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Correlating Structure with Thermal Properties for a Series of 1-Alkyl-4-methyl-1,2,4-triazolium Ionic Liquids

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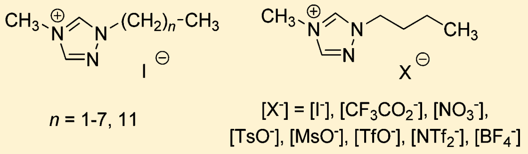
Ⓢ *Supporting Information*

ABSTRACT: Thermal properties (T_m and T_d) are reported for a series of 1-alkyl-4-methyl-1,2,4-triazolium ionic liquids where the alkyl chain length R and anion [X^-] were varied. The highest melting transitions were observed when a longer alkyl chain or smaller anion was employed. Thermal stability was the greatest when anions with weak hydrogen bonding capability were used. Correlations were also made between ^{1}H NMR chemical shift values in acetone-d_6 and the hydrogen bonding capability of the anion.



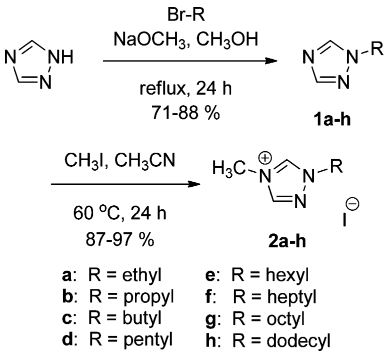
While the ionic liquid field has been dominated by the 1,3-dialkylimidazolium cation, there remains a strong desire to explore other classes of ionic liquids in order to tailor physical properties for specific applications.[1,2] Nitrogen-rich ionic liquids in particular have gained interest due to their potential advantages over conventional energy-rich materials, the properties of which include higher densities and heats of formations, improved thermal stabilities and lower vapor pressures and flammabilities.[3] Within this group, 1,2,4-triazolium-based ionic liquids are of interest since the nitrogen-rich heterocycle possesses a large, positive heat of formation (ΔH_f° (1,2,4-triazole) = 109 kJ/mol compared to ΔH_f°(imidazole) = 58.5 kJ/mol).[4] Additionally, since molecular nitrogen is a primary product of decomposition for the 1,2,4-triazole ring, the corresponding 1,2,4-triazolium ionic liquids have been envisioned as a more environmentally acceptable alternative to many materials currently used in the propellant and explosives industries.[3]

While the interest in 1,2,4-triazolium-containing ionic liquids has increased over the past decade, the majority of research has focused on materials specifically designed for energetic and electrochemical applications.[3,5,6] Shreeve and co-workers recently reviewed their work on "energy-rich" triazolium ionic liquids in which a number of amino-, nitro-, or azido-substituted 1,2,4-triazolium cations were combined with energy-rich anions such as perchlorate or nitrate.[7] Shreeve has also explored the properties of several fluoroalkylated 1,2,4-triazolium salts as well as the free-radical polymerization of 1-vinyl-1,2,4-triazolium monomers in an attempt to make energy-rich polymeric materials.[8−10] The utility of the 1,2,4-triazolium ring in "tunable" aryl/alkyl ionic liquids has also recently been explored by Strassner.[11]

Despite these advances in the chemistry and applications of 1,2,4-triazolium ionic liquids, we are interested in exploring a more fundamental structure−activity study. In this paper, the preparation of a series of 1-alkyl-4-methyl-1,2,4-triazolium ionic liquids is reported where we attempt to correlate thermal properties such as melting point (T_m) (or glass transition T_g) and thermal stability (T_d) with variations in ionic liquid structure. The two parameters of interest include (1) the length of the *N*-1 alkyl chain R and (2) the anion [X^-]. While both of these structural features have a profound influence on the thermal properties of 1,3-dialkylimidazolium ionic liquids, a similar study has yet to be reported for the 1,4-dialkyl-1,2,4-triazolium system.[12−14]

A number of methods have been reported for the regioselective *N*-1 alkylation of 1,2,4-triazole, the majority of which employ basic conditions such as sodium alkoxide, sodium hydroxide, or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).[15−17] We found that Shreeve's procedure (Scheme 1) provided the highest yields of 1-alkyl-1,2,4-triazoles **1a−h** after high vacuum distillation.[8] For each synthetic experiment, 1,2,4-triazole was alkylated at the *N*-1 position with the appropriate 1-bromoalkane in the presence of sodium methoxide. The resulting 1-alkyl-1,2,4-triazoles **1a−h** were then quaternized at the *N*-4 position with methyl iodide to provide the desired 1-alkyl-4-methyl-1,2,4-triazolium iodides **2a−h**. All of the ionic liquids were solids at room temperature with the exception of

Scheme 1. Synthesis of 1-Alkyl-4-methyl-1,2,4-triazolium Ionic Liquids 2



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2b (R = propyl), which was a viscous, yellow oil. Compound identification and purity were determined by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis.

