH_2$, 2F). Anal. Calcd (%) for $C_{23}H_{28}F_{18}N_6O_8S_4$ (986.06): C, 28.00; H, 2.86; N, 8.52. Found: C, 27.57; H, 2.70; N, 8.36.

**(25) 1,1′-(2,2,3,3,4,4,5,5-Octafluorohexane-1,6-diyl)-bis(3-butyl-1*H*-imidazolium-1-yl) Di[bis(trifluoromethanesulfonyl)amide] (25).** 75% yield, colorless solid. $^1$H NMR ($CD_3CN$): $\delta$ 8.68 (s, 2H), 7.54 (s, 2H), 7.53 (s, 2H), 5.03 (m, 4H), 4.21 (t, $J$ = 7.2 Hz, 4H), 1.87 (m, 4H), 1.34 (m, 4H), 0.94 (t, $J$ = 7.3 Hz, 6H). $^{13}$C NMR: $\delta$ 139.39, 125.35, 123.10, 51.08, 49.06, 32.29, 19.94, 12.60. $^{19}$F NMR: $\delta$ –80.10 [s, $N(SO_2CF_3)_2$, 12F], –117.85 (s, $-CF_2CH_2$, 4F), –124.86 [s, $-(CF_2)_2CF_2CH_2$, 4F]. Anal. Calcd (%) for $C_{24}H_{28}F_{20}N_6O_8S_4$ (1036.05): C, 27.80; H, 2.72; N, 8.11. Found: C, 27.82; H, 2.63; N, 7.99.

**(26) 1,1′-(2,2,4,4,5,5,7,7-Octafluoro-3,6-dioxaoctane-1,8-diyl)-bis(3-butyl-1*H*- imidazolium-1-yl) di[bis(trifluoromethanesulfonyl)amide].** 75% yield, colorless solid. $^1$H NMR ($CD_3CN$): $\delta$ 8.7 (s, 2H), 7.5 (s, 2H), 7.5 (s, 2H), 4.94 (t, $J_{HF}$ = 9.5 Hz, 4H), 4.2 (t, $J$ = 7.0 Hz, 4H), 1.92 (m, 4H), 1.3 (m, 4H), 0.93 (t, $J$ = 7.3 Hz, 6H). $^{13}$C NMR: $\delta$ 138.28, 125.18, 124.13, 51.92, 48.85, 32.11, 19.76, 13.40. $^{19}$F NMR: $\delta$ –75.84 (s, $-OCF_2CF_2O$, 4F), –80.10 [s, $N(SO_2CF_3)_2$, 12F], –89.11 (s, $-CH_2CF_2O$, 4F). Anal. Calcd (%) for $C_{24}H_{28}F_{20}N_6O_{10}S_4$ (1068.04): C, 26.97; H, 2.64; N, 7.86. Found: C, 26.58; H, 2.37; N, 7.59.

**(31) 1,1′-(1,4-Phenylenebismethylene)bis(3-butyl-1*H*-imidazolium-1-yl) Di[bis(trifluoromethanesulfonyl)amide].** 85% yield, colorless solid. $^1$H NMR ($CD_3CN$): $\delta$ 8.52 (s, 2H), 7.41 (s, 4H), 7.39 (s, 2H), 7.35 (s, 2H), 5.32 (s, 4H), 4.12 (t, $J$ = 7.2 Hz, 4H), 1.81 (m, 4H), 1.33 (m, 4H), 0.93 (t, $J$ = 7.3 Hz, 6H). $^{13}$C NMR: $\delta$ 136.54, 135.81, 130.32, 123.51, 118.86, 53.35, 50.61, 32.46, 20.02, 13.63. $^{19}$F NMR: $\delta$ –80.06 [s, $N(SO_2CF_3)_2$, 12F]. Anal. Calcd (%) for $C_{26}H_{32}F_{12}N_6O_8S_4$ (912.10): C, 34.21; H, 3.53; N, 9.21. Found: C, 33.99; H, 3.32; N, 9.07.