Thermal transitions (T_m or T_g) of the 1-alkyl-4-methyl-1,2,4-triazolium liquids **2a−h** were determined by differential scanning calorimetry (DSC), the results of which are summarized in Table 1. The ability to correlate melting point and structure for ionic liquids is critical since many of the prospective applications rely heavily on the depressed melting points (T_m) and viscosities that result from decreased symmetry and weak intermolecular interactions between the cation and anion. An initial decrease in melting point (T_m) value was observed when the alkyl chain R was increased from R = methyl (literature T_m = 122 °C), ultimately resulting in a glass transition (T_g) value of −53.2 °C for 1-propyl-4-methyl-1,2,4-triazolium iodide **2b** (lit.[10] T_g −52 °C).This initial decrease in thermal transition is attributed to a disruption of symmetry properties, resulting in poorer crystal packing and a decrease in ionic interactions. Upon further increasing the alkyl chain from **2b** (R = propyl) to **2h** (R = dodecyl), a steady rise in T_m value was observed. As the chain length and mass of the compound increases, a greater amount of energy is needed to overcome the growing number of van der Waals interactions.

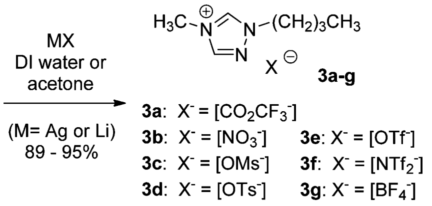
Table 1. Thermal Properties of 1-Alkyl-4-methyl-1,2,4-triazolium Ionic Liquids 2

compd	R	T_m (°C)	T_d (°C)
	methyl	122[a]	
2a	ethyl	33.9	194
2b	propyl	−53.2 (T_g)	194
2c	butyl	54.7	194
2d	pentyl	70.3	188
2e	hexyl	96.3	184
2f	heptyl	108.4	181
2g	octyl	113.2	180
2h	dodecyl	126.7	177

[a] Reference 10.

Thermal decomposition (T_d) values for the 1,2,4-triazolium iodides **2** were determined by thermogravimetric analysis (TGA) and are also summarized in Table 1. Although there is not a large variation, a small but consistent decrease in T_d value was observed as the chain length was increased from **2c** (R = butyl) to **2h** (R = dodecyl). We speculate that this trend may be due to an increase in the stability of the degradation product(s), however a comprehensive decomposition study was beyond the scope of this work. Both of the observed trends in T_m and T_d values are comparable to compiled data for a number of analogous 1,3-dialkylimidazolium ionic liquids.[12] All thermal measurements (DSC and TGA) were completed in duplicate with an error of ±2 °C on samples that had been stored in a vacuum oven at 60 °C for 48 h.

Scheme 2. Synthesis of 1-Butyl-4-methyl-1,2,4-triazolium Ionic Liquids 3



To probe the effects of anion selection, a series of 1-butyl-4-methyl-1,2,4-triazolium ionic liquids **3** was prepared (Scheme 2). From the previously prepared 1-butyl-4-methyl-1,2,4-triazolium iodide **2c**, anion-exchange reactions using the appropriate silver or lithium salt were performed to achieve the desired triazolium-based ionic liquids **3a−g**.[18−20] The anions were chosen to encompass a wide variety of sizes and hydrogen bond capabilities and included trifluoroacetate $[CF_3CO_2^-]$, nitrate $[NO_3^-]$, mesylate $[OMs^-]$, tosylate $[OTs^-]$, triflate $[OTf^-]$, bis(trifluoromethylsulfonyl)imide $[NTf_2^-]$, and tetrafluoroborate $[BF_4^-]$. Compound identification and purity were determined by ^{1}H and ^{13}C NMR spectroscopy and high-resolution mass spectrometry (HRMS). The amount of residual iodide in each ionic liquid was determined to be less than 0.01% w/w by ion chromatography.[21]

1-Butyl-4-methyl-1,2,4-triazolium ionic liquids **2c** and **3a−g** were analyzed by ^{1}H NMR spectroscopy, and a summary of the chemical shift values for triazolium ring protons H^3 and H^5 in acetone-d_6 and DMSO-d_6 (0.05 M of ionic liquid) is provided in Table 2. In general, the 1,2,4-triazolium ring protons appeared further downfield in acetone-d_6. The effect of solvent on the chemical shift values of imidazolium ring protons has been reported by Lue and Gibson, and their results are consistent with the findings reported here.[18,22] Ions are better solvated in DMSO-d_6 and thus cause a decrease in hydrogen bonding interaction between the anion and the cation. This results in chemical shift values that appear further upfield with little change being observed when the anion is varied. Use of acetone-d_6 resulted in tighter ion pairs and downfield chemical shift values that are more dependent upon the choice of anion due to poorer solvation.

Table 2. Triazolium Ring ^{1}H NMR Chemical Shift Data for 1-Butyl-4-methyl-1,2,4-triazolium Ionic Liquids 3

		acetone-d_6 (ppm)		DMSO-d_6 (ppm)	
compd	anion	H^3	H^5	H^3	H^5
3a	$[CF_3CO_2^-]$	9.19	11.02	9.17	10.18
3b	$[NO_3^-]$	9.20	10.80	9.14	10.06
2c	$[I^-]$	9.21	10.73	9.14	10.05
3c	$[OMs^-]$	9.23	10.68	9.14	10.06
3d	$[OTs^-]$	9.18	10.54	9.13	10.05
3e	$[OTf^-]$	9.06	10.01	9.12	10.02
3f	$[NTf_2^-]$	9.06	9.99	9.12	10.02
3g	$[BF_4^-]$	9.03	9.87	9.11	10.01

The chemical shift values are strongly dependent upon the hydrogen-bonding capability of the anion, with the largest separation in values and greatest downfield shifts observed for the more acidic H^5 proton in the weakly solvating acetone-d_6.[17,23] In this series, the largest chemical shift value was observed at 11.02 ppm when the strongly coordinating trifluoroacetate $[CF_3CO_2^-]$ was employed. Conversely, ionic liquids which employed anions with the weakest hydrogen bonding capability, namely triflate $[OTf^-]$, bis(trifluoromethylsulfonyl)imide $[NTf_2^-]$, and tetrafluoroborate $[BF_4^-]$, provided the furthest upfield shifts at 10.01 ppm, 9.99 ppm and 9.87 ppm, respectively. Overall, the chemical shift of the H^5 proton generally increased in acetone-d_6 with increasing anion basicity and ability to hydrogen bond: $[CF_3CO_2^-]$ > $[NO_3^-]$ > $[I^-]$ > $[OMs^-]$ > $[OTs^-]$ > $[OTf^-]$ > $[NTf_2^-]$ >

[BF$_4^-$].[20] The separation of chemical shift values between H^3 and H^5 was observed to decrease with decreasing hydrogen bonding ability, presumably due to increased delocalization of the cation in the ring, resulting in a greater similarity in chemical environment for the two protons. In comparison to values reported for analogous 1-butyl-3-methylimidazolium ionic liquids, hydrogen bonding capability had a greater effect on the magnitude of the chemical shift values of the 1,2,4-triazolium ionic liquids. We speculate that this finding is due to the increased acidity of the triazolium ring.[23,24]

Correlation between anion hydrogen bond ability and the ^{1}H NMR chemical shift values of the H^2 proton for a series of 1-butyl-4-methylimidiazolium ionic liquids was reported by Spange.[25,26] In their study, they determined a hydrogen bond accepting capability parameter β^N, which was based upon UV/vis absorption data of a solvochromatic dye, normalized with ^{1}H NMR data. The chemical shift values for the H^5 proton of our 1,2,4-triazolium ionic liquids **2c** and **3a−g** in acetone-d_6 were plotted against Spange's β^N values (Figure 1), and a reasonable correlation (r^2 = 0.93) was found. Thus, it appears that the relationship between ^{1}H NMR chemical shift values and anion hydrogen bonding ability reported for imidazolium ionic iquids is translatable to the 1,2,4-triazolium system reported here.

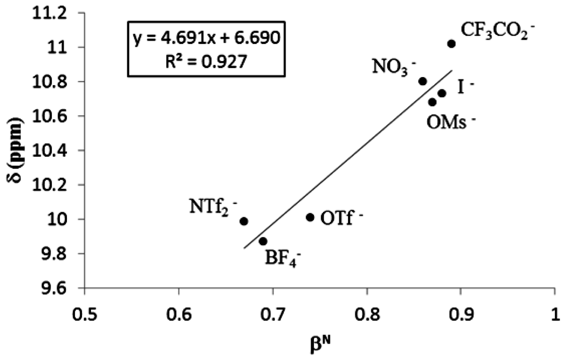


Figure 1. Correlation of the ^{1}H NMR chemical shift values of the H^5 proton with the hydrogen-bond accepting parameter β^N.