**(32) 1,1′-(1,4-Phenylenebismethylene)bis(3-decyl-1*H*-imidazolium-1-yl) Di[bis(trifluoromethanesulfonyl)amide].** 80% yield, colorless solid. $^1$H NMR ($CD_3CN$): $\delta$ 8.52 (s, 2H), 7.40 (s, 4H), 7.39 (s, 2H), 7.34 (s, 2H), 5.32 (s, 4H), 4.11 (t, $J$ = 7.2 Hz, 4H), 1.81 (m, 4H), 1.28 (m, 28H), 0.88 (t, $J$ = 7.0 Hz, 6H). $^{13}$C NMR: $\delta$ 136.36, 135.64, 130.15, 123.51, 118.11, 53.18, 50.69, 32.46, 30.32, 30.01, 29.91, 29.84, 29.41, 26.56, 23.23, 14.23. $^{19}$F NMR: $\delta$ –80.07 [s, $N(SO_2CF_3)_2$, 12F]. Anal. Calcd (%) for $C_{38}H_{56}F_{12}N_6O_8S_4$ (1080.29): C, 42.22; H, 5.22; N, 7.77. Found: C, 42.49; H, 5.19; N, 7.70.

**(33) 1,1′-(1,4-Phenylenebismethylene)bis(3-tetradecyl-1*H*-imidazolium-1-yl) Di[bis(trifluoromethanesulfonyl)amide].** 83% yield, colorless solid. $^1$H NMR ($CDCl_3$) $\delta$ (ppm): 8.78 (s, 2H), 7.43 (s, 4H), 7.42 (s, 2H), 7.26 (s, 2H), 5.36 (s, 4H), 4.15 (t, $J$ = 7.0 Hz, 4H), 1.87 (m, 4H), 1.28 (m, 44H), 0.90 (t, $J$ = 6.5 Hz, 6H). $^{13}$C NMR: $\delta$ 135.54, 133.60, 129.84, 122.87, 117.56, 52.98, 50.32, 31.82, 29.91, 29.57, 29.54, 29.47, 29.36, 29.24, 29.20, 28.75, 26.07, 25.58, 13.99. $^{19}$F NMR: $\delta$ –78.88 [s, $N(SO_2CF_3)_2$, 12F]. Anal. Calcd (%) for $C_{46}H_{72}F_{12}N_6O_8S_4$ (1192.41): C, 46.30; H, 6.08; N, 7.04. Found: C, 46.59; H, 5.99; N, 7.37.

**(34) 1,1′-(1,4-Phenylenebismethylene)bis(3-tetradecyl-1*H*-imidazolium-1-yl) Dihexafluorophosphate.** 80% yield, colorless solid. $^1$H NMR ($CDCl_3$): $\delta$ 8.44 (s, 2H), 7.24 (s, 4H), 7.19 (s, 2H), 7.11 (s, 2H), 5.21 (s, 4H), 4.09 (t, $J$ = 7.2 Hz, 4H), 1.82 (m, 4H), 1.24 (m, 42H), 0.87 (t, $J$ = 6.5 Hz, 6H). $^{13}$C NMR: $\delta$ 136.61, 135.89, 130.39, 124.05, 53.41, 50.93, 32.74, 30.57, 30.49, 30.47, 30.45, 30.42, 30.31, 30.16, 29.67, 26.81, 23.48, 14.47. $^{19}$F NMR: $\delta$ –70.23 to –72.75 (d, $J_{P-F}$ = 710.6 Hz, 12F). Anal. Calcd (%) for $C_{42}H_{72}F_{12}N_4P_2$ (922.50): C, 54.65; H, 7.86; N, 6.07. Found: C, 54.43; H, 7.85; N, 5.99.