As before, all samples were stored in a vacuum oven at 60 °C for 48 h prior to thermal analysis. All thermal measurements (DSC and TGA) were completed in duplicate with an error of ±2 °C. When comparing the thermal transitions of the 1-butyl-4-methyl-1,2,4-triazolium ionic liquids **3**, as determind by DSC, all compounds exhibited an endothermic transition which corresponded to a melting point (T_m). Melting point correlations in imidazolium-containing ionic liquids have been difficult to establish, but the size of the anion appears to be of greater importance than hydrogen bonding ability.[18,20,27] This general trend was also observed for 1-butyl-4-methyl-1,2,4-triazolium ionic liquids **3** (Table 3). Implementation of larger anions such as bis(trifluoromethylsulfonyl)imide [NTf$_2^-$] and trifluoroacetate [CF$_3$CO$_2^-$] resulted in ionic liquids that exhibited reduced T_m values, presumably due to the disruption of crystal lattice packing. Ionic liquids containing smaller anions such as iodide [I$^-$], nitrate [NO$_3^-$] and tetrafluoroborate [BF$_4^-$] displayed the highest melting transitions. Within the sulfonate anion series, use of the tosylate [OTs$^-$] anion provided a T_m value that was higher than expected, an observation that we postulate is due to the ability of the phenyl rings of the tosylate group to participate in π-stacking interactions.

Table 3. Thermal Properties of 1-Butyl-4-methyl-1,2,4-triazolium Ionic Liquids 3

compd	anion	T_m (°C)	T_d (°C)
3a	[CF$_3$CO$_2^-$]	−74.0	167
3b	[NO$_3^-$]	9.2	190
2c	[I$^-$]	54.7	194
3c	[OMs$^-$]	−58.0	254
3d	[OTs$^-$]	−40.6	264
3e	[OTf$^-$]	−68.1	310
3f	[NTf$_2^-$]	−70.2	316
3g	[BF$_4^-$]	−16.1	272

Unlike melting point values, thermal stability can be directly correlated to the ability of an anion to hydrogen bond.[12,18,20] In the 1-butyl-4-methyl-1,2,4-triazolium ionic liquid series **3**, use of a strongly coordinating anion such as trifluoroacetate [CF$_3$CO$_2^-$] led to the poorest thermal stability (T_d = 167 °C) whereas use of weaker anions such as triflate [OTf$^-$] or bis(trifluoromethylsulfonyl)imide [NTf$_2^-$] lead to T_d values in excess of 300 °C. Overall, the T_d values observed for ionic liquids **3** are comparable with the reported values for other 1,2,4-triazolium-containing ionic liquids,[8,10] but they are generally less stable than the analogous 1-butyl-3-methylimidazolium ionic liquids, many of which are stable in excess of 400 °C.[12,20]

In summary, a series of 1-alkyl-4-methyl-1,2,4-triazolium ionic liquids was prepared and analyzed by ^{1}H NMR spectroscopy, DSC and TGA. Two parameters were targeted as part of this structure−activity study: the length of the alkyl chain R at position *N*-1 and the anion [X$^-$]. The highest melting transitions (T_m or T_g) were observed when ionic liquids with long alkyl chains or large anions were tested. Comparison of the ^{1}H NMR chemical shift values of the acidic H^5 proton for 1-butyl-4-methyl-1,2,4-triazolium ionic liquids **2c** and **3a−g** indicated a correlation with the hydrogen bonding ability of the anion. The highest thermal stability (T_d) was observed when weakly coordinating anions (such as bis(trifluoromethylsulfonyl)imide [NTf$_2^-$] or triflate [OTf$^-$]) were employed.

■ EXPERIMENTAL SECTION

General Experimental Methods. All commercial reagents were used without further purification. All solvents were reagent or HPLC grade. Anhydrous acetone and acetonitrile (CH$_3$CN) were used without further purification. ^{1}H and ^{13}C NMR spectra were obtained on a 400 MHz spectrometer at ambient temperature. Chemical shift values are reported in parts per million relative to using residual solvent signals as internal standards (acetone-d_6: ^{1}H, 2.05 ppm; ^{13}C, 29.84 ppm, DMSO-d_6: ^{1}H, 2.50 ppm; ^{13}C, 39.52 ppm, or CDCl$_3$: ^{1}H, 7.27 ppm; ^{13}C, 77.00 ppm). Ionic liquids **2** and **3** were stored in a vacuum oven at 60 °C for 48 h prior to spectroscopic and thermal analyses. Differential scanning calorimetry (DSC), at a heating rate of 10 °C/min on 5−10 mg samples, was performed to determine thermal transitions (T_m and T_g). Reported values were determined from the second heating cycle. Thermal stabilities were studied under a constant nitrogen flow (50 mL/min) using a thermogravimetric analyzer (TGA) at a heating rate of 10 °C/min. All thermal experiments were completed in duplicate and values are reported with an error of ±2 °C. High resolution mass spectrometry (HRMS) was conducted on a MALDI-TOFMS in the positive or negative ion mode.

Preparation 1-Alkyl-1,2,4-triazoles 1a−h. Triazoles **1a**,[16] **1b**,[10] **1c**,[8] **1d**,[15] **1e**,[28] **1f**,[8] and **1g**[29] have been previously reported. The synthesis of 1-docedyl-1,2,4-triazole **1h** has not been previously reported. 1-Dodecyl-1,2,4-triazole **1h** was prepared by following Shreeve's method as described below.[8]

*1-Dodecyl-1,2,4-triazole (**1h**).* To a solution of 1,2,4-triazole (1.00 g, 14.4 mmol) in methanol (15 mL) was added sodium methoxide solution (2.7 mL of 5.4 M solution in methanol, 14.3 mmol). 1-Bromododecane (3.46 g, 14.6 mmol) was then added dropwise using an addition funnel. The resulting solution was allowed to stir at room temperature for 2 h followed by warming to 60 °C, where the stirred solution was held for 24 h. The methanol was then removed under reduced pressure, and the resulting oily solid was purified by high vacuum distillation (105−108 °C, 0.1 mmHg) to afford a colorless oil, which solidified upon cooling to give a white solid (2.91 g, 85% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1 H), 7.91 (s, 1 H), 4.12 (t, J = 7.3 Hz, 2 H), 1.80−1.91 (m, 2 H), 1.17−1.32 (m, 18 H), 0.80−0.89 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 143.1, 53.3, 35.8, 32.0, 29.7, 29.7, 29.6, 29.48, 29.46, 29.1, 28.9, 26.4, 22.8, 14.3. Anal. Calcd for $C_{14}H_{27}N_3$: C, 70.83; H, 11.46; N, 17.70. Found: C, 70.59; H, 11.37; N, 17.88.

Preparation of Ionic Liquids 2a−h. 1-Alkyl-4-methyl-1,2,4-triazolium iodides **2** were prepared by following a modification of Shreeve's procedure.[10] 1-Propyl-4-methyl-1,2,4-triazolium iodide **2b** has been previously reported.[10] The remaining ionic liquids **2a** and **2c−h** have not been reported. Representative procedures for ionic liquids **2a** and **2c** are provided below along with reaction yields and characterization data for the remaining ionic liquids **2d−h**.

*1-Ethyl-4-methyl-1,2,4-triazolium Iodide (**2a**).* In a 50-mL round-bottomed flask equipped with a magnetic stir bar was dissolved 1-ethyl-1,2,4-triazole (**1a**) (1.40 g, 14.0 mmol) in anhydrous acetonitrile (20 mL) under nitrogen. Methyl iodide (3.07 g, 22.0 mmol) was then added, and the resulting stirred solution was warmed to 60 °C and held for 24 h. The solvents and excess methyl iodide were removed under reduced pressure to afford **2a** as a light yellow solid (3.29 g, 95% yield): ^{1}H NMR (400 MHz, acetone-d_6) δ 10.67 (s, 1 H), 9.27 (s, 1 H), 4.59 (q, J = 7.2 Hz, 2 H), 4.19 (s, 3 H), 1.60 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, acetone-d_6) δ 146.1, 143.8, 48.5, 35.3, 14.1. Anal. Calcd for $C_5H_{10}IN_3$: C, 25.12; H, 4.22; N, 17.58. Found: C, 24.95; H, 4.38; N, 17.31.

*1-Butyl-4-methyl-1,2,4-triazolium Iodide (**2c**).* In a 25 mL round-bottomed flask was dissolved 1-butyl-1,2,4-triazole (**1c**) (1.00 g, 7.99 mmol) in anhydrous acetonitrile (10 mL). Iodomethane (2.27 g, 15.0 mmol) was then added, and the resulting stirred solution was warmed to 60 °C and held for 24 h. The solvent and excess iodomethane was then removed under reduced pressure to afford a light orange solid (1.96 g, 92% yield): ^{1}H NMR (400 MHz, acetone-d_6) δ 10.73 (s, 1 H), 9.31 (s, 1 H), 4.58 (t, J = 7.2 Hz, 2 H), 4.21 (s, 3 H), 1.99 (m, 2 H), 1.43 (m, 2 H), 0.95 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, acetone-d_6) δ 146.2, 144.1, 52.8, 35.2, 31.3, 19.9, 13.6. Anal. Calcd for $C_7H_{14}IN_3$: C, 31.48; H, 5.28; N, 15.73. Found: C, 31.78; H, 5.27; N, 15.41.