**(35) 1,1′-(2,3,5,6-Tetrafluoro-1,4-phenylenebismethylene)bis(3-butyl-1*H*-imidazolium-1-yl) Di[bis(trifluoromethanesulfonyl)-amide].** 85% yield, colorless solid. $^1$H NMR ($CD_3CN$): $\delta$ 8.61 (s, 2H), 7.45 (s, 2H), 7.44 (s, 2H), 5.51 (s, 4H), 4.15 (t, $J$ = 7.2 Hz, 4H), 1.83 (m, 4H), 1.33 (m, 4H), 0.96 (t, $J$ = 7.3 Hz, 6H). $^{13}$C NMR: $\delta$ 148.83, 145.48, 136.98, 123.96, 123.68, 50.66, 41.56, 32.39, 19.91, 13.59. $^{19}$F NMR: $\delta$ –80.16 [s, ($N(SO_2CF_3)_2$, 12F], –142.37 (s, F-Ph, 4F). Anal. Calcd (%) for $C_{26}H_{28}F_{16}N_6O_8S_4$ (984.06): C, 31.71; H, 2.87; N, 8.53. Found: C, 31.60; H, 2.80; N, 8.40.

**(36) 1,1′-(2,3,5,6-Tetrafluoro-1,4-phenylenebismethylene)bis(3-decyl-1*H*-imidazolium-1-yl) Di[bis(trifluoromethanesulfonyl)-amide].** 80% yield, colorless solid. $^1$H NMR ($CD_3CN$): $\delta$ 8.61 (s, 2H), 7.44 (s, 2H), 7.42 (s, 2H), 5.51 (s, 4H), 4.14 (t, $J$ = 7.2 Hz, 4H), 1.86 (m, 4H), 1.33 (m, 28H), 0.92 (t, $J$ = 6.4 Hz, 6H). $^{13}$C NMR: $\delta$ 147.94, 144.55, 136.86, 123.86, 123.59, 50.83, 41.49, 32.46, 30.29, 30.01, 29.91, 29.84, 29.40, 26.51, 23.22, 14.22. $^{19}$F NMR: $\delta$ –80.14 [s, ($N(SO_2CF_3)_2$, 12F], –142.37 (s, F-Ph, 4F). Anal. Calcd (%) for $C_{38}H_{52}F_{16}N_6O_8S_4$ (1152.25): C, 39.58; H, 4.55; N, 7.29. Found: C, 39.47; H, 4.61; N, 7.32.

**(37) 1,1′-(2,3,5,6-Tetrafluoro-1,4-phenylenebismethylene)bis(3-tetradecyl-1*H*-imidazolium-1-yl) Di[bis(trifluoromethanesulfonyl)amide].** 85% yield, colorless solid. $^1$H NMR ($CD_3CN$): $\delta$ 8.56 (s, 2H), 7.41 (s, 2H), 7.39 (s, 2H), 5.48 (s, 4H), 4.10 (t, $J$ = 7.2 Hz, 4H), 1.83 (m, 4H), 1.33 (m, 44H), 0.87 (t, $J$ = 6.5 Hz, 6H). $^{13}$C NMR: $\delta$ 148.77, 145.34, 137.66, 124.66, 124.39, 51.63, 42.30, 31.09, 31.04, 31.01, 30.98, 30.86, 30.72, 30.21, 27.32, 24.04, 15.02. $^{19}$F NMR: $\delta$ –80.10 [s, ($N(SO_2CF_3)_2$, 12F], –142.40 (s, F-Ph, 4F). Anal. Calcd (%) for $C_{46}H_{68}F_{16}N_6O_8S_4$ (1264.37): C, 43.66; H, 5.42; N, 6.64. Found: C, 43.66; H, 5.32; N, 6.58.

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**Supporting Information Available:** Representative $^1$H, $^{19}$F NMR spectra, DSC and TGA scans for new dicationic ionic liquids **6**, **8**, **20**, **21**, **23**, **24**, **25**, **33**, **35**, and **37.** (PDF). This information is available free of charge via the Internet at http://pubs.acs.org.

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