*1-Pentyl-4-methyl-1,2,4-triazolium Iodide (**2d**).* 1-Pentyl-4-methyl-1,2,4-triazole (**2d**) was obtained as a light yellow solid (97% yield) following the general method described above: ^{1}H NMR (400 MHz, acetone-d_6) δ 10.74 (s, 1 H), 9.34 (s, 1 H), 4.56 (t, J = 7.2 Hz, 2 H), 4.22 (s, 3 H), 1.98−2.08 (m, 2 H), 1.32−1.42 (m, 4 H), 0.90 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, acetone-d_6) δ 146.1, 143.9, 53.0, 35.3, 28.9, 28.6, 22.6, 14.0. Anal. Calcd for $C_8H_{16}IN_3$: C, 34.18; H, 5.74; N, 14.95. Found: C, 33.95; H, 5.75; N, 14.90.

*1-Hexyl-4-methyl-1,2,4-triazolium Iodide (**2e**).* 1-Hexyl-4-methyl-1,2,4-triazolium iodide (**2e**) was obtained as a white solid (93% yield) after recrystallization from hot acetonitrile following the general method described above: ^{1}H NMR (400 MHz, acetone-d_6) δ 10.70 (s, 1 H), 9.25 (s, 1 H), 4.58 (t, J = 7.2 Hz, 2 H), 4.20 (s, 3 H), 1.99−2.07 (m, 2 H), 1.28−1.46 (m, 6 H), 0.87 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 142.6, 53.0, 35.7, 31.0, 28.7, 25.8, 22.3, 13.9. Anal. Calcd for $C_9H_{18}IN_3$: C, 36.62; H, 6.15; N, 14.24. Found: C, 36.36; H, 6.26; N, 14.19.

*1-Heptyl-4-methyl-1,2,4-triazolium Iodide (**2f**).* 1-Heptyl-4-methyl-1,2,4-triazolium iodide (**2f**) was obtained as a white solid (93% yield) after recrystallization from hot acetonitrile following the general method described above: ^{1}H NMR (400 MHz, acetone-d_6) δ 10.72 (s, 1 H), 9.28 (s, 1 H), 4.56 (t, J = 7.4 Hz, 3 H), 4.19 (s, 3 H), 1.95−2.03 (m, 2 H), 1.21−1.45 (m, 8 H), 0.85 (t, J = 7.3 Hz, 3 H); ^{13}C NMR (100 MHz, acetone-d_6) δ 146.1, 143.9, 53.1, 35.2, 32.2, 29.4, 29.3, 26.6, 23.1, 14.2. Anal. Calcd for $C_{10}H_{20}IN_3$: C, 38.85; H, 6.52; N, 13.59. Found: C, 38.85; H, 6.53; N, 13.48.

*1-Octyl-4-methyl-1,2,4-triazolium Iodide **2g**.* 1-Octyl-4-methyl-1,2,4-triazolium iodide (**2g**) was obtained as an off-white solid after recrystallization from hot acetonitrile (87% yield) following the general method described above: ^{1}H NMR (400 MHz, acetone-d_6) δ 10.71 (s, 1 H), 9.26 (s, 1 H), 4.58 (t, J = 7.2 Hz, 2 H), 4.20 (s, 3 H), 1.99−2.07 (m, 2 H), 1.21−1.46 (m, 10 H), 0.85 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, acetone-d_6) δ 146.2, 144.0, 53.1, 35.3, 32.4, 29.7, 29.6, 29.4, 26.7, 23.2, 14.3. Anal. Calcd for $C_{11}H_{22}IN_3$: C, 40.88; H, 6.86; N, 13.00. Found: C, 40.67; H, 6.99; N, 12.93.

*1-Dodecyl-4-methyl-1,2,4-triazolium Iodide (**2h**).* 1-Dodecyl-4-methyl-1,2,4-triazolium iodide (**2h**) was obtained as a white solid after recrystallization from hot acetonitrile (84% yield) following the general method described above: ^{1}H NMR (400 MHz, acetone-d_6) δ 10.57 (s, 1 H), 9.15 (s, 1 H), 4.57 (t, J = 7.08 Hz, 2 H), 4.19 (s, 3 H), 1.97−2.07 (m, 2 H), 1.21−1.45 (m, 18 H), 0.86 (t, J = 6.3 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.0, 142.8, 49.9, 32.0, 29.8, 29.6, 29.5, 29.4, 29.1, 19.7, 14.2. Anal. Calcd for $C_{15}H_{30}IN_3$: C, 47.50; H, 7.97; N, 11.08. Found: C, 47.51; H, 8.01; N, 11.14.

Preparation of Ionic Liquids 3a−h. Anion-exchange reactions followed the general guidelines of previously published procedures.[18−20,27] The quantity of residual iodide was determined by ion chromatography under the following conditions: 4.5 mM CO_3^{2-}/1.4 mM HCO_3^- eluent concentration, 1.2 mL/min flow rate, 31 mA suppressor current. After chromatographic calibration via aqueous standards prepared by serial dilution of 1000 ppm [I^-] stock (from sodium iodide), 10−15 mg of each ionic liquid **3a−h** was dissolved in 1 mL of DI water and injected.[21] The amounts of residual iodide in each ionic liquid were determined to be less than the method detection limit, which was 0.01% w/w.

*1-Butyl-4-methyl-1,2,4-triazolium Trifluoroacetate (**3a**).* In a 25 mL round-bottomed flask was dissolved 1-butyl-4-methyl-1,2,4-triazole iodide (**2c**) (1.00 g, 3.74 mmol) in anhydrous acetone (10 mL). Silver trifluoroacetate (0.84 g, 3.87 mmol) was then added, and the resulting mixture was allowed to stir overnight at room temperature in the dark. The solids were then filtered, and the solvent was removed under reduced pressure to give a light yellow oil (0.88 g, 93% yield): ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.18 (s, 1 H), 9.17 (s, 1 H), 4.37 (t, J = 7.2 Hz, 2 H), 3.90 (s, 3 H), 1.82 (m, 2 H), 1.28 (m, 2 H), 0.90 (t, J = 7.1 Hz, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 157.9 (q, J = 31 Hz, C=O), 145.5, 143.1, 117.4 (q, J = 285 Hz, CF_3), 51.2, 33.9, 30.2, 18.6, 13.2; HRMS (MALDI-TOF) m/z $[M-CO_2CF_3]^+$ calcd for $C_7H_{14}N_3$ 140.1188, found 140.1191.

*1-Butyl-4-methyl-1,2,4-triazolium Nitrate **3b**.* In a 25 mL round-bottomed flask was dissolved 1-butyl-4-methyl-1,2,4-triazole iodide (**2c**) (1.00 g, 3.74 mmol) in anhydrous acetone (10 mL). Silver nitrate (0.65 g, 3.82 mmol) was then added, and the resulting mixture was allowed to stir overnight at room temperature in the dark. The solids were then filtered, and the solvent was removed under reduced pressure to give a clear, yellow oil (0.72 g, 95% yield): ^{1}H NMR (400 MHz, acetone-d_6) δ 10.80 (s, 1 H), 9.20 (s, 1 H), 4.52 (t, J = 7.2 Hz, 2 H), 4.13 (s, 3 H), 1.96 (m, 2 H), 1.38 (m, 2 H), 0.94 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, acetone-d_6) δ 146.5, 145.1, 52.6, 34.7, 31.4, 19.9, 13.6; HRMS (MALDI-TOF) m/z $[M - NO_3]^+$ calcd for $C_7H_{14}N_3$ 140.1188, found 140.1190.

*1-Butyl-4-methyl-1,2,4-triazolium Mesylate (**3c**).* In a 25 mL round-bottomed flask was dissolved 1-butyl-4-methyl-1,2,4-triazole iodide (**2c**) (1.00 g, 3.74 mmol) in anhydrous acetone (10 mL). Silver mesylate (0.81 g, 3.97 mmol) was then added, and the resulting mixture was allowed to stir for 48 h at room temperature in the dark. The solids were then filtered, and the solvent was removed under reduced pressure to give a clear, colorless oil (0.83 g, 89% yield): ^{1}H NMR (400 MHz, acetone-d_6) δ 10.65 (s, 1 H), 9.32 (s, 1 H), 4.51 (t, J = 7.0 Hz, 2 H), 4.14 (s, 3 H), 1.95 (m, 2 H), 1.41 (m, 2 H), 0.94 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, acetone-d_6) δ 146.6, 145.1, 52.5,

40.1, 34.8, 31.4, 19.9, 13.6; HRMS (MALDI-TOF) *m/z* [M − SO_3CH_3]$^+$ calcd for $C_7H_{14}N_3$ 140.1188, found 140.1188.

*1-Butyl-4-methyl-1,2,4-triazolium Tosylate (**2d**).* To a 25 mL round-bottomed flask was dissolved 1-butyl-4-methyl-1,2,4-triazole iodide (**2c**) (1.00 g, 3.74 mmol) in anhydrous acetone (10 mL). Silver tosylate (0.41 g, 3.82 mmol) was then added, and the resulting mixture was allowed to stir overnight at room temperature in the dark. The solids were then filtered, and the solvent was removed under reduced pressure to afford a light yellow oil (1.05 g, 89% yield): ^1H NMR (400 MHz, acetone-d_6) δ 10.54 (s, 1 H), 9.18 (s, 1 H), 7.65 (d, *J* = 7.8 Hz, 2 H), 7.12 (d, *J* = 7.8 Hz, 2 H), 4.42 (t, *J* = 7.3 Hz, 2 H), 4.09 (s, 3 H), 2.31 (s, 3 H), 1.87 (m, 2 H), 1.33 (m, 2 H), 0.86 (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR (100 MHz, acetone-d_6) δ 146.7, 144.9, 139.2, 129.0, 126.7, 52.5, 34.8, 31.4, 21.2, 19.9, 13.7; HRMS (MALDI-TOF) *m/z* [M − *p*-SO_3PhCH_3]$^+$ calcd for $C_7H_{14}N_3$ 140.1188, found 140.1189; [M − $C_7H_{14}N_3$]$^-$ calcd for $C_7H_7SO_3$ 171.0116, found 171.0111.

*1-Butyl-4-methyl-1,2,4-triazolium Triflate (**3e**).* To a 25 mL round-bottomed flask was dissolved 1-butyl-4-methyl-1,2,4-triazole iodide (**2c**) (0.50 g, 1.87 mmol) in DI water (5 mL). Silver triflate (0.50 g, 1.97 mmol) was then added, and the resulting mixture was allowed to stir for 48 h at room temperature. The solids were then filtered, and the solvent was removed under reduced pressure to afford a clear, yellow oil (0.38 g, 93% yield): ^1H NMR (400 MHz, acetone-d_6) δ 10.01 (s, 1 H), 9.06 (s, 1 H), 4.52 (t, *J* = 7.3 Hz, 2 H), 4.13 (s, 3 H), 1.97 (m, 2 H), 1.42 (m, 2 H), 0.95 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, acetone-d_6) δ 146.3, 144.0, 121.9 (q, *J* = 310 Hz, CF_3), 52.9, 34.8, 31.4, 19.9, 13.6; HRMS (MALDI-TOF) *m/z* [M − SO_3CF_3]$^+$ calcd for $C_7H_{14}N_3$ 140.1188, found 140.1188.

*1-Butyl-4-methyl-1,2,4-triazolium Bis(trifluoromethylsulfonyl)-imide (**3f**).* To a 25 mL round-bottomed flask equipped with a magnetic stir bar was dissolved 1-butyl-4-methyl-1,2,4-triazole iodide (**2c**) (1.00 g, 3.74 mmol) in DI water (5 mL). To this stirred solution was added a solution of lithium bis(trifluoromethylsulfonyl)imide (1.13 g, 3.93 mmol) in DI water (2 mL). After several minutes, a biphasic mixture was observed. After 24 h of stirring at room temperature, chloroform (20 mL) was added, and the resulting mixture was transferred to a separatory funnel. The organic phase was separated and washed twice with DI water (10 mL each) and the solvent removed under reduced pressure, resulting in **3f** as a clear yellow oil (1.45 g, 92% yield): ^1H NMR (400 MHz, acetone-d_6) δ 9.99 (s, 1 H), 9.06 (s, 1 H), 4.61 (t, *J* = 7.2 Hz, 2 H), 4.21 (s, 3 H), 2.04 (m, 2 H), 1.46 (m, 2 H), 0.95 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, acetone-d_6) δ 146.4, 143.7, 120.9 (q, *J* = 320 Hz, CF_3), 53.0, 34.9, 31.3, 19.8, 13.6; HRMS (MALDI-TOF) *m/z* [M − NTf_2]$^+$ calcd for $C_7H_{14}N_3$ 140.1188, found 140.1184; [M − $C_7H_{14}N_3$]$^-$ calcd for $C_7F_6NS_2O_4$ 279.9172, found 279.9167.

*1-Butyl-4-methyl-1,2,4-triazolium Tetrafluoroborate (**3g**).* To a 25 mL round-bottomed flask was dissolved 1-butyl-4-methyl-1,2,4-triazole iodide (**2c**) (1.00 g, 3.74 mmol) in anhydrous acetone (10 mL). Silver tetrafluoroborate (0.74 g, 3.82 mmol) was then added, and the resulting mixture was allowed to stir overnight at room temperature in the dark. The solids were then filtered and the solvent was removed under reduced pressure to give a clear, yellow oil (0.78 g, 91% yield): ^1H NMR (400 MHz, acetone-d_6) δ 9.87 (s, 1 H), 9.03 (s, 1 H), 4.52 (t, *J* = 7.3 Hz, 2 H), 4.12 (s, 3 H), 1.93 (m, 2 H), 1.40 (m, 2 H), 0.94 (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR (100 MHz, acetone-d_6) δ 146.2, 143.8, 52.8, 34.7, 31.4, 19.8, 13.7; HRMS (MALDI-TOF) *m/z* [M − BF_4]$^+$ calcd for $C_7H_{14}N_3$ 140.1188, found 140.1189.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Spectroscopic data (^1H and ^{13}C NMR) for triazole **1h** and triazolium ionic liquids **2a,c−h** and **3a−g**. Representative DSC thermograms for ionic liquids **2a,c−h** and **3a−g**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